

Norit Electronic Version

Infosheet

Food

Norit Activated Carbon for Purification of Edible Oils

1. Introduction

Crude vegetable oils and marine oils can be polluted by carcinogenic Polycyclic Aromatic Hydrocarbons (PAH) and/or persistent organic pollutants (POP) such as dioxins, furans, Polychlorinated Biphenyls (PCB), pesticides and herbicides, etc.

Contamination of crude vegetable oils by Polycyclic Aromatic Hydrocarbons (PAH) is usually caused by smoke drying or direct heating of raw materials by exhaust gases. Occasionally excessive PAH contamination is caused by inadequate cleaning of tankers used for transport.

Major examples of PAH contaminated oils (depending on the source):

- Coconut oil by smoke drying of the copra
- Olive pomace oil by direct drying with combustion gases
- Fish oil by environmental pollution

Occasionally PAH contamination occurs in following oils:

- Sunflower oil by direct drying with combustion gases
- Rapeseed oil by direct drying with combustion gases or environmental pollution.
- Palm/palm kernel oil by contamination of transport containers
- Soybean oil by direct drying with combustion gases

The contamination of the fish oil is strongly dependant on the level of pollution of the water and the age of the fish. Cod Liver oil being a well known source for healthy poly unsaturated fatty acids (PUFA-Omega 3 for functional foods) originating from the North Sea contains traces of dioxins/furans, PCB , flame retardants, PAH etc. as these pollutants accumulate in the liver with the age of the cod.

Other sources of fish (haring, menhaden) are processed by fisheries into fish oil and meal. The oil may be destined for processing fish feed for fish farms and is subjected to EU limits on dioxins and PCB (see 2.2).

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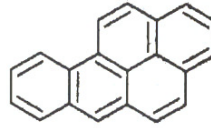
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2. Acceptable Limits on Carcinogenic and Toxic Substances

2.1 Polycyclic aromatic hydrocarbons (PAH)

Benzo(a)pyrene (BaP) is regarded as marker for the occurrence and the effect of 15 polycyclic aromatic hydrocarbons (PAH) being potentially genotoxic and carcinogenic. The maximum permitted level of BaP is regulated in the EU in the EC Regulation No. 1881/2006:

- 2.0 µg/kg BaP in oils and fats intended for direct human consumption or use as an ingredient in foods.

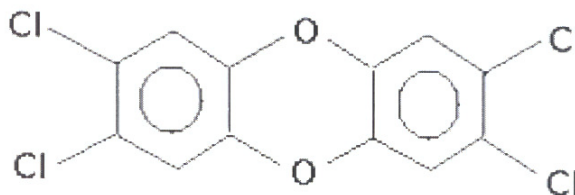


Benzo-alpha-Pyrene (BaP)

2.2 Dioxins/furans and Polychlorbiphenyls (PCB)

The maximum permitted levels for dioxins/furans and PCB for edible oils and edible oil derivatives are also regulated in the EU. EC regulation No. 1881/2006 prescribes regulated limits on PCDD (dioxins) and PCDF (furans) together with the sum of PCDD/F and dioxin like PCB for oils intended for direct human consumption or use as an ingredient in foods. Commission Directive 2006/13/EC prescribes the maximum permitted levels on PCDD/F and the sum of PCDD/F and dioxin like PCB of oils when used in animal feed. A survey of maximum permitted limits is listed in the table below.

Undesirable substances	Product	Max. content pg/g WHO TEQ	Intended use
PCDD / PCDF	Vegetable oils and their by products	0.75	Human consumption
Sum of PCDD/F and dioxin like PCB	Vegetable oils and their by products	1.5	Human consumption
PCDD / PCDF	Marine oils	2.0	Human consumption
Sum of PCDD/F and dioxin like PCB	Marine oils	10.0	Human consumption
PCDD / PCDF	Vegetable oils and their by products	0.75	Animal feed
Sum of PCDD/F and dioxin like PCB	Vegetable oils and their by products	1.5	Animal feed
PCDD / PCDF	Fish oils	6.0	Animal feed
Sum of PCDD/F and dioxin like PCB	Fish oils	24.0	Animal feed



2, 3, 7, 8 - p - TCDD

Most toxic dioxin

3. The Purpose of Activated Carbon

3.1 The removal of PAH from vegetable oils

The traditional use of activated carbon in edible oil refining processes is decolourisation of vegetable oils to support the decolorizing effect of bleaching earth. The significance of activated carbon for this purpose has been reduced substantially with the quality improvement of available activated bleaching earth types being capable to do most of the bleaching alone. However in case of very high concentrations of persistent pigments such as chlorophylls, xanthophylls and carotene, activated carbon can be used to improve the bleaching effect or support the thermal decomposition of pigments such as carotene in the deodorization process step.

Due to the existing FEDIOL limits on PAH, removal of PAH has become the main target for PAC in the edible oil refining industry. The majority of the present light PAH (up to 4-rings) in contaminated oils is usually volatile enough to be stripped off during the deodorization process step along with other volatile compounds. However the balance of persistent light PAH compounds together with the remaining heavy PAH compounds (5-rings and higher) must be removed by adsorption of activated carbon during the bleaching process step in order to comply with agreed quality standards for refined edible oils.

3.2 The removal of dioxins, furans and PCB from fish oils

Crude fish oil destined for making fish feed must be purified with activated carbon to comply with the EU regulated limits. The original natural character of the fish oil should however remain as much as possible. Therefore typical refining steps such as degumming, de-acidification, bleaching and de-odorizing are omitted when “detoxifying” crude fish oil.

This is different when refining fish oils destined for human consumption; these are intensively refined similar to vegetable oil refining processes, thus including bleaching and deodorization. In case refined fish oils must comply with EU regulated limits on dioxins and PCB, activated carbon is used in conjunction with bleaching earth and the bleached oil is finally de-odorized.

4. Activated Carbon in Process

Edible oil purification including activated carbon is typically done with powdered activated carbon (PAC). Granular activated carbon is usually not applied because of many operational constraints.

- The use of PAC for edible oil refining is always in conjunction with bleaching earth. PAC dosing can be done at the same time as bleaching earth to the bleacher. For relative small scale operations, ready-for-use bleaching earth/activated carbon mixtures are offered by established bleaching earth manufacturers (e.g. under brand name TONSIL). Performance improvements may occur when dosing of PAC with some delay after bleaching earth, respectively using a two stage bleaching process with the majority of the carbon in the second stage. A two stage bleaching process may be required when the spent bleaching earth and spent carbon have to follow separate disposal ways. A diagram of such a concept is shown in figure 1.
- The use of PAC for detoxification of crude fish oil is without bleaching earth, eventually following active silica pre-treatment. The purpose for the silica: selective removal phospholipids from the crude oil being inhibitors for the activated carbon. The purpose for the carbon is: selective removal of persistent organic pollutants (dioxins, PCB, ...)
- Operation usually under vacuum to avoid oxidation of the oil, sometimes under nitrogen. In any case, presence of oxygen during the adsorption process should be minimized
- Contact time 20-30 min. for decolourisation of vegetable oils and fish oil purification, for heavy PAH contaminated vegetable oils at minimum 45 min.

- Dosing rates of PAC:
 - For decolourisation: 5-10 % portion in a mixture with bleaching earth. Dosage adsorbent mixture usually 0.5-1.5 % (5-15 kg/ton).
 - For PAH removal: PAC dosing up to 0.5 % (5 kg/ton) for coconut oils. Other PAH contaminated oils (except olive pomace oil) usually require less to meet the FEDIOL requirements on PAH (see chapter 2.). The bleaching earth dosage is at minimum 1.5 times higher than of that of the PAC dosage.
 - For dioxin/PCB removal from fish oils: 0.1 – 0.3 % (1-3 kg/ton)
- Recommended temperatures for refining including bleaching earth: roughly from 80 °C to 100 °C, based on the recommended bleaching earth treatment for the corresponding type of oil. For crude fish oil detoxification (without bleaching earth): 70-80 °C.
- Filtration of the adsorbent mixture is usually done with pressure leaf filters, membrane presses or pulse tube filters in special cases where a minimum of filter aid is to be used (see chapter 7 below).

Separated waste handling

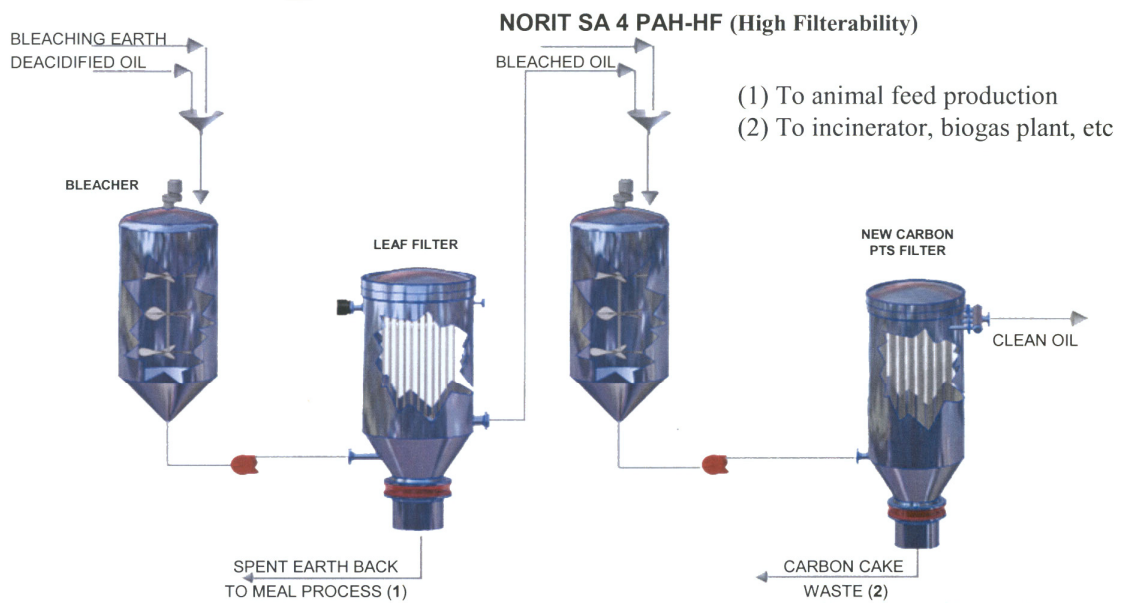


Figure 1 : Process diagram for a two stage bleaching process

5. Critical Carbon Properties

- Adsorptive properties: dedicated pore structure for PAH, dioxins and PCB. The recommended Norit carbons have specified values on PAH adsorption given on each certificate of analysis and a proven performance on dioxin and PCB adsorption from fish oil.
- pH/reaction: no acid reaction to maintain the chemical composition of the oil.
- Filtration behavior: plays a dominant role, high pollution levels ask for high dosing rates. *High filterability* carbons can reduce operating costs substantially, see chapter 7 below.
- Purity: the powdered carbon should be guaranteed free from dioxins, higher aromatic hydrocarbons and other hazardous substances. The recommended Norit carbons are frequently controlled on the presence of higher hydrocarbons and dioxins to ensure a food safe operation according to the principles of HACCP guidelines.

6. Recommended Norit Carbon Grades

- Norit SA 4 PAH, standard grade.
Features: Proven performance on PAH, dioxin and PCB adsorption. Specified values on PAH adsorption, good filtration properties, guaranteed purity to ensure a food safe operation.
- Norit SA 4 PAH-HF, high filterability grade.
Same features as for Norit SA 4 PAH but with a manipulated particle size distribution to ensure excellent filtration properties, see chapter 7 below.
- Both upgraded qualities were developed with the focus on adsorption of hazardous organic substances, not with focus on decolourisation. If decolourisation is the only objective, it is recommended to perform tests under practical circumstances including other Norit alternatives.

7. The use of High Filterability Carbons in Edible Oil Refining Processes

The net benefit expected when using a high filterability carbon such as Norit SA 4 PAH-HF include the following:

- ❑ Higher throughput since more batches can be filtered in the same time period. This also means that existing equipment may be suitable for expanded production capacity eliminating the need for additional capital investment for filtration equipment.
- ❑ Lower energy cost since lower pressure is needed to maintain the desired flow rates through the filter.
- ❑ Allows for the possibility of filtering higher viscosity oils without the need to increase the temperatures too much with risk for product degradation due to prolonged exposure to high temperatures.
- ❑ Less sensitive to bleed through of fines, in case this is taking place when compressible filtercakes shift or crack at higher operating pressures.

Norit SA 4 PAH-HF used with the proper filtration equipment can eliminate the need to use filter aid or avoid the use of a surplus of bleaching earth in contradiction to conventional PAC grades. This can also benefit the customer in the following ways:

- ❑ Reduction in the volume of solid waste thus reducing the disposal cost.
- ❑ Reduction in oil retention due to minimization of the filter cake solids content.
- ❑ Reduction in the purchase and storage of filter aids particularly if they are totally eliminated.
- ❑ Increase in the filtration cycle time since more carbon can be deposited onto the filters before having to be sluiced off.

This infosheet (21-03, issue 10-07) replaces infosheets 21-01 and 21-02.