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RESEARCH ARTICLE OPEN ACCESS

A preliminary study on the decontamination properties of different sorbent materials used for oil bleaching against mineral oils and selected alkylated polycyclic aromatic hydrocarbons[☆]

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Abstract – Mineral oils are complex mixtures of saturated (MOSH) and aromatic hydrocarbons (MOAH) of petrogenic origin, which can contaminate edible oils. Some MOAH (>3 benzene rings) are suspected genotoxic carcinogens, as are polycyclic aromatic hydrocarbons (PAHs) with the same ring number, but without alkylation, mainly originating from the pyrolysis of organic matter. Heavy PAHs can be removed during oil bleaching, but no information is available on MOH and selected alkylated PAHs. Therefore, this study aimed to investigate the adsorption properties of activated carbon, and other sorbents commonly used for oil bleaching, against MOAH and selected alkylated compounds. For this purpose, batch experiments were carried out on mixtures of the target analytes in hexane (model system) using different contact times and sorbent amounts. On-line HPLC-GC-FID was used for quantification. Activated carbon alone or in combination with acid activated bleaching earth proved able to remove not only parent PAHs, but also MOAH and single alkylated PAHs, according to their ring number and alkylation degree. Natural and acid activated bleaching earths alone removed 30–45% of perylene and 7-methylbenzo[a]pyrene. Further studies are needed to better understand the decontamination properties of different sorbent materials and their behavior in the oil matrix.

Keywords: Mineral oil saturated hydrocarbons (MOSH) / mineral oil aromatic hydrocarbons (MOAH) / parent and alkylated polycyclic aromatic hydrocarbons (PAHs) / oil bleaching / adsorption

Résumé – Une étude préliminaire sur les propriétés de décontamination de différents matériaux absorbants utilisés pour le blanchiment des huiles, face aux huiles minérales et à certains hydrocarbures aromatiques polycycliques alkylés. Les huiles minérales sont des mélanges complexes d'hydrocarbures saturés (MOSH) et aromatiques (MOAH) d'origine pétrogénique, qui peuvent contaminer les huiles alimentaires. Certains MOAH, notamment ceux à plus de trois cycles benzéniques, sont classés cancérogènes génotoxiques, similaires aux hydrocarbures aromatiques polycycliques (HAP) non substitués issus de la pyrolyse. Bien que les HAP lourds puissent être éliminés lors du blanchiment des huiles, peu d'informations existent sur la décontamination des MOH et des HAP alkylés spécifiques. Cette étude visait à évaluer l'efficacité d'adsorbants comme le charbon actif et autres adsorbants couramment utilisés pour le blanchiment de l'huile pour éliminer les MOAH et certains HAP alkylés des huiles comestibles. Des expériences en batch ont été réalisées avec des mélanges cibles dans de l'hexane (système modèle), en testant divers temps de contact et quantités d'adsorbants. La quantification a été effectuée *via* HPLC-GC-FID. Le charbon actif, seul ou combiné à des terres de blanchiment activées par acide, s'est montré efficace pour éliminer les HAP parentaux, les MOAH et certains HAP alkylés selon leur structure. Terres décolorantes naturelles et activées par l'acide seules ont réduit à elles seules 30-45% du pérylène et du 7-méthylbenzo[a]pyrène. Des recherches supplémentaires sont nécessaires pour approfondir la compréhension des mécanismes d'adsorption et leur efficacité dans la matrice huileuse.

Mots-clés : Hydrocarbures saturés d'huile minérale (MOSH) / hydrocarbures aromatiques d'huile minérale (MOAH) / hydrocarbures aromatiques polycycliques parentaux et alkylés (HAP) / blanchiment des huiles / adsorption

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[☆] Contribution to the Topical Issue: "Contaminants in oils and fats / Contaminants des huiles et corps gras".
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1 Introduction

Vegetable oils and fats can be contaminated with parent polycyclic aromatic hydrocarbons (PAHs) originated from incomplete combustion of organic matter, and mineral oil hydrocarbons (MOH) originated during petroleum diagenesis (Purcaro *et al.*, 2016; Gharbi *et al.*, 2017).

Heavy PAHs (>3 benzene rings) are recognized as genotoxic and carcinogenic compounds. Their presence in foods (including fats and oils) has been regulated for years at the European level, and maximum limits in various food products have recently been updated (EU Regulation 2023/915). MOH consists of complex mixtures of mineral oil saturated hydrocarbons (MOSH), including linear, branched and cyclic compounds able to bioaccumulate in human tissue and organs, and mineral oil aromatic hydrocarbons (MOAH), mostly composed of alkylated aromatic hydrocarbons (>98%) with 1–7 benzene rings, and a small percentage (<2%) of parent PAHs (EFSA, 2012; EFSA 2023). Since MOAH may contain alkylated PAHs with more than 3 benzene rings and low alkylation degree, having toxicity similar to heavy parent PAHs of the same ring number, their presence in food is of high concern. According to a draft regulation circulated to stakeholders in 2024, starting from the beginning of 2026, maximum limits equal to the limit of quantification reported in the Joint Research Centre (JRC) "Guidance on sampling, analysis and data reporting for the monitoring of mineral oil hydrocarbons in food and food contact materials" (Bratinova *et al.*, 2023), will be introduced for the MOAH in different foodstuffs, depending on the fat content (Craig, 2024).

Due to their lipophilic nature and the numerous sources of contamination along the entire processing chain, MOH and PAHs are common contaminants of vegetable oils and fats (Purcaro *et al.*, 2016; Brühl, 2016; Menegoz Ursol *et al.*, 2024; Barp and Moret, 2024). Special attention must be paid to the harvesting phase, due to accidental leaks of lubricants and hydraulic oils, or contact with lubricated parts of harvesting machineries (Menegoz Ursol *et al.*, 2023).

Bleaching is part of the refining process of crude edible oils and fats, which make use of different sorbents (mainly bleaching earths and activated carbon) to remove pigments (chlorophyll, carotenes) and contaminants. Sorbent materials may retain contaminants physically (van der Waals' forces), chemically (electrochemical bonding), or by molecular sieves during filtration (contaminants are trapped inside the pores of the sorbent). The adsorption process depends on several parameters such as temperature, pH, contact time, concentration of the adsorbate and sorbent, solubility of the adsorbate in the medium, surface area and particle size, and effectiveness of agitation (Ab Razak *et al.*, 2021; Bello, 2021). Recently, Menegoz Ursol *et al.* (2025) reported that the bleaching step reduced the presence of some alkylated PAHs in an olive pomace oil, but concluded that further studies are needed to confirm this result. Indeed, while there is established literature on the removal of parent heavy PAHs during oil bleaching (Gong *et al.*, 2007; Ma *et al.*, 2017; Kiralan *et al.*, 2019), studies on the impact of bleaching on different alkylated PAHs and total MOHs are lacking.

The main objective of this work was therefore to investigate and compare the decontamination properties of different sorbent materials, commonly used for oil bleaching, towards a mixture of selected PAHs (both alkylated and non-alkylated), mineral oil, and their mixtures, also in the presence of other matrix components such as *n*-alkanes. A model system was created with the target analytes in a solvent (*n*-hexane) instead of vegetable oil, and batch experiments were carried out to compare the adsorption properties of the tested sorbent materials.

2 Materials and methods

2.1 Reagents and standards

HPLC grade *n*-hexane and dichloromethane (distilled when necessary), as well as all other solvents used (toluene and cyclohexane), were from Sigma-Aldrich (St. Louis, Missouri, USA).

The PAH10 standard mixture consisted of pentylbenzene (PB), 2-methylnaphtalene (2MN), 1-methylnaphthalene (1MN), 2,6-dimethylnaphthalene (2,6DMN), 1,3,5-tritert-butylbenzene (TBB), 2-methylanthracene (2MA), 9,10 dimethylanthracene (9,10DMA), chrysene (Ch), perylene (Per), and 7-methylbenzo[a]pyrene (7MBaP), all purchased from Sigma-Aldrich.

Table 1 indicates the concentration of each single stock PAH solution that was prepared in toluene, how the stock standard solution containing all the PAHs was prepared, and the final concentration of each PAH in the stock PAH10 mix in cyclohexane.

The stock standard solution was stored at 4 °C and diluted (just before use) with *n*-hexane to prepare the working solution at approximately 100 ng/mL of each PAH component.

The mineral oil standard was a Gravex oil (a naphthenic-based process oil containing 27.0% of MOAH) supplied by a manufacturer. The stock standard solution of Gravex was prepared by weighing 25 mg of the Gravex oil into a 250 mL flask and taking it to volume with cyclohexane, then stored at 4 °C. The working Gravex solution, used alone or with the PAH10 mix, was prepared by diluting the stock solution 1 to 10 to obtain a 25 µg/mL Gravex solution in *n*-hexane (containing around 7 µg/mL of MOAH).

2.2 Sorbent materials to be tested

Five commercial sorbent materials used for oil bleaching were tested for their ability to remove the target analytes (PAH10, Gravex oil and *n*-alkanes). Table 2 lists the 5 materials kindly furnished by Unigrà SpA and the available information.

Bleaching earths are generally composed of one or more types of clay minerals, with the most abundant being calcium montmorillonite (also called bentonite), attapulgite, and sepiolite. The adsorptive capacity of these materials depends on factors such as their structure, surface area, particle size distribution, porosity, and surface activity (Hales, 2016). Both natural and acid-activated bleaching earths are available on the market. The natural bleaching earth is a type of bentonite or attapulgite clay, which has a natural adsorption capacity and only requires physical treatment, such as mining, crushing, drying, grinding and sizing (Zschau, 2001). Activated

Table 1. Preparation of the PAH10 stock solution.

Polycyclic aromatic hydrocarbon	Acronym	Single stock PAH solutions in toluene (μg/mL)	μL added to a 10 mL flask taken to volume with cyclohexane	Stock PAH10 solution in cyclohexane (μg/mL)
Pentylbenzene	PB	2628	40	10.5
2-Methylnaphthalene	2MN	2944	35	10.3
1-Methylnaphthalene	1MN	978	100	9.8
2,6-Dimethylnaphthalene	2,6DMNa	2659	40	10.6
1,3,5-Tritert-butylbenzene	TBB	2534	40	10.1
2-Methylanthracene	2MA	2601	40	10.4
9,10 Dimethylanthracene	9,10DMA	1024	100	10.2
Chrysene	Ch	2429	40	9.7
Perylene	Per	1377	75	10.3
7-Methylbenzo[a]pyrene	7MBaP	1508	70	10.6

Table 2. Description and physical characteristics of tested sorbent materials.

Sorbent type	Code	Description and physical characteristics
Natural bleaching earth	NBE	Steam activated bleaching earth, characterized by fast filtration capacity and good bleaching power. Surface area (BET): 180±20 m^2/g; pH: 7.0±1.0; granulometry: 25-150 μm; moisture content: <30% (measured humidity*: 7.69±0.11)
Acid activated bleaching earth/ activated carbon (5%)	AABE/AC	Highly active bleaching earth manufactured by acid activation of calcium bentonite, containing 5% of AC with a highly porous inner structure, suitable for the removal of both polar and non-polar components as PAHs. Surface area (BET): 187 m^2/g; pH: 3.5; granulometry: 25-150 μm. Free moisture (2h, 110 °C): 11%.
Activated carbon	AC	Powdered activated carbon produced from specially selected grades of bituminous coal. Surface area (BET): 1100±1200 m^2/g; pH in water solution: 8.0; granulometry: 75-200 μm. Moisture content: <5% (measured humidity*: 2.85±0.08).
Amorphous silica powder	AmSi	Filtration aid used to treat oils/fats that have undergone interesterification or hydrogenation treatments in order to facilitate filtration and remove catalyst residue (0.1% of the oil weight). Surface area: 680 m^2/g; pH in 10% water solution: 3.0; particle size d50: 17-23 μm. (Measured humidity*: 54.73±0.09)

*Humidity was measured as weight loss after heating at 110 °C for 2h (data are expressed as mean and standard deviation of 2 replicates).

bleaching earth, which usually contains a higher proportion of montmorillonite, undergoes a chemical treatment (treatment with inorganic acid, followed by washing and drying) able to increase its bleaching potential towards pigments in oil and other colloidal impurities (Chew and Nyam, 2020). The typical amount added for bleaching is 1% of the weight of the oil.

Activated carbon (AC) is usually used in conjunction with activated bleaching earths to effectively remove heavy PAHs that activated bleaching clay alone cannot adsorb. In bleaching treatments, AC is typically used in amounts comprised between 0.1 and 0.5% of the oil weight (Zschau, 2001).

2.3 Decontamination trials

All glassware to be used in the decontamination trials was thoroughly washed with acetone and *n*-hexane before use. To assess the removal properties of the investigated sorbent materials towards alkylated and non-alkylated PAHs and mineral oil (Gravex), batch adsorption experiments were carried out. More precisely, a specific amount of the investigated sorbent (as indicated in Tab. 3) was weighed in a 25 mL dark vial, added with a magnetic stir bar, and 20 mL of the working PAH10 mix in *n*-hexane (100 ng/mL each) or 20 mL of the working Gravex solution at 25 μg/mL, or a combination of both in the presence of a mixture of *n*-alkanes. After closing the vial, the sample solution was thermostatted at 30 °C and agitated (magnetic stirring) for different times (30, 60, 120 min). After a short rest (1 min) to decant the sorbent powder, a portion of the solution was withdrawn with a pipette and loaded onto a syringe fitted with a 0.22 μL cellulose filter, then filtered directly into an autosampler vial. In addition, prior to each treatment, 2 mL of the solution was placed in an autosampler vial and injected directly into the LC-GC-FID (as a reference standard).

Table 3. Outline of the batch experiments.

Trial	Tested sorbent	Sorbent amount (mg)	Target analytes (adsorbate)	Contact time (min) at 30 °C	Total PAH(µg/mL)	Total MOAH (µg/mL)	Total MOSH (µg/mL)	Total *n*-alkanes (µg/mL)
A	All	100, 500	PAH10 (100 ng/mL each)	30, 60, 120	1.0	–	–	–
B	All	100, 500	PAH10 (100 ng/mL each)	30, 60, 120	1.0	–	–	–
C	All	500	PAH10 (100 ng/mL each) Gravex (10 µg/mL)*n*-alkanes (100 ng/mL each)	30, 60, 120	1.0	2.7	7.3	1.6
D	AC	10, 25,50, 100, 500	PAH10 (100 ng/mL each)	60	1.0	–	–	–
E	AC	25, 50, 100, 250, 500, 750, 1000	PAH10 (100 ng/mL each) Gravex (10 µg/mL) *n*-alkanes (100 ng/mL each)	60	1.0	2.7	7.3	1.6
F	AC	10, 25, 50, 100, 250, 500, 750, 1000	Gravex (10 µg/mL)	60	–	2.7	7.3	–

Blank tests were performed by placing 500 mg of each sorbent material in contact with 20 mL of *n*-hexane for two hours.

2.4 Separation and quantitative determination of selected PAHs and MOH

High performance liquid chromatography (HPLC) coupled on-line with gas chromatography (GC) and a flame ionization detector (FID) was used for separating and analysing the selected mixture of PAHs and mineral oil. The two-channel on-line HPLC-GC-FID system, able to process both MOSH and MOAH within the same GC run, was from Brechbühler (LC-GC 9000, Zurich, Switzerland), and included an HPLC unit equipped with a Phoenix 9000 pump and a GC Trace 1310 series from Thermo Fisher Scientific (Waltham, Massachusetts, USA). The HPLC column was a 25 cm × 2.1 mm ID, 5 µm particle size, packed with Lichrospher Si-60 column by DGB (Schlossboeckelheim, Germany). The feeding of the two GC channels was managed by a switching valve system. Each GC channel included a 10 m × 0.53 mm ID deactivated retention gap to allow large volume injection (LVI) (Biedermann & Grob, 2012), followed by a steel T-piece connected in turn with a solvent vapour exit (SVE) heated at 140 °C for vapour discharge, and with a 10 m × 0.25 mm ID GC column by Mega (Legnano, Milan, Italy) with a stationary phase of PS-255 (1% vinyl, 99% methyl polysiloxane), 0.15 µm film thickness. MOSH and MOAH separation by the HPLC was accomplished by setting a gradient starting with 100% *n*-hexane, kept for 0.1 min, and reaching a 70:30 dichloromethane/*n*-hexane (*v/v*) ratio after 0.5 min, while using an eluent flow of 300 µL/min. The MOSH fraction was eluted from 2.1 to 3.6 min, while the MOAH from 3.8 to 5.3 min. After transferring the MOAH fraction, a backflush with 100% dichloromethane at a flow rate of 500 µL/min was performed for 9 min, and then the column was reconditioned with *n*-hexane for 6.5 min at a flow rate of 700 µL/min, and for 1.5 min at the initial flow rate. Fraction transfer from HPLC to GC occurred by exploiting partially concurrent eluent evaporation through the Y-interface (Biedermann & Grob, 2009). During the fraction transfer, the GC worked at a constant pressure of 90 kPa, lowered to 60 kPa during the GC run. The temperature gradient started from 51 °C and was kept constant for 8.5 min, then raised at a rate of 20 °C/min, until reaching the final temperature of 350 °C, which was maintained constant for 5 min. The FID was heated at 360 °C. Data were acquired and processed with Chromeleon 7 Chromatography Data System (CDS) from Thermo Fisher Scientific (Waltham, Massachusetts, USA).

3 Results and discussion

3.1 Sorbent comparison

In the first part of this work, the decontamination properties of 5 sorbent materials commonly used for oil bleaching were tested by performing batch experiments in a model system consisting of the target analytes (PAH10 mixture, MOH from Gravex oil, and a combination of these in the presence of *n*-alkanes) dissolved in 20 mL of *n*-hexane, which simulated about 20 g of oil. The PAH10 mixture included 2 parent PAHs and 8 alkylated PAHs (PAH10), all listed in Table 1.

The use of solvent instead of vegetable oil in the model system allowed to eliminate the interference of the matrix (due to the presence of olefins coeluting with the MOAH and the PAHs) and speed up the analysis time. Epoxidation to eliminate olefins was not applied, since it also affects PAHs (Nestola and Schmidt, 2017; Bauwens *et al.*, 2023).

According to the information furnished by the company that supplied the sorbent materials, the optimal amount of bleaching earth to be used corresponds to 1% of the weight of the oil (200 mg for our model system). In bleaching treatments, AC is typically used in amounts comprised between 0.1 and 0.5% of the oil weight (Zschau, 2001). Its quantity can be more precisely calculated by considering the concentration of BaP present in the sample, according to the following formula:

$\%\ AC\ on\ fat\ weight = [(ng/mg\ BaP)/8]\quad 0.1$

Based on this formula and the BaP concentration in the model system, the optimal amount of AC resulted to be

250 mg. According to the manufacturer's information, the amount of amorphous silica to be used was 0.1% of the oil weight (20 mg). In conclusion, with the exception of amorphous silica, which was tested using amounts of sorbent 5 to 25 times greater than those generally used to treat 20 mg of oil, the other sorbents were tested in a range of concentrations that encompasses the optimal amount recommended for oil bleaching.

Batch experiments were carried out to compare the removal properties of all the sorbents as schematized in Table 3.

First, the PAH10 mixture in *n*-hexane (containing about 100 ng/mL of each PAH) was placed in contact (magnetic stirring) with 100 (trial A) and 500 mg (trial B) of each sorbent material. These high concentrations of PAH10 (100 µg/kg each) were used to simulate the worst case of a highly contaminated crude edible oil. Parent PAH concentrations even higher than those considered in this work have been reported in the literature in oils subjected to drying with direct contact with combustion fumes, such as olive pomace oil (Barranco *et al.*, 2004) and coconut oil. Van Duijn and Den Dekker (2010) reported a maximum level of 73 µg/kg for BaP in crude coconut oil. Next, a more complex solution including the same PAH10 mixture, the Gravex oil at 10 µg/mL and a mixture of even *n*-alkanes from *n*-C_{10} to *n*-C_{40} (each at 100 ng/mL), was placed in contact with 500 mg of each sorbent material.

Preliminary blank experiments showed that all sorbents, with the exception of AABE/AC, which gave two humps in the first part of the LC-GC-FID chromatogram of the MOSH fraction, did not release appreciable interference in *n*-hexane. Repeatability tests (4 replicates) performed on the PAH10 mixture in contact with 10 mg of AC sorbent for 60 min showed a residual standard deviation (RSD) lower than 10%.

As TBB, probably due to its high steric hindrance, was never removed, to avoid variations due to possible solvent evaporation, its area ratio in the reference and sample ($A_{TBB\ reference}/A_{TTB\ sample}$) was used to normalize all PAH areas in the treated sample. To evaluate the influence of contact time, each batch experiment was performed by placing the sorbent in contact for 30, 60 and 120 min. Since no significant differences ($p < 0.05$) were observed at varying contact times, percentage removal rates were calculated by comparing the average area of the target compounds after treatment with the sorbent to the area of the reference standard that was not subjected to decontamination. With few exceptions, relative standard deviations (RSD) of PAH10, MOAH, and *n*-alkane areas were below 12%, 15% and 7%, respectively.

Figure 1 shows PAH10 removal rates obtained in trials A, B, and C.

With the exception of amorphous silica, the percentage removal rate of PAHs increased as the amount of sorbent material increased. With the exception of PB, probably because of its long alkyl chain, even when 100 mg of sorbent (half the optimal amount to be used for bleaching oils) was used, samples treated with AC or AABE/AC showed almost complete removal of PAHs.

The removal properties of AC against heavy parent PAHs in both polar (water) and non-polar (oil) environments are well known, but this is the first evidence of clear removal of low alkylated PAHs. Concerning the other sorbent materials, NBE and AABE showed a similar behavior and reached a removal rate higher than 10% only for heavier PAHs (starting from Ch) when using 500 mg of the sorbent. Per and 7MBaP reached a removal rate around 30–45%. AmSi showed negligible removal for all PAHs, even at the highest amount (500 mg).

Figure 2 shows an overlay of the MOSH and MOAH traces of the reference (mixture of PAHs, Gravex oil and *n*-alkanes) and the same sample after treatment with 500 mg of AC and AABE/AC (trial C). As visible from the chromatographic traces, all PAHs elute in the MOAH fraction, while *n*-alkanes elute in the MOSH fraction. Unlike other sorbent materials, AABE/AC released light hydrocarbons giving interference especially in the MOSH fraction.

Interestingly, 500 mg of AC (2 times the optimal amount according to the formula) was able to remove all of the PAH10, except TBB and PB, and part of the MOH from the Gravex (46% of the MOAH and 11% of the MOSH). AABE/AC showed lower removal for the MOH (18% of the MOAH) and negligible removal for the MOSH. Other sorbent materials have proven unable to remove MOH.

The capacity of ACs to remove *n*-alkanes has been reported by other researchers (Nwali, 2014; Bergaoui *et al.*, 2018), but no information was available for the other tested sorbents. This is of interest because of their presence in varying amounts in vegetable oils and fats and the possible competing effect against PAHs and MOH.

AABE and AmSi showed poor affinity towards *n*-alkane. They removal rates were all less than 5%, close to the variability of the data. Interestingly, NBE showed a certain capacity to remove long-chain *n*-alkanes, which became well evident (>10% of removal) starting from *n*-C_{18}, reaching maximum removal rates around 80% for *n*-C_{40}. This could be due to a different composition of the earths or the fact that acid activation treatment may have changed the surface chemical composition, making it more polar (Hussin *et al.*, 2011) and thus less likely to retain *n*-alkanes.

As expected from literature data, AC showed high removal rates, particularly for longer carbon chains. This is probably because long carbon chains establish more interactions with the active sites of the sorbent materials and are therefore better retained. Solubility is another factor that must be considered. Indeed, as the length of the hydrocarbon chain increases, solubility in solvent decreases (Jennings and Weispfennig, 2005). Compared to AC, AABE/AC showed removal rates > 10% starting from *n*-C_{20}, instead of *n*-C_{16}, reaching removal rates > 90% starting from *n*-C_{34} instead of *n*-C_{28}. Since the commercial mixture contained only 5% of AC (corresponding to 50 mg), this result was surprising. Further studies are needed to investigate the behavior of different ACs and bleaching earths and their combination.

Figure 3 shows the removal rates of each *n*-alkane for NBE, AABE/AC and AC (trial C), showing how they clearly increase with increasing carbon chain length.

3.2 Focus on the activated carbon

Later, attention was focused on better investigating the decontamination properties of increasing amounts of AC against the target analytes. This experimental part included trials D (PAH10 only), E (mixture of PAH10, Gravex and

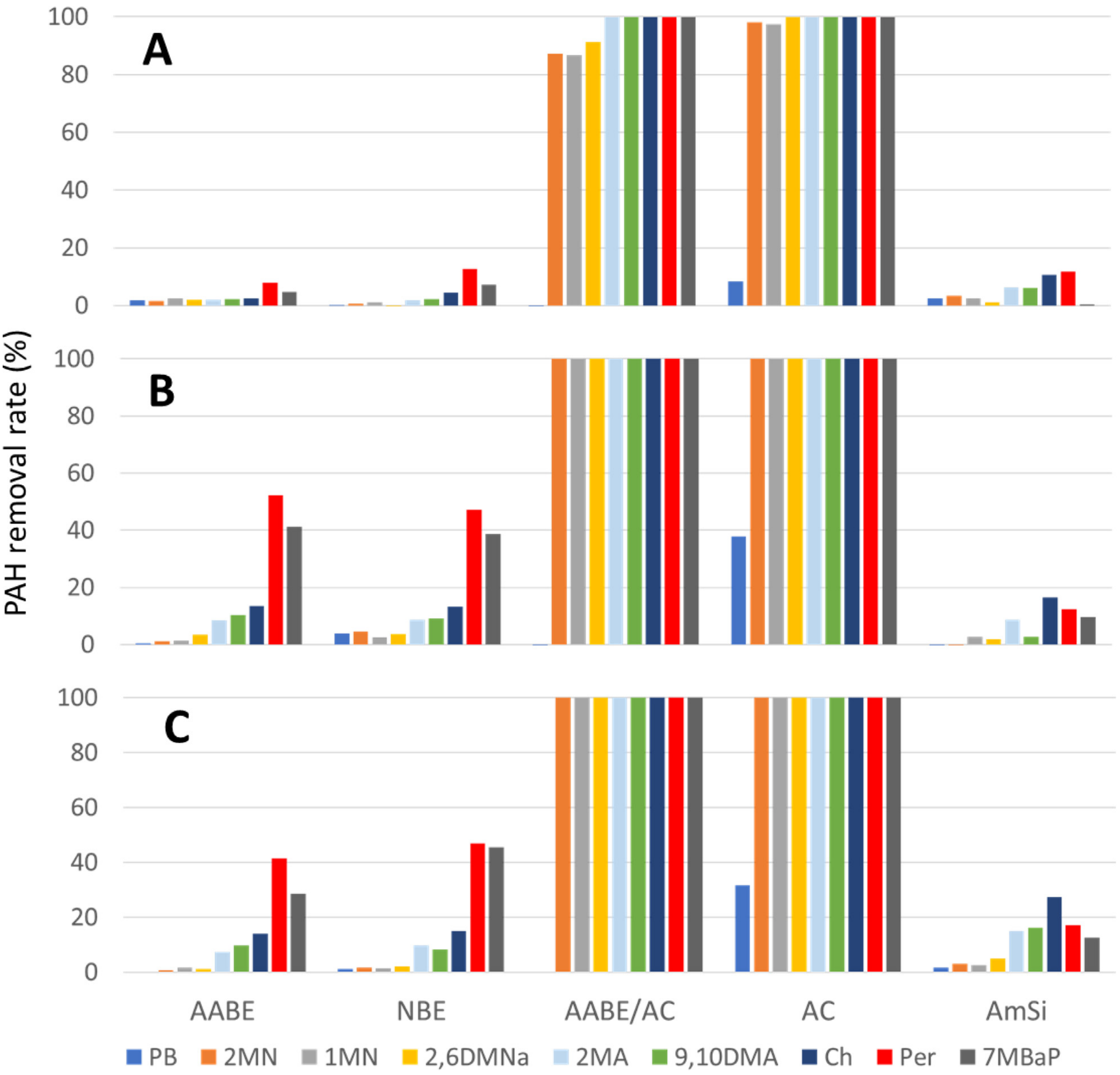

Fig. 1. Average removal rates of PAH10 obtained with different sorbent materials in trial A, B and C. Data are the average of three replicates at different contact times (RSD < 12%). PB, pentylbenzene; 2MN, 2-methylnaphtalene; 1MN, 1-methylnaphthalene; 2,6DMN, 2,6-dimethylnaphthalene; TBB, 1,3,5-tritert-butylbenzene; 2MA, 2-methylanthracene; 9,10DMA, 9,10 dimethylanthracene; Ch, chrysene; Per, perylene; 7MBaP,7-methylbenzo[a]pyrene.

n-alkanes), and F (Gravex only). Since no appreciable differences were observed from previous trials using different contact times, these batch experiments were conducted using a single contact time of 60 min.

Figure 4 reports the comparison of percentage removal rates of the lighter PAH10 at increasing AC amounts for trial D (only PAH10) and for trial E (PAH10 in the presence of MOH and *n*-alkanes). Since, starting from 2MA, complete removal (100%) was achieved in both cases with only 10 mg of AC, data referring heavier PAHs are not shown. The removal rates observed for the lighter PAHs in the presence of compounds that can compete for the active sites of the sorbent (MOH and n-alkanes), were not significantly lower than those obtained for PAH10 alone, when considering the RSD of 4 replicates of the same sample (10%).

As previously observed, the decontamination capacity against PAH10 increased as sorbent amount increased. The higher affinity towards heavier PAHs can be explained by taking into consideration the type of interactions that take place. The delocalized electrons present on the aromatic rings are able to give $\pi - \pi$ interactions with the delocalized electrons present in the active sites of the carbon (Dowaidar *et al.*, 2007). Thus, as the number of aromatic rings increases, this effect becomes increasingly relevant, leading to a better decontamination capacity against heavier PAHs.

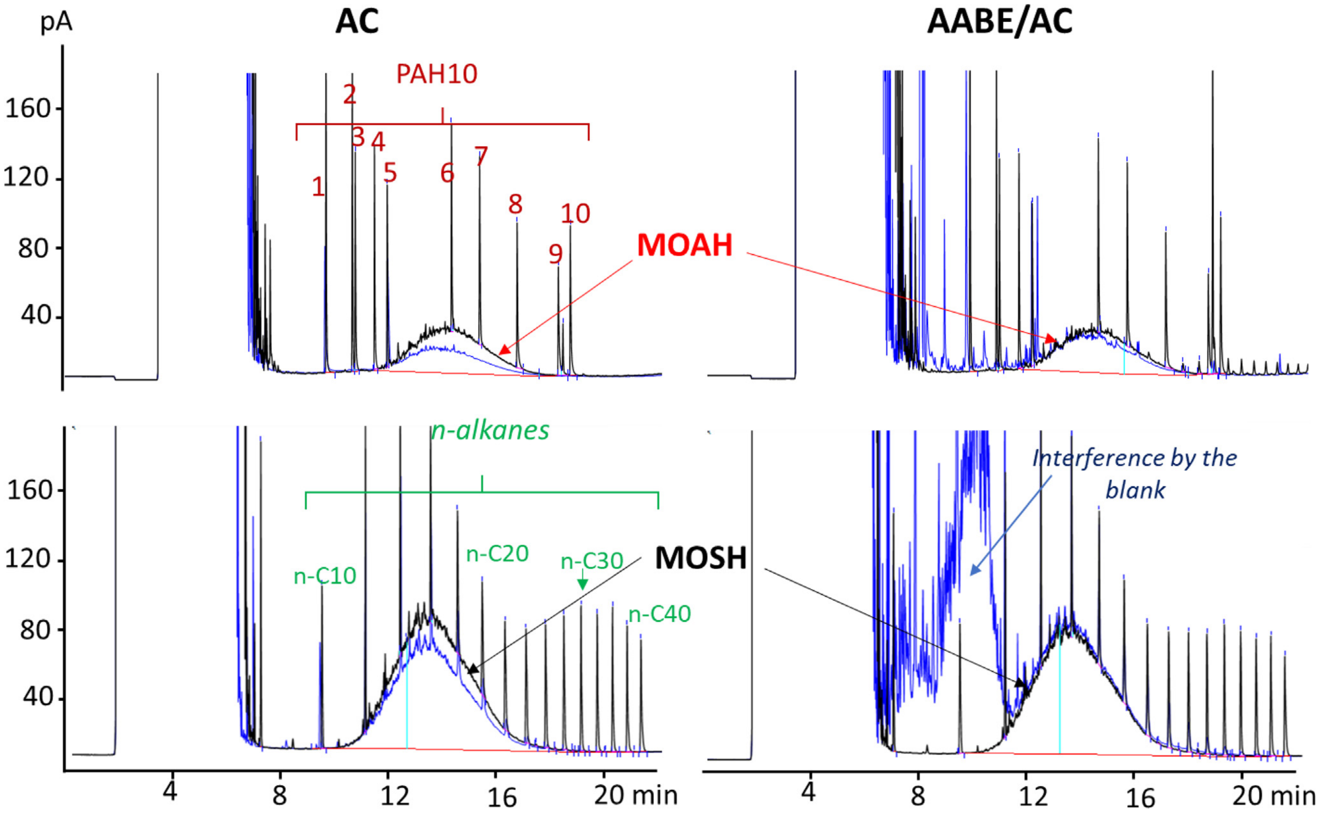

Fig. 2. Overlay of the LC-GC-FID chromatograms (MOAH and MOSH fractions) of the reference solution of trial C (in black) and the corresponding samples after treatment with AC and AABE/AC (in blue). 1, pentylbenzene; 2, 2-methylnaphtalene; 3, 1-methylnaphthalene; 4, 2,6-dimethylnaphthalene, 5, 1,3,5-tritert-butylbenzene; 6, 2-methylanthracene, 7, 9,10 dimethylanthracene; 8, chrysene; 9, perylene; 10, 7-methylbenzo[a]pyrene.

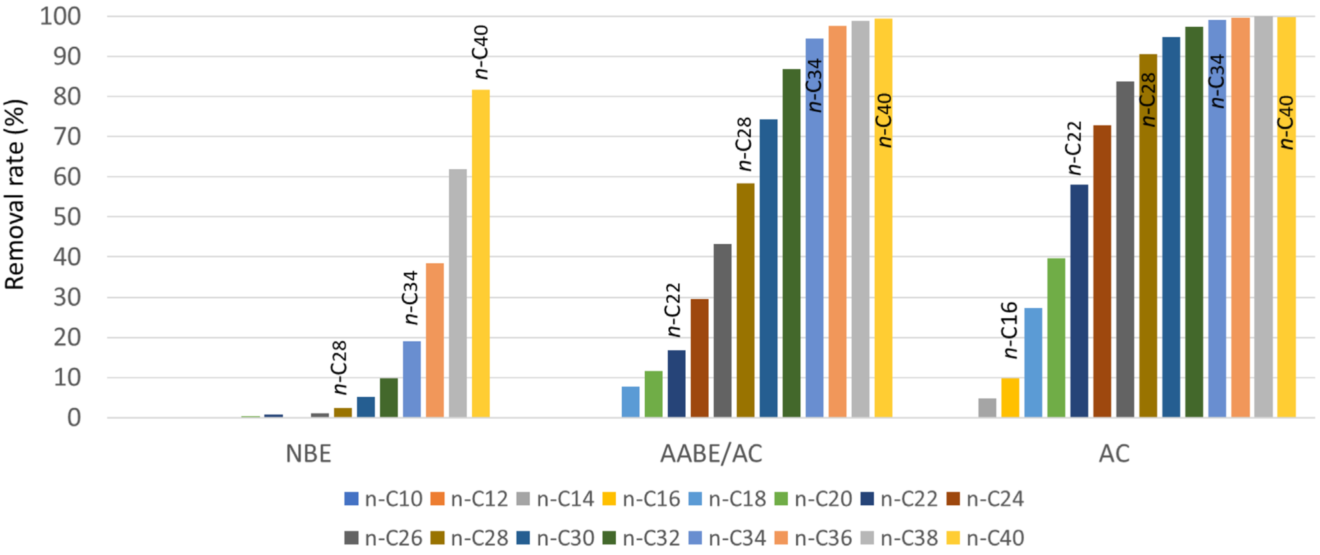

Fig. 3. Average *n*-alkane removal rates obtained with 500 mg of NBE, AABE/AC and AC (trial C). Data are the average of three replicates at different contact times (RSD < 7%).

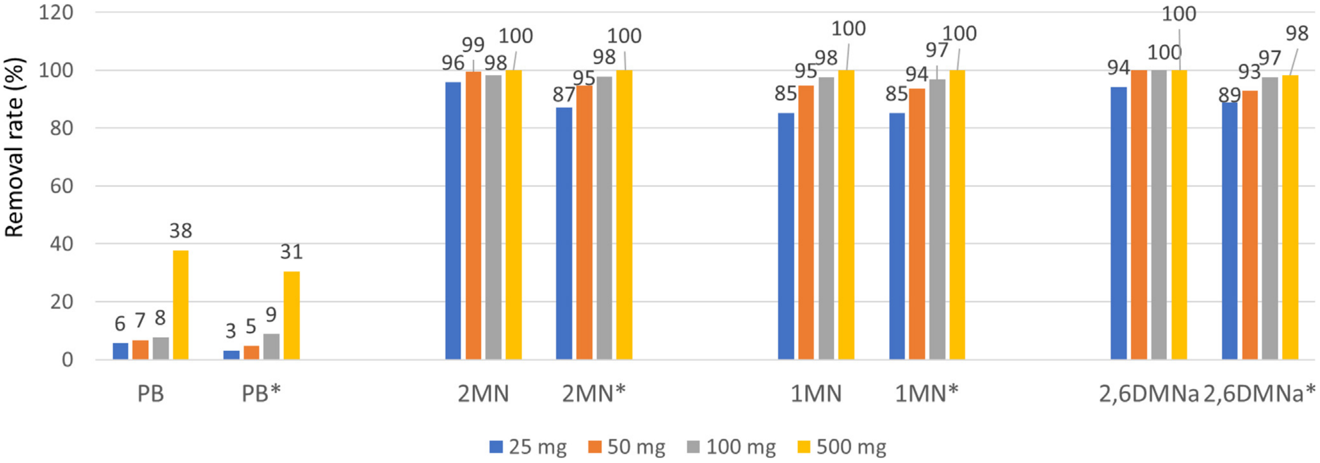

Fig. 4. Lighter PAH10 removal rate at increasing AC amounts in trial D (only PAH10) and in trial E* (PAH10 in the presence of MOH and *n*-alkanes). The asterisk indicates the presence of MOH and *n*-alkanes. PB, pentylbenzene, 2MN, 2-methylnaphthalene, 1MN, 1-methylnaphthalene, 2,6DMN, 2,6-dimethylnaphthalene.

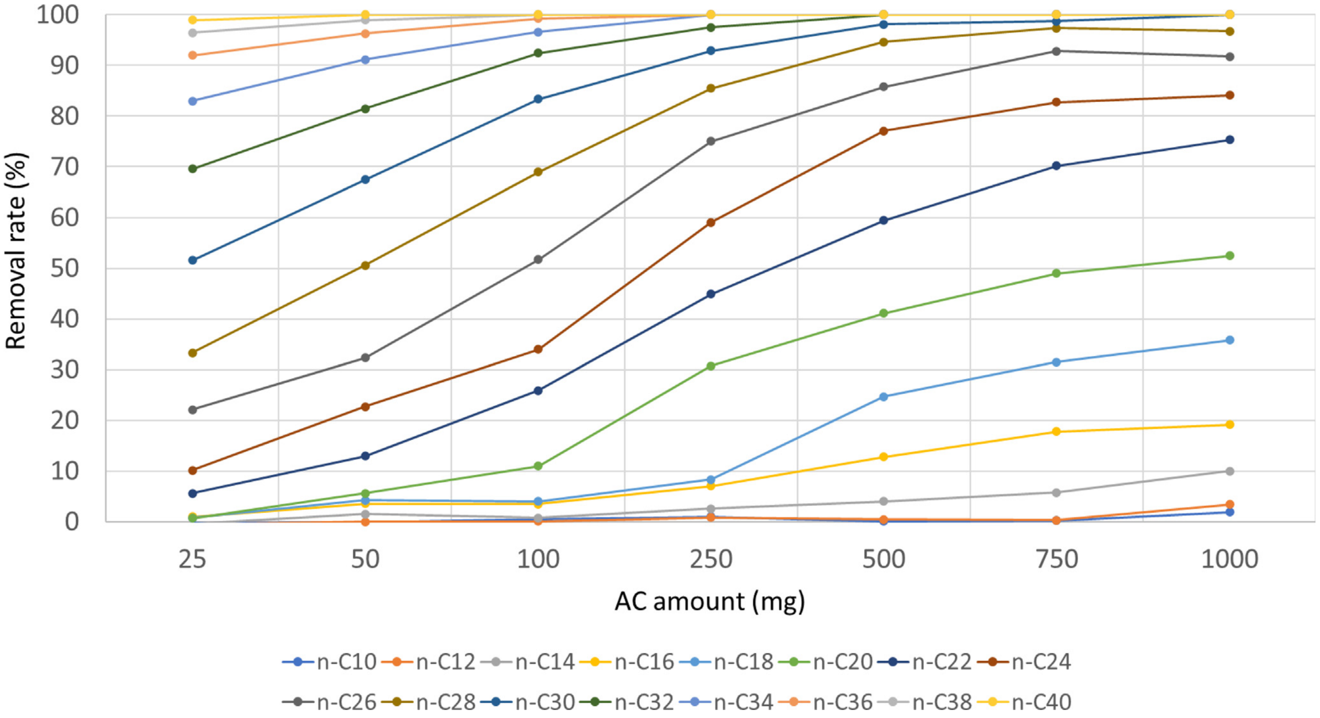

Fig. 5. Trend of *n*-alkane removal as the amount of AC increases (trial E).

Figure 5 shows the trend of each single *n*-alkanes, which indicates that the amount of AC to achieve complete removal (100%) decreases with increasing carbon chain length. Heavier hydrocarbons required lower amounts of sorbent to achieve complete removal, while lighter ones require higher amounts. Lighter hydrocarbons such as *n*-C_{10} and *n*-C_{12}, were hardly removed at all.

Figure 6 compares MOSH and MOAH removal rates at increasing AC amount when Gravex was present in the solution alone (trial F) or mixed with PAH10 and *n*-alkanes (trial E). MOH removal at increasing AC amount, in the tested concentration range, was well described with a logarithmic trend for the MOAH and a linear trend for the MOSH, with coefficient of correlations higher than 0.98 in all cases. It was surprising to observe that part of the MOSH were also removed, although at much lower levels than the MOAH. When using the optimal AC amount (250 mg), calculated based on the formula previously reported, MOAH removal was around 40%, while MOSH removal was below 10%. In the presence of PAH10 (at 100 ng/mL each) and *n*-alkanes, the removal rate was clearly lower, confirming a competitive behavior. Probably this is because of the higher affinity of PAHs for active carbon sites.

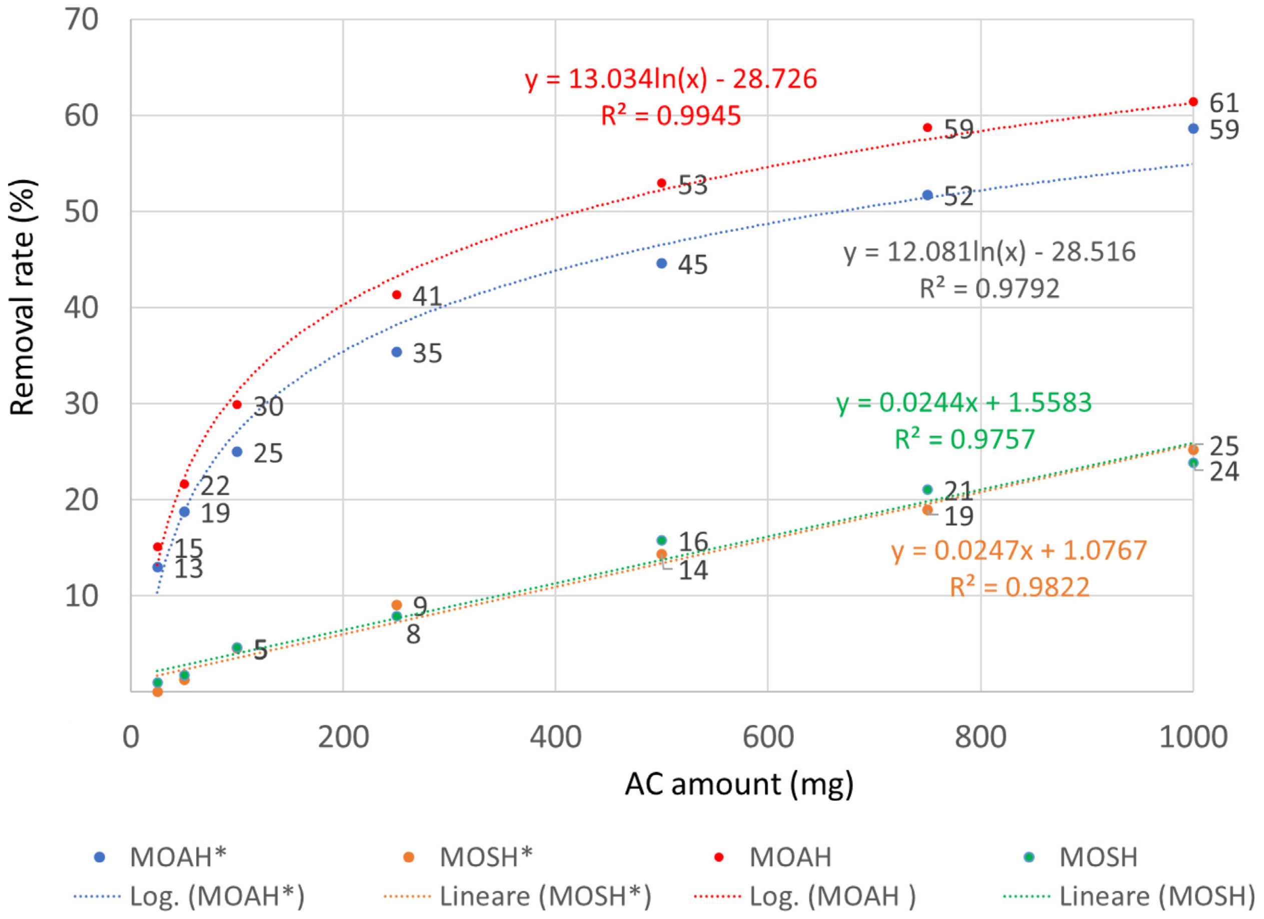

Fig. 6. MOSH and MOAH removal rates with increasing amount of AC in the presence (trial E)* or absence (trial F) of PAH10 and *n*-alkanes.

It is important to underline that further work is needed to translate the results obtained in hexane to a real oil matrix. However, based on some preliminary results, that will be the object of a forthcoming paper, a good correlation was found between the results obtained in *n*-hexane and vegetable oil. Percentage removal rates obtained for a wider range of alkylated PAHs were lower than those obtained in solvent, but still satisfactory, especially for little alkylated compounds with 3 or more benzene rings.

4 Conclusions

The presence of contaminants in oils, such as PAHs and MOH, is a current problem due to their hazardousness to human health. In this work, the decontamination properties of different sorbent materials, commonly used for oil bleaching, were tested against selected mixtures of alkylated PAHs and MOH, using a simple model system in which vegetable oil was replaced by a non-polar solvent (*n*-hexane). Among the tested sorbents, only AC and AABE/AC possess relevant decontamination properties. The ability of AC to remove not only parent PAHs but also alkylated PAHs and MOH was confirmed, with higher percentage removal rates for the MOAH. The MOSH fraction showed an appreciable removal rate only when an amount of AC much higher than that commonly used during the bleaching step was used. Further studies including a higher number of alkylated and non-alkylated PAHs are needed to understand the effect of the alkylation degree. Compounds with longer alkyl substituents (PB) or high steric hindrance are poorly removed. TBB, a monoaromatic compound of high steric hindrance was never removed. MOH removal also depends on the co-presence of heavy PAHs (alkylated and non-alkylated), with higher affinity toward AC. The effect of *n*-alkanes deserves further investigation. The results obtained with this basic research hint at the possibility to remove the most toxic MOAH components (polyaromatic compounds with 3 or more benzene rings with low alkylation degree) by exploiting the adsorption properties of activated carbon. The developed model system allowed to simplify and speed up the analysis work by avoiding matrix interferences (mainly from olefins), but results obtained must be translated to the actual matrix (edible oils or fats) and several other parameters here neglected (matrix composition, temperature effect, water addition, vacuum applied, etc.) need to be investigated.

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Conflicts of interest

The authors declare no competing interests.

Author contribution statement

Sabrina Moret: conceptualization, methodology, writing-original draft preparation, supervision, funding acquisition.

Anna Piazza: investigation, formal analysis, validation, data curation, visualization.

Marouane Bouguerra: formal analysis, data curation, validation.

Laura Barp: conceptualization, supervision, writing – Review & Editing.

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