SELECTIVE ADSORPTION OF DIOXINS AND PCB'S FROM MARINE OILS ON ACTIVATED CARBON

Bruno De Meulenaer[1], Jeroen Maes[1], Peter Van Heerswynghels[2], Wim De Greyt[2], Leo Goeyens[3], Isabelle Windal[3], Gauthier Eppe[4], Edwin De Pauw[4], André Huyghebaert[1]

[1]Laboratory of Food Chemistry and Analysis, Departement of Food Technology and Nutrition, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium; [2]De Smet Group, Da Vincilaan 2-bus G1, B-1935 Zaventem, Belgium; [3]Scientific Institute of Public Health, Juliette Wytsmanstraat 14, B-1050 Brussels, Belgium; [4]Laboratory of Mass Spectrometry, Department of General and Physical Chemistry, Liège University, Sart Tilman, B-4000 Liège, Belgium

Introduction

Marine oils are an excellent source of ω-3 fatty acids, such as EPA and DHA. These fatty acids are claimed to have various nutritional benefits, such as reduced risk for cardiac diseases, anti carcinogenic properties and many others. Because of their health protecting and promoting effects, the market share of foods enriched in ω-3 fatty acids is becoming more important. Moreover, commercial interest in using marine oils for food and feed supplementation is growing as well.

Two main issues should be taken into account however, considering these marine oils as a source of ω-3 fatty acids : their low oxidative stability and their high degree of contamination with persistent organic pollutants such as dioxins and PCB's. Oil processors face problems in this respect, since high temperature striping is not applicable because of to high losses in ω-3 fatty acids (EPA and DHA). Other techniques such as thin film-short path evaporation are quite expensive. Therefore, selective adsorption of persistent organic pollutants on activated carbon powder seems to be the method of choice nowadays. Activated carbon was shown to be very effective in removing dioxins and coplanar PCB's from oils. Its removal efficiency towards mono-ortho PCB's was however very low.

Therefore this paper focuses on the use of activated carbons to remove dioxins and PCB's and particularly the mono-ortho PCB's from marine oils using newly developed activated carbon types. In addition, the effects of the various evaluated activated carbon types on the quality parameters of the oil are investigated.

Materials and methods

Activated carbon treatment. To an appropriate amount of activated carbon powder (0.1 and 0.5 % on oil basis), which was initially deaerated in a rotary evaporator under reduced pressure (55mbar), 300 g of preheated marine oil (70°C) was added without altering the vacuum. This mixture was rotated at constant speed and constant temperature for 30 minutes. After the activated carbon treatment, the mixture was filtered over a Buchner filter, using a conventional Whatman N°1 filter paper, under vacuum. Filtered oil samples were stored at 4°C under a protective nitrogen atmosphere and protected from light for further analysis.

Four different types activated carbon were used as summarized in table 1.

Persistent organic pollutant analysis. Both instrumental and bioanalytical techniques were used for dioxin and PCB analysis. For the instrumental methods, HR-GC-MS was used as described earlier

by De Pauw et al[1]. For the bioanalytical method or chemical activated luciferase gene expression (CALUX) as previously described by Van Overmeire et al[2].

Table 1. Types, codes and properties of the evaluated activated carbon powders

Type of activated carbon	Code	Properties
Norit SA4 PAH	AC-1	Steam activation, for removal of polyaromatic hydrocarbons
Norit EXP 21 A	AC-2	Experimental type
Norit EXP 21 B	AC-3	Experimental type
Norit CA3	AC-4	Chemical activation

Oil composition and quality parameters. Fatty acid profile, free fatty acid content, peroxide value, p-anisidine value, oxidative stability index and the specific extinction at 232 and 268 nm were determined according to AOCS official methods[3]. Colour measurements were made using a Lovibond Tintometer type E.

Results and discussion
In the initial experiments, ten marine oils (essentially cod liver and menhaden oil) from several sources were screened for their dioxin and PCB levels using the CALUX bioassay. Dioxin levels varied between 4-28 pg PCDD/F (WHO) TEQ per g fat while PCB levels ranged between 5-9.3 pg PCB (WHO) TEQ per g fat. These data confirm the high dioxin and PCB contamination levels of marine oils previously reported and illustrate the need for removal of these contaminants during refining.
A cod liver oil from the Baltic seas was selected as a feedstock for the adsorption experiments using the four types of activated carbon powers (Table 1) at two concentration levels : 0.1 % and 0.5 %. Results on selected oil quality parameters are summarized in Table 2 and data on contaminant levels are represented in Table 3.
No significant changes in fatty acid composition are noted, especially not for the EPA and DHA levels. The oxidative status of the oils, as evaluated by the peroxide value, the p-anisidine value and the specific extensions measurements, did not change either. The oxidative stability however seemed to decrease for some of the activated carbon types in a concentration dependent manner. Remarkably, a similar trend with regard to the colour parameters could be noticed.
As for the removal of the contaminants, it is obvious that dioxin removal is more efficient compared to the PCB removal. From the HRGC-MS data it could be concluded that the adsorption of PCB's was less efficient, essentially because of the lower adsorption of the mono-ortho PCB's.
Removal efficiencies seemed to be strongly dependent upon the activated carbon load, for most carbon types and for most contaminants.
Comparing the contamination levels obtained via the bioassay and the instrumental method, some important differences are notices as well. For the dioxin fraction probably some other Ah agonists are thought to affect the CALUX signal. For the PCB levels reported, the underestimated levels are predominantly method specific[4].

Conclusions
The evaluated activated carbon types were able to remove dioxins in a sufficient manner, while the removal of the mono-ortho PCB's was significantly less efficient.

Table 2: Overview of the selected quality parameters of the purified fish oils in phase 2.

	Feedstock	AC-1 (0.1 %)	AC-1 (0.5%)	AC-2 (0.1 %)	AC-2 (0.5%)	AC-3 (0.1 %)	AC-3 (0.5 %)	AC-4 (0.1%)	AC-4 (0.5%)
FFA (% oleic acid)	0,17	0,19	0,18	0,17	0,16	0,19	0,19	0,19	0,21
Peroxide value (meq O2/kg)	13,59	13,16	14,40	13,00	13,26	13,21	15,20	14,85	16,83
p-Anisidine value	18,01	16,58	15,19	17,44	17,30	17,40	17,83	16,72	15,70
OSI (h) at 80°C	5,98	5,28	4,55	5,87	5,53	4,68	4,72	6,60	6,40
Specific extinction at 232 nm	7,47	7,67	7,89	7,38	7,66	7,49	7,50	7,50	7,70
Specific extinction at 268 nm	0,82	0,82	0,81	0,85	0,86	0,85	0,84	0,83	0,85
Color (Lovibond) at 1"									
Yellow	50	50	30	50	15	50	30	40	40
Red	5,5	5,0	4,1	4,0	1,7	4,5	3,6	4,3	4,2
FAME analysis (%)									
C16:1	5.9	6.0	6.0	6.4	6.1	5.8	6.1	6.2	6.2
C18:1	17.1	16.8	17.4	17.1	17.4	17.3	17.8	17.6	17.2
C18:2	2.8	2.9	3.0	2.7	2.9	2.7	2.8	3.0	2.7
C18:3	0.8	1.3	0.9	0.9	1.1	0.9	0.9	0.9	1.0
C18:4	2.5	2.3	2.3	2.5	2.7	2.6	2.4	2.6	2.7
C20:1	10.4	10.3	10.2	10.4	10.3	10.8	10.0	9.6	10.5
C22:1	13.0	13.7	13.7	13.1	13.3	13.6	13.8	12.9	13.0
EPA	9.8	9.4	9.4	9.7	9.7	9.6	9.8	9.7	9.8
C22:5	2.1	2.3	2.2	1.9	2.0	2.1	2.2	2.1	2.3
DHA	11.4	11.5	11.6	11.1	11.3	11.6	11.3	11.1	11.7

Table 3: Contaminant level of purified oils using the CALUX and HR-GC-MS (pg WHO TEQ per g fat).

	Feedstock	AC-1 (0.1 %)	AC-1 (0.5 %)	AC-2 (0.1 %)	AC-2 (0.5%)	AC-3 (0.1%)	AC-3 (0.5 %)	AC-4 (0.1%)	AC-4 (0.5%)
Total PCDD/F via CALUX	16.8	4.8	2.0	4.3	1.3	3.7	1.7	12.0	6.3
Relative removal (%)		71	88	74	92	78	90	29	63
Total PCB via CALUX	7,3	3.2	2.0	2.1	1.6	3.1	1.7	6.0	6.0
Relative removal (%)		56	72	71	78	58	77	18	18
Total PCDD/F via HRGC-MS	5.40	0.80	0.17	0.43	N.D.	0.89	0.09	4.25	1.76
Relative removal (%)		85	97	92	100	84	98	21	67
Total coplanar PCB via HRGC-MS	14.32	10.84	3.42	8.54	0.93	10.83	4.06	14.13	10.58
Relative removal (%)		24	76	40	94	24	72	1	26
Total mono-ortho PCB via HRGC-MS	3.74	3.35	3.01	3.5	2.69	3.55	3.53	3.42	3.45
Relative removal (%)		10	20	6	28	5	6	9	8
Total PCB via HRGC-MS	18.06	14.19	6.43	12.04	3.62	14.38	7.59	17.55	14.03
Relative removal (%)		21	64	33	80	20	58	3	22

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