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Super-Critical Fluid Extraction (SFE) with CO2 as decontamination step for recycling polyethylenes for food contact

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ABSTRACT

The recycling of polyolefins remains a significant challenge in the context of food contact materials (FCM) due to contamination by both volatile and non-volatile compounds. Supercritical Fluid Extraction (SFE) with carbon dioxide (CO_2) has emerged as a promising technology for being included as an efficient step of decontamination or postconsumer polyolefins, ensuring their safety and quality for food contact applications. This study evaluates the capability of SFE to decontaminate postconsumer polyolefin-based materials, including multilayer polyethylene (PE) and polyamide 6,6 (PA-6,6) plastic bags, high density polyethylene (HDPE) containers, and postconsumer HDPE packaging, all previously in contact with food. A non-targeted analytical approach was applied using headspace solid-phase microextraction gas chromatography-mass spectrometry (HS-SPME-GC-MS) and ultrahigh performance liquid chromatography coupled to a quadrupole-time-of-flight mass spectrometer (UPLC-QTOF-MS) to detect and semi-quantify contaminants before and after SFE treatment and a total of 121 compounds were detected in this non-target analysis. Among them, several common plastic additives and various food-derivative compounds, degradation or oxidation products of these additives were found. The results demonstrated up to 99 % decontamination efficiency for volatile compounds and 75 % for non-volatiles, based on the total concentration of compounds before and after the SFE process. These efficiencies highlight the potential of SFE as a critical step for enhancing the quality of recycled polyolefins. The study underscores the role of SFE in advancing the recyclability of polyolefins within the framework of a circular economy. By addressing contamination challenges—both chemical and structural—and enabling the safe reuse of materials in food contact applications, this technology contributes to reducing plastic waste and promoting sustainable material management.

1. Introduction

Plastics have revolutionized modern life due to their versatility, durability, and cost-effectiveness (Hopewell et al., 2009), but their extensive use in food contact materials (FCMs), cosmetic and pharma has raised significant environmental and safety concerns (Ragaert et al., 2017). Among these materials, polyolefins such as polyethylene (PE) and polypropylene (PP) dominate the market due to their chemical stability, lightweight nature, and adaptability, comprising approximately 70 % of all FCMs (*Circular Polyolefins* — PCEP.Eu, 2024; Geueke et al., 2018). However, in a circular economy, the plastic waste needs to be correctly processed, being recycling processes one of the most attractive approaches to provide a new life to plastics. Among the different technologies, mechanical recycling is one promising

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Abbreviations: $SCCO_2$, Super-critical CO_2 extraction; FCM, food contact materials; SFE, supercritical Fluid Extraction; HS-SPME-GC-MS, Headspace Solid-Phase Microextraction coupled with Gas Chromatography-Mass Spectrometry; UPLC-MS/QTOF, Ultra-Performance Liquid Chromatography coupled with Quadrupole-Time of Flight Mass Spectrometry; IAS, Intentionally Added Substances; NIAS, Non-Intentionally Added Substances; PP, polypropylene; PE, polyethylene; PET, polyethylene terephthalate; NIAS, non-intentionally added substances; IAS, intentionally added substances; CO_2-sc, CO_2 in a supercritical state; MBPR, Manual Back-Pressure Regulator; ABPR, Automatic Back-Pressure Regulator; DE, decontamination efficiency.

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alternative. However, recycling polyolefins remains a formidable challenge, particularly when considering compliance with the stringent safety and quality standards that recycled materials require, either in food contact applications, cosmetic or pharma products (Geueke et al., 2018; Pérez-Bondía et al., 2024). Unlike polyethylene terephthalate (PET), which has achieved substantial success as FCM recycling due to its simpler composition and low contamination levels (Pérez-Bondía et al., 2024).

The main recycling barriers arise from contamination by non-intentionally added substances (NIAS) and intentionally added substances (IAS), which can migrate into food and pose potential health risks (Nerín et al., 2022; Oldring et al., 2023). These challenges result from the inherent characteristics of polyolefins' chemical structure and their high capacity for chemical absorption and diffusion of substances, making their decontamination and requalification for food contact applications a critical focus in the field of plastic recycling (Novák et al., 2016). In addition to organic contaminants, recent reviews have also highlighted the role of inorganic impurities such as heavy metals, which can accumulate during recycling and are equally important to assess alongside volatile and non-volatile organic substances when evaluating decontamination efficiency (Undas et al., 2023).

Analytical chemistry plays a crucial role in ensuring the safety of recycled FCMs. Advanced techniques such as gas chromatography-mass spectrometry (GC-MS) and liquid chromatography coupled to high-resolution mass spectrometry (LC-MS/QTOF) are indispensable for untargeted analysis, identification and quantification of IAS and NIAS in polyolefins (Oldring et al., 2023; Vera et al., 2018) before and after the recycling process. These methods enable non-targeted screening and semi-quantification of a wide range of volatile and non-volatile contaminants, offering critical insights into the chemical composition of post-consumer recycled materials (Su et al., 2021; Vera et al., 2023). Such analyses are essential to assess the suitability of recycled polyolefins for food contact applications and to comply with the stringent regulatory standards established by the EU (EC, 2011). However, it is also important to note that in the United States, the Food and Drug Administration (FDA) provides clearance of recycling processes through the issuance of non-objection letters (NOLs), which serve as the U.S. equivalent to EFSA evaluations in Europe (Cecon et al., 2021).

The European Union has developed a comprehensive legislative framework, primarily Regulation EU 10/2011 (EC, 2011), and its 19 amendments, which governs the use of plastic materials intended for food contact. This regulation includes a positive list of authorized substances known as Intentionally Added Substances (IAS), such as monomers, stabilizers, antioxidants and many plastic additives. However, the safety of recycled materials is further complicated by the presence of Non-Intentionally Added Substances (NIAS), which may originate from polymer degradation, additives, impurities, or chemical interactions during the material's lifecycle (Nerin et al., 2013, 2022). These substances pose potential risks due to their migration into food, emphasizing the critical need for thorough risk assessment and compliance verification. As part of this evaluation, both EFSA and FDA require the performance of a challenge test, in which surrogate contaminants are introduced into plastics to demonstrate the decontamination efficiency of the recycling process before it can be approved for food contact use (Cecon et al., 2021).

In parallel, circular economy has emerged as a central framework for addressing the environmental challenges posed by plastic waste (Rhodes, 2018). EU initiatives such as the European Strategy for Plastics in a Circular Economy (Plastics Strategy - European Commission, 2024) aim to promote the recycling and reuse of plastics, with specific targets for increasing the use of recycled materials in packaging. For polyolefins, achieving these targets requires overcoming technical barriers related to contamination and ensuring compliance with safety regulations. The successful integration of recycled polyolefins into FCMs would not only reduce the environmental footprint of plastic production but also create economic opportunities through the development of sustainable material recovery processes (Rhodes, 2018). Beyond food applications, recent industry-based frameworks such as those developed by the Cospatox consortium and the Elipso-FEBEA working group are establishing safety guidelines for contact-sensitive applications like cosmetics, further broadening the scope of recycling safety assessments (CosPaTox, 2024; Elipso/FEBEA, 2024).

To address these challenges, innovative decontamination technologies are being explored. Supercritical Fluid Extraction (SFE) with carbon dioxide (CO_2) has been widely used to extract valuable substances from vegetables (Giménez-Rota et al., 2020; Langa et al., 2019; Mur et al., 2021, 2022), materials (Batlle et al., 2005), food and in many other sectors(Nerín et al., 2002). It is also a common technology applied to extract caffeine from coffee at industrial level and for sure to other industrial applications and it has recently gained attention as a promising decontamination technology for postconsumer polyolefins (Alassali et al., 2020; Singh et al., 2023). Besides, this process does not require the use of toxic solvents, making it an eco-friendly alternative that combines efficiency with sustainable chemistry, thereby minimizing environmental impact. This technique utilizes supercritical CO_2 as a solvent to extract volatile and non-volatile contaminants from plastics, offering a sustainable and efficient alternative to traditional cleaning methods (Ahmad et al., 2019). Unlike other decontamination processes, such as thermal desorption or solvent washing, SFE operates under relatively mild conditions, preserving the polymer's structural integrity while achieving high decontamination efficiencies (Singh et al., 2023). The scalability and tunability of SFE make it a potentially key technology for the recycling of polyolefins, particularly for high-value applications like FCMs. Its effectiveness has been demonstrated in the removal of additives such as phthalates, stabilizers, plasticizers, antioxidants, and hydrocarbon fractions, but these target studies have focused exclusively on the control of IAS (Alassali et al., 2020; Salafranca et al., 1999; Singh et al., 2023).

This study aims to evaluate the capability of SFE to remove both IAS and NIAS contaminants from different polyolefins like PE-PA-6,6-PE bags, HDPE containers and post-consumer HDPE closures. As a novel approach, a non-targeted analysis was carried out to identify and semi quantify volatile compounds by Headspace Solid-Phase Microextraction coupled with Gas Chromatography-Mass Spectrometry (HS-SPME-GC-MS) and non-volatile compounds through Ultra-Performance Liquid Chromatography coupled with Quadrupole-Time of Flight Mass Spectrometry (UPLC-MS/QTOF). This research contributes to the development of sustainable strategies for the recycling of FCM plastics, with implications for both public health and global environmental goals.

2. Material and methods

2.1. Chemicals and reagents

Ethanol absolute (HPLC quality) from Panreac (Barcelona, Spain and ultrapure water from a Mili-Q Ultramatric Wasserlab GR 216071 (Madrid, Spain) were used to prepare the aqueous simulants. Methanol was purchased from Panreac (Barcelona, Spain). Standards were purchased from Sigma-Aldrich (Madrid-Spain): C7-C40 alkanes solution, 2-methyl-1,3-dioxolane (CAS: 497–26–7), toluene (108−88−3), benzaldehyde (100−52−7), hexadecane (544−76−3), acetophenone (98−86−2), D-limonene (5989–27–5), (-)-β-pinene (19902–08–0), p-cymene (99−87−6), estragole (140−67−0), hexadecanoic acid, methyl ester (112−39−0), 2-tridecanone (593−08−8), nonanoic acid (112−05−0), α-terpineol (8000–41–7), nonanal (124−19−6), benzoic acid (65−85−0), 2,4-di-tert-butyl phenol (96−76−4), 1-hexadecanol (36653–82–4), naphthalene (91−20−3), BHT (128−37−0), dibutyl phthalate (84−74−2), 2,6-diisopropylnaphthalene (24157–81–1), N,N bis (2-hydroxyethyl) dodecanamine (120−40−1), hexadecanamide (629−54−9), oleamide (301−02−0), erucamide (112−84−5), bis(2-ethylhexyl) adipate (103−23−1), docosanamide (3061–75–4), Irgafos 168 OXO (95906–11–9), Irgafos 168 (31570–04–4), caffeine

(58–08–2), caprolactam (105–60–2), hexadecylamine (143–27–1), 7,9-Di-tert-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione (82304–66–3), Ralox 35 (6386–38–5), N,N′-1,2-Ethanediylbis[octadecanamide] (110–30–5), Irganox 1076 (2082–79–3), triethanolamine (102–71–6), glyceryl octadecanoate (31566–31–1) and glyceryl dihexadecanoate (27638–00–2).

2.2. Samples

Four polyolefin samples were analyzed. Sample 1 (S1) consisted of HDPE closures of commercial soft-drinks, sample 2 (S2) HDPE rigid containers, sample 3 (S3) PE-PA-6,6-PE bags (PE is the outer layer and PA-6,6 is the inner layer. The approximate ratio by weight was 85/15 PE/PA-6,6) and sample 4 (S4) post-consumer collected HDPE closures. All the above-mentioned samples were previously in contact with food.

2.3. Carbon Dioxide Supercritical Extraction

Fig. 1 presents a schematic diagram of the system where the main components of the supercritical fluid extraction (SFE) system are illustrated. The equipment corresponds to a laboratory-scale unit from TharSFC (Thar Instruments, USA), located at the Sustainable Chemistry Laboratory of the I3A Institute (University of Zaragoza) and operated by the GATHERS research group. This equipment is designed for the selective extraction of volatile and semi-volatile compounds, particularly from solid matrices using supercritical CO_2 as solvent.

At the start of the process, CO_2 is supplied from a pressurized cylinder then compressed by a P200 high-pressure CO_2 pump and directed through a heat exchanger that raises its temperature. A six-zone temperature controller ensures precise thermal regulation throughout the system, supported by two power control relay boxes. When needed, a cosolvent pump (Series III 310SFX01, 10 mL) introduces an auxiliary solvent to improve extraction efficiency. Once the CO_2 is both heated and pressurized, it enters the reactor, a 1 L stainless steel vessel equipped with a screw-cap lid for hermetic sealing and surrounded by a heating jacket for temperature control. The CO_2 enters the reactor from the bottom at supercritical conditions and acts as a selective solvent for the target compounds. The extracted materials exit the reactor through the top, passing through an automated backpressure regulator until they reach two cyclone collectors (500 mL) arranged in series where the compounds are collected. Pressure at each outlet is regulated by manual back-pressure regulators, rated up to 10,000 PSI. The system also includes a SITRANS F C mass flowmeter (SIEMENS) and a specialized software ensuring a precise control during the entire extraction process.

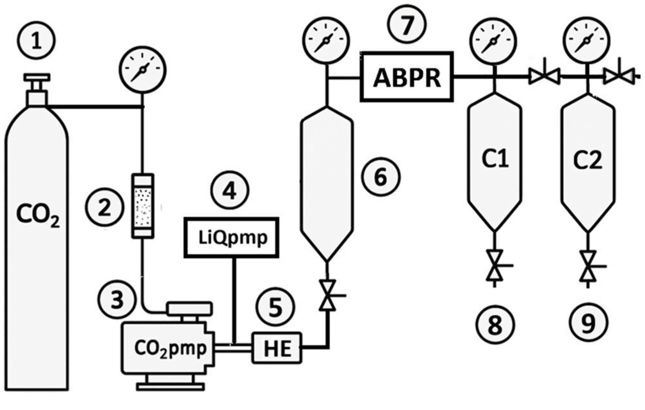


Fig. 1. SFE reactor used. 1) CO_2 Cylinder/Bottle 2) Refrigerating Batch 3) CO_2 Pump 4) Cosolvent pump 5) Heat Exchanger 6) Reactor 7) Automatic Back-Pressure Regulator (ABPR) 8 and 9) Collectors.

2.4. Optimization approach

Considering the diversity of samples in terms of both material type and conformation and given that this study represents a proof of concept, optimization efforts were focused exclusively on Sample 4 (post-consumer bottle closures), as it was available in the largest quantity. Parameters such as particle size, washing efficacy post-reactor processing, and various reactor operating conditions were systematically evaluated to find the best conditions of use with these samples.

Particle size was studied to improve the contact between the plastic and CO_2 in a supercritical state. Three sample preparation methods for closures prior to their introduction into the reactor were evaluated: (i) whole closures without any pretreatment, (ii) chopped closures with sizes ranging from 0.3 to 1 cm, and (iii) ground closures with particle sizes smaller than 0.3 cm. An additional sample preparation was conducted by rinsing the samples exiting the reactor with cold ultrapure water, allowing them to dry, and subsequently washing them with ultrapure water under agitation for 2 h at 70 °C (iv). Additionally, SFE repeatability was evaluated by introducing the same batch of sample on three different days to have three fully independent replicates. In all cases, the sample was mixed with inert glass beads to favour the better access of CO2 flow to all plastic particles.

The decontamination efficacy of supercritical CO_2 was evaluated by testing three discrete reactor operating conditions. This experimental design drew upon established parameters for supercritical fluid extraction (SFE) on recycled high-density polyethylene (rHDPE) and low-density polyethylene (LDPE) (Salafranca et al., 1999). Conditions were structured to systematically vary the two most critical parameters governing SFE efficiency, residence time and solvent power (temperature and pressure), while covering both static (contaminant dissolution) and dynamic (contaminant removal) extraction phases. The following conditions were explored: conditions 1 (Starter), conditions 2 (4 +4) and conditions 3 (90 ºC). The three conditions were designed to establish a baseline protocol with four progressive cycles (Condition 1), to assess the effect of extending the treatment time (Condition 2), and finally to explore the impact of increasing pressure and temperature within a shorter treatment to intensify the extraction (Condition 3). This way, the combination of static and dynamic extraction was covered.

Condition 1: The cleaning process was carried out in four cycles, each lasting 1 h, with 30 min of dynamic operation and 30 min of static operation per cycle. During these cycles, CO_2 was pumped until the following pressures reached in the reactor: 150 bar in the first cycle, 250 bar in the second cycle, 350 bar in the third and fourth cycles. The reactor temperatures were maintained at 40, 60, 80 and 80 °C, respectively. The CO_2 flow rate was kept constant at 35 g/min throughout the process. The operating conditions in the collectors (C1 and C2) were set to 90 bar and 45 °C, and 30 bar and 30 °C, respectively. The total processing time was 4 h for each plastic load. At the end of each process, after depressurizing the equipment, the extracted residues were collected from the collectors (C1 and C2), along with the cleaned plastic material that remained in the reactor.

Condition 2: Additional tests under the same conditions were conducted applying the same conditions but with a double number of cycles (4 +4).

Condition 3: Another test was carried out with only 4 cycles but with higher pressure and temperature conditions: 150 bar in the first cycle, 250 bar in the second, 400 bar in the third cycle, and 400 bar in the fourth cycle, along with reactor temperatures of 40, 60, 90 and 90 °C, respectively.

2.5. Sample treatment

Soft-drink bottles (S1) were stored upside down for 10 days at 40ºC to provide a controlled worst-case beverage exposure. After that, closures were cleaned with ultrapure water and milled with liquid nitrogen (once dried) to reduce its size and homogenize them. Due to the small number of closures, the particle size was not reduced as expected to 0.3 cm.

HDPE rigid containers (S2) posed significant challenges during mechanical processing due to their thickness, making it difficult to reduce the material to small pieces. Attempts to mill the sample with liquid nitrogen were unsuccessful, and manual cutting with a ceramic knife yielded pieces of approximately 0.5 × 0.5 cm at best. However, it was not feasible to process the entire sample into small pieces for reactor introduction. As a result, the sample was introduced into the reactor in larger pieces ranging from 1 to 5 cm.

PE-PA-6,6-PE bags (S3) were cut into small pieces of approximately 0.5 × 0.5 cm using scissors prior to being subjected to supercritical fluid extraction (SFE).

Post-consumer HDPE closures (S4) were first cleaned with ultrapure water and then dried before treatment. Subsequently, S4 underwent different treatments to study the optimal reactor conditions: (i) no treatment (whole closures), (ii) mechanically cut into pieces between 0.3 and 1 cm, (iii) ground with liquid nitrogen to 0.3 cm, and (iv) ground with liquid nitrogen to 0.3 cm and washed with ultrapure water in the ultrasound bath at 60°C for 1 h.

The analysis of polymer samples, both pre- and post-reactor treatment, required two distinct chromatographic methods to quantify a broad spectrum of contaminants. For volatile contaminants, samples were analyzed directly and in triplicate using HS-SPME-GC-MS to ensure high sensitivity and analytical reproducibility. Similarly, for the quantification of non-volatile compounds, a 1.0 g aliquot of each sample was first subjected to an accelerated solvent migration procedure, involving extraction with 18 mL of 95 % ethanol for 2 h at 70ºC. The resulting ethanol extract was then analyzed by UPLC-MS/QTOF.

2.6. *HS-SPME-GC-MS analysis*

An amount of 0.1 g of the milled samples was weighed in 20 mL vials and submitted to headspace-solid-phase-microextraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS). A DVB/CAR/PDMS 50/30 µm fiber was used due to its proven highly efficacy extraction capacity for low and high molecular mass molecules (Chen et al., 2019; Estremera et al., 2024; Su et al., 2020). The CTC Analytics Pal RSI 85 from CTC Analytics AG (Zwingen, Switzerland) coupled to GC-MS equipment GC 8890 gas chromatograph from Agilent (Palo Alto, CA, USA) with an Agilent ultrainert liner (id = 0.75 and 4 mm) was used for the analysis. Compounds were separated with a HP-5 MS column from Agilent (30 cm×0.25 mm, 0.25 µm film thicknesses). The ramp temperature started at 50°C for 5 min, and increased at a rate of 8°C min^{-1} up to a 300°C and held for 10 min. Splitless mode was used and the injector had a temperature of 250°C. Helium was the carried gas used with a flow of 1.2 mL/min. Adsorption was performed at 80ºC for 20 min and the stirring rate conditions were 600 rpm. An Agilent 5977B Mass Spectrometer in SCAN mode from 45 to 450 *m/z* was used with a source temperature of 250ºC to perform the analysis of substances.

2.7. *UPLC-MS/QTOF analysis*

An AcquityTM system coupled to Xevo G2 QTOF detector, both from Waters (Milford, MA, USA) were used to carry out the analysis of non-volatile compounds. BEH C18 column (100 mm×2.1 mm×17 µm) at 40ºC with a flow rate of 0.3 mL/min was used for chromatographic separation. Mobile phases were water (A) and methanol (B) both with 0.1 % formic acid. The gradient started at 95–5 % A-B and shifted to 100–0 % A-B in 7 min, then kept for 4 min and dropped to the initial phase in 2 min, making a total run of 13 min. The injection volume was 10 µL.

Regarding the instrumental parameters, electrospray interface was used. The mass range considered was from 50 to 1200 Da. Acquisition was performed in MS^{E} mode which alternates two functions, one at low energy (6 V) to obtain the exact mass precursor ion spectra and other at high ramp energy (10–30 V) to obtain the exact mass fragment ions. Source temperature 150ºC, desolvation gas temperature 450ºC and desolvation gas flow 650 L/h.

Leucine enkephalin was employed for online mass correction and a text mix solution from Waters was injected every 25 injections to ensure mass accuracy of the results and several QC pooled samples were injected for each simulant. MassLynx version 4.2. software from Waters was used for acquisition.

2.8. *Identification and quantification of compounds*

2.8.1. *Identification and quantification of volatile compounds by MS-DIAL*

Chromatograms were processed using MS DIAL software version 4.9 (Tsugawa et al., 2015) to identify, deconvolute and perform the alignment of characteristic peaks. MS DIAL parameters were set as follows: a minimum detected peak height of 2000, a sigma window value of 0.5 and 10 EI spectra cut off. Alignment was performed with a retention time tolerance of 0.075 min and an EI similarity tolerance of 70 %. Identification was carried out with NIST 20 modified library and retention index (RI) experimentally calculated, with a RI tolerance of 30. Additionally, peaks with a maximum/mean sample fold change of less than 5 and those that were not present in all three replicates were removed.

To improve the reliability of the identification, mass spectra and retention index (RI) of all the candidates were manually checked. Moreover, identification workflow described in the literature (Su et al., 2019) was used along with the identification confidence proposed (Schymanski et al., 2014). It contains 5 levels. Level 1: Confirmed by a reference standard with MS, MS/MS and retention index match (For GC); Level 2: Probable structure which is subdivided into 2a (MS and MS/MS or retention index) and 2b (No other structure fits the experimental information); Level 3: Tentative candidate where exists evidence for possible structure but insufficient information for one exact structure only; Level 4: Unequivocal molecular formula; and Level 5: Exact mass (*m/z*).

Once the tentative identification was performed, suitable and available standards were prepared to quantify or semi quantify each compound. In absence of pure standard, the identified compounds were quantified with another one with similar chemical structure.

2.8.2. *Identification and quantification of non-volatile compounds*

The identification was performed through the following steps (Nerín et al., 2022): comparison of extraction chromatograms with blanks and subsequent peak detection for the extracted compounds; determination of the molecular formula; database search to propose possible structures corresponding to the identified formula; verification of the proposed structure through the MassFragment® tool, comparing it to the compound's mass spectrum; and, when a commercial standard was available, injection of the standard to confirm retention time and mass spectrum consistency.

For the quantification of the detected compounds, calibration curves were generated using the standards of the corresponding compounds at increasing concentrations. In cases where the standard was not available, quantification was performed using a standard with a similar molecular structure.

2.9. *Risk assessment*

To assess the potential risk of the identified compounds, each substance was first checked against the positive list established in Regulation (EU) No 10/2011 (EC, 2011) in order to determine its specific migration limits (SML). Compounds not included in this legislation were evaluated using the Threshold of Toxicological Concern (TTC) approach, based on Cramer's classification through the Toxtree® software. This system, together with recommendations from Plastics Europe, classifies compounds into three categories and establishes maximum daily human exposure values: 1.8 mg/kg for Class I, 0.54 mg/kg for Class II, and 0.09 mg/kg for Class III (Koster et al., 2011; Patlewicz et al., 2008).

2.10. Decontamination efficacy calculation

Decontamination efficacy (DE) was calculated as the percentage of decrease of total concentration of semi quantified substances, as shown in Eq. 1 where "C_{after}" is referred to the total concentration of substances after SFE extraction and "C_{before}" to the total concentration before.

$$Decontamination\ efficiency(\%) = \left(1 - \frac{C_{after}}{C_{before}}\right) \times 100 \tag{1}$$

Eq. 1**:** Calculation of decontamination efficacy

The uncertainty was estimated using standard error propagation (Ku, 1966) considering the standard deviations of the three replicates before (SD_{before}) and after (SD_{after}) as shown in Eq. 2.

$$\sigma_{decontamination} = 100 \quad \times \quad \sqrt{\left(\frac{SD_{before}}{C_{before}}\right)^2 + \quad \left(\frac{SD_{after}}{C_{after}}\right)^2 \times \quad \left(\frac{C_{after}}{C_{before}}\right)^2} \tag{2}$$

Eq. 2**:** Estimation of total uncertainty in decontamination efficacy

3. Results

3.1. SFE optimization

The initial experimental conditions for SFE were taken from previous studies working with SFE extraction applied to HDPE and other polymers(Salafranca et al., 1999). Although the main goal of such studies was to apply an exhaustive extraction to measure the contamination degree of the postconsumer polymers, the lessons learned assessed us to select the same optimum temperature as that obtained years ago. In those studies, the temperature was shown as a very critical parameter, as depending on it, the polymer melted inside the reactor. Temperature ranged between 50 and 100 ºC. At low temperature, the SF has a high density and consequently shows high extraction ability. However, the diffusivity of SF is quite low and the extraction is not efficient. At high temperature the density, and consequently the solvation power, decreases, but this effect is stronger than the increase in diffusivity. An optimum value was found at 80 ºC and this was the selected temperature. Extraction time and extraction mode such as static and dynamic or a combination of both, also played an important role. In the modern pilot installations of SFE, as that used in this work, applying both extraction modes in sequential cycles increases the efficiency and save time, as the polymer remains in the same reactor over the whole process. For this reason, sequential cycles applying a gradient of temperature were tested instead of one fixed temperature. A progressive variation of pressure and temperature within a single multi-cycle experiment was considered more practical and representative of a real cleaning process than conducting separate experiments under fixed conditions. This approach reduces material consumption and total processing time while allowing the evaluation of extraction efficiency under gradually intensified conditions. Additionally, it mimics a stepped elution profile, where more volatile or weakly bound substances are removed in the initial cycles, and compounds with stronger retention are extracted in the later, more intense cycles.

The particle size significantly impacts the decontamination rate by controlling the available surface area-to-volume ratio. A smaller particle size enhances the rate of contaminant diffusion from the polymer bulk to the surface for extraction.

DE (decontamination efficacy) subjected to different sample preparation approaches and reactor conditions, focused on the removal of volatile compounds, are shown in Fig. 2. The results highlight the critical role of sample preparation, particularly particle size reduction, and reactor conditions in optimizing contaminant removal.

Whole closures, processed without being milled or any other pretreatment, exhibit the lowest DE, with a value around 30 %. The high variability, as indicated by the standard deviation, might be due to the variability in polymer particle surface area across the experimental runs. This outcome can be attributed to the limited surface area exposed to the reactor environment, which hinders the interaction between the material and the supercritical CO_2. When the closures were cryogenically chopped into smaller pieces ranging from 0.3 cm to 1 cm, the DE increases significantly to approximately 55 %. This improvement underscores the positive impact of particle size reduction on decontamination, as the increased surface area facilitates better interaction with the CO_2 and the reactor's mechanisms. The variability in this condition is also reduced compared to whole closures, indicating more uniform input and thus more uniform contaminant removal.

Further size reduction to particles smaller than 0.3 cm yields near-complete decontamination, with efficacies higher than 95 %. This dramatic improvement highlights the critical importance of maximizing the exposed surface area. This fact emphasizes the idea of applying SFE step to flakes of polymer, e.g. from HDPE bottles, where the surface exposed is much higher than that of small plastic pieces from the closures. The additional washing step with water did not lead to a noticeable increase in efficacy.

Reactor *condition 2 (4 +4)* demonstrates DE similar to those achieved at *conditions 3 (90ºC)* with both reaching 96 % for ground closures smaller than 0.3 cm. This parity between the two sets of conditions highlights the robustness and flexibility of the reactor system in achieving effective contaminant removal from finely ground particles. However, it is worth noting that the SFE conditions, such as temperature, pressure, and the number of cycles, could be further optimized to reach values closer to 100 %.

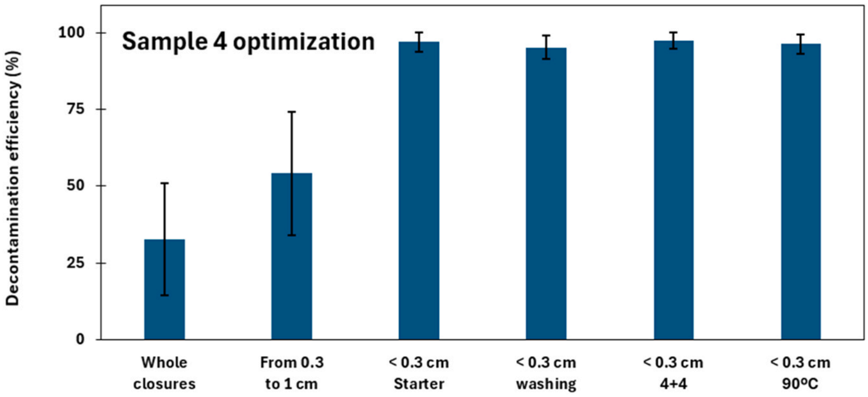


Fig. 2. Decontamination efficacies of different sample preparation procedures and reactor conditions: whole closures, particles from 0.3 to 1 cm, < 0.3 cm and < 0.3 cm washing, under Condition 1; < 0.3 cm under Condition 2 (4 +4) and < 0.3 cm under Condition 3 (90ºC).

To assess whether the differences observed are statistically significant, a one-way analysis of variance (ANOVA) was performed highlighting a significant effect of reactor condition on the total concentration of migrants ($p < 0.001$). Additionally, post-hoc comparisons with Turkey HSD revealed that all modified conditions (whole closures, particles 0.3–1 cm, particles < 0.3 cm, reactor conditions 1, 2 and 3) differed significantly from the initial stage. Among decontamination conditions, 'whole closures' and 'particles 0.3–1 cm' did not differ significantly ($p = 0.194$). However, both are significantly different from the rest of the conditions. In fact, once the particle size is < 0.3, no significant differences were observed ($p > 0.1$) between the treatments applied (conditions 1, 2 and 3).

3.2. Volatile compounds

A total of 65 volatile compounds were identified and semi-quantified after migration in the four different samples. Detailed information on each compound and its decontamination levels is provided in Table S1. Quantification was performed using the standards listed in Table S2. The decontamination efficacy may be seen by comparing the chromatograms of the samples before and after treatment with SFE along with a blank of the SPME fiber, as shown in Fig. 3, where a high number of chromatographic peaks disappear after the recycling process.

Among the identified compounds, a range of volatile substances originated both from the food items themselves and from the FCMs were found. Food-derivative compounds include linalool, which is a common component of essential oils (Aprotosoaie et al., 2014), vanillin widely used as flavoring agent (Walton et al., 2003), estragole, found in herbs and D-limonene and citral which are found primarily in citrus fruits (Lin et al., 2024) and of course very common in soft drinks and many food products.

On the other hand, several volatile compounds originated from the polyolefin additives were identified. Degradation products of Irgafos 168 like 2,4-Di-tert-butylphenol and 2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)- (Estremera et al., 2024) were identified. IAS like Butylated Hydroxytoluene (BHT), a known antioxidant (Estremera et al., 2024; Su, Vera, Salafranca, et al., 2021), showed up to 99 % decontamination efficacy. A variety of aromatic compounds, such as Benzene 1,2,4-trimethyl- (MW = 120 g/mol) and Benzene methanol, α,α,4-trimethyl- (MW = 150 g/mol), were identified as compounds, likely coming from aromatic polymers or adhesives used in packaging. These compounds are of concern due to their potential to be contaminants of the food, especially since they are not commonly present themselves in food products.

Most of them showed high levels of decontamination, up to 99 %, except for sample S2.

Fig. 4 shows heat maps showing each sample's compound decontamination percentages plotted against the volatile compounds' polarity and molecular weight.

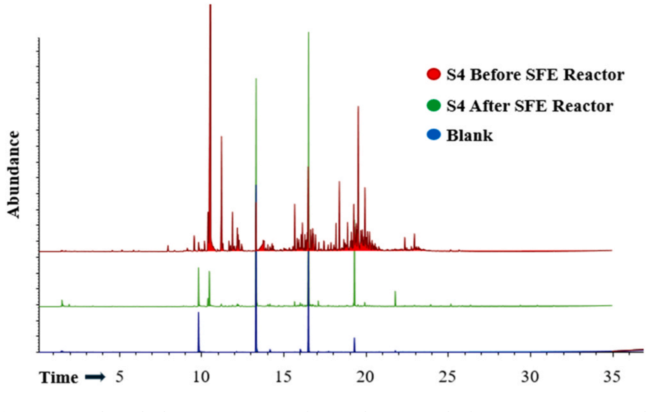


Fig. 3. Overlayed chromatograms of Sample 4 (S4) before SFE reactor (red), after SFE reactor (green) and blank.

The efficiency for S2 is lower, primarily because of its extreme rigidity, which prevented the reduction of sample size to 0.3 cm. A larger or non-uniform particle size results in a significantly reduced specific surface area available for contact with the CO_2. This limitation means that the CO_2 cannot penetrate the sample matrix effectively or quickly, leading to poor mass transfer and thus lower decontamination efficiency, regardless of the contaminant's intrinsic properties (LogP and Molecular Weight, Mw). The physical barrier imposed by the sample's structure overrides the chemical parameters. Similar behavior could be explained for S1

For S3, the expectation that lower Mw and LogP would guarantee better decontamination is confounded by its extreme flexibility. This characteristic also prevented the sample from being milled to the optimal 0.3 cm size. The resulting non-optimal, likely irregular or agglomerated, sample geometry leads to an inconsistent or reduced effective surface area and potential channeling of the CO_2 flow. In this scenario, the CO_2 bypasses large portions of the sample material, resulting in incomplete contaminant extraction. While lower Mw and LogP theoretically favor better solubility and diffusivity in CO_2, the physical impediment of the sample's preparation and structure dictates the observed, non-optimal efficiency.

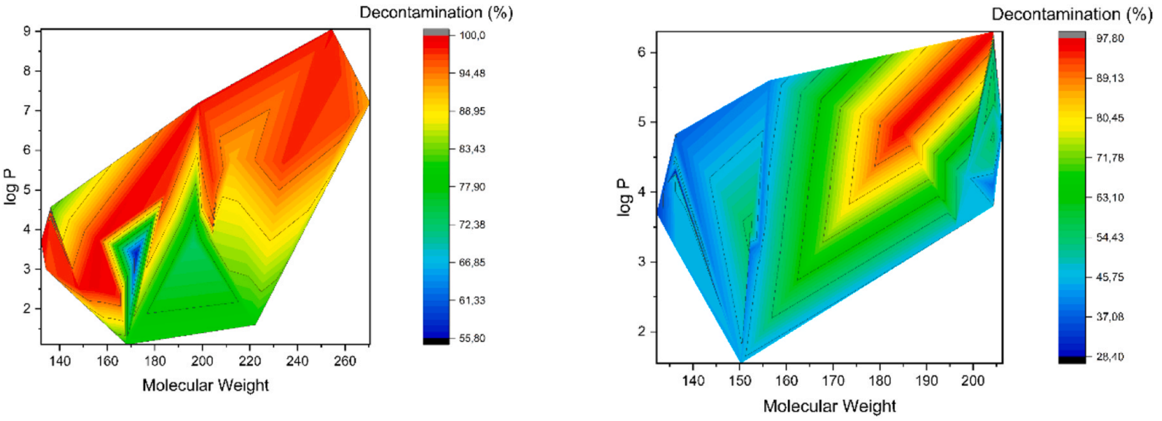
The better performance of S4 is mechanistically explained by its proper particle size reduction to 0.3 cm. This optimal preparation guarantees maximal specific surface area, minimized diffusion path length (the distance the CO_2 must travel to reach and extract the contaminant from the center of the particle is significantly reduced) and enhanced mass transfer (the combined effect of large surface area and short diffusion paths facilitates rapid and complete mass transfer of the contaminant into the CO_2 phase).

In general, higher decontamination efficiency is observed for compounds with lower molecular weight and low logP values, suggesting that more volatile and polar compounds are more easily removed. In the case of sample S4, a more uniform decontamination pattern is observed, which could indicate that the conditions or treatments applied in this sample are more effective across a broader range of compounds.

3.3. Non-Volatile compounds

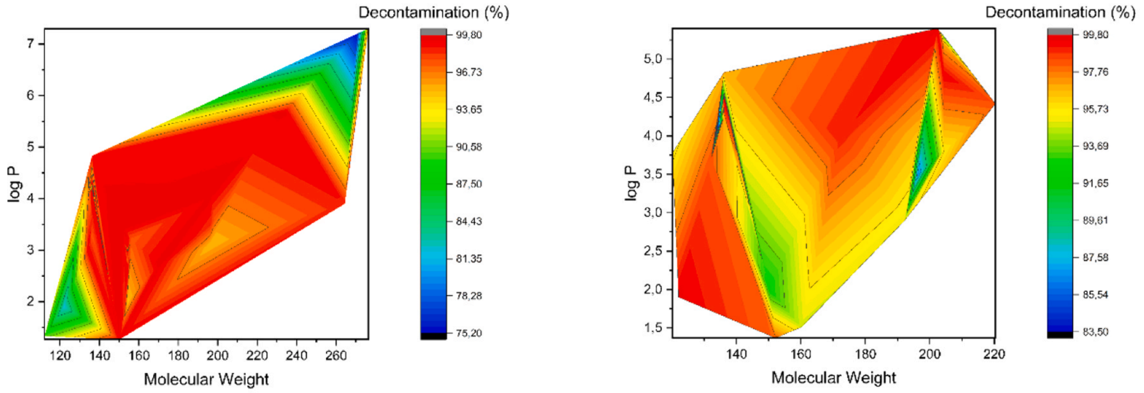
A total of 56 non-volatile compounds were detected in the migration samples, and 15 out of them remained unidentified (Detail information can be found in Table S3 and the quantification standards in Table S4). A general overview of decontamination efficacy can be seen in Fig. 5. Among the identified compounds, 26 % were additives commonly used in plastic manufacturing, while 74 % were classified as non-intentionally added substances (NIAS). Among the identified additives, the following ones can be mentioned: compound N,N-bis(2-hydroxyethyl) hexylamine, which belongs to the group of N,N-bis(2-hydroxyethyl) alkyl amines, widely used as antistatic agents, antioxidants such as Irganox 1016 and Irgafos 168 were identified, along with slip agents including stearamide, hexadecanamide, oleamide, and erucamide. Lubricants like octadecanamide N,N′-1,2-ethanediylbis- and 1-monopalmitin, a compound with applications as a lubricant, emulsifier, or surfactant in industrial settings, were also detected. The plasticizer bis(2-ethylhexyl) adipate, used to enhance the flexibility of packaging materials, was identified as well (Gupta et al., 2024; Hahladakis et al., 2018; Ignacio et al., 2023; Otoukesh et al., 2020; Vera et al., 2023).

As NIAS, triethanolamine was identified, which could be a byproduct of the dissociation of the dimer triethanolamine-perchlorate, sodium salt (substance FCM No. 1080). This substance is used as an additive in poly (vinyl chloride) (PVC) bottles for water, oil, vinegar, or juices. According to the literature (Silano et al., 2020), when in contact with water, this compound completely dissociates into triethanolamine, sodium cations, and perchlorate, confirming the migration of triethanolamine. Therefore, it is possible that this molecule could come from the contamination



1: Heat map for the S1

2: Heat map for the S2



3: Heat map for the S3

4: Heat map for the S4

Fig. 4. Heat map for each sample showing the decontamination percentage of volatile compounds analyzed by HS-SPME-GC-MS plotted against their log P and molecular weight.

of the analyzed polyethylene (PE), given its capacity to absorb substances from other materials that were in contact with it. Other examples of contamination could be the compound 1,2,2,6,6-Pentamethyl-4-piperidinyl 2-methyl-2-propenoate, which is used as a light stabilizer for coatings and inks, and also the caffeine, detected in the migration of two samples. These substances could come from food residues left in the packaging from prior use and not being completely eliminated in the samples 3 and 4 (Di Bella et al., 2014; Liu et al., 2002; Silano et al., 2020).

Several groups of linear amines (compounds 9, 11, and 15 from Table S4) and their oxidized forms (compounds 10 and 12), as well as linear amides (compounds 12, 18, 40, 42, 43, 46, and 47) and compounds derived from oleamide and erucamide (compounds 31, 32, 34, 35, 36, 41, and 44) were also identified. These substances could be originated from impurities or degradation products of hexadecanamide, stearamide, erucamide, and oleamide, above mentioned, which are widely used as slip agents (Bhunia et al., 2013; Vera et al., 2019). Besides, two common degradation compounds were identified: 7.9-Di-tert-butyl-1-oxaspiro[4.5]deca-6.9-diene-2.8-dione and 3.5-Di-tert-butylbenzaldehyde, which are degradation products of the antioxidants Irganox 1010 and BHT respectively. Another substance, 2,6-Di-tert-Butyl-4-[3,5-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzylidene]-2,5-cyclohexadienone, although not reported in the literature, seems to be a degradation product, due to its structural similarity to the previously mentioned compounds.

Additionally, compound 49 was identified as the oxidized form of the antioxidant Irgafos 168, resulting from the addition of one oxygen atom. Finally, compounds 50 and 53 were identified as break-down products of N,N′-1,2-Ethanediylbis[octadecanamide] (Gupta et al., 2024; Hahladakis et al., 2018; Vera et al., 2019). Most of the compounds found were expected, as polyolefins need a series of additives, such as antioxidants, slip agents and others, on top of the absorbed contaminants. Applying SFE as a decontamination step for recycling showed that additivation with antioxidant steps will certainly be needed as part of the recycling step. This is demonstrated by the removal of Irganox 1076 with a 99.49 % for S3 and 94.84 % for S4 and Irgafos 168 with a 62–81 % across the four samples (Table S3)

Fig. 6 shows a heat map showing each sample’s compound decontamination percentages plotted against the non-volatile compounds’ polarity and molecular weight.

For non-volatile compounds, a generally lower level of decontamination is observed compared to volatile ones. Decontamination is more effective for compounds with intermediate molecular weight and low to moderate logP values. Compounds of heavier molecular weight and very high logP (more lipophilic) are more resistant to decontamination.

In S1, the decontamination pattern shows moderate variability across the chemical space. Higher efficiencies (65–95 %) are achieved for compounds of intermediate molecular weight and log P values, while extremes show lower performance (<40 %). This indicates that the decontamination process in S1 is somewhat selective, with reduced efficiency for very small or highly hydrophobic molecules. In contrast to the apparent uniformity of the heat map, the overall decontamination for S2 was poor and highly variable. This was mainly due to the inability to properly reduce the particle size during processing, which limited the efficiency of contaminant removal. As a result, S2 consistently

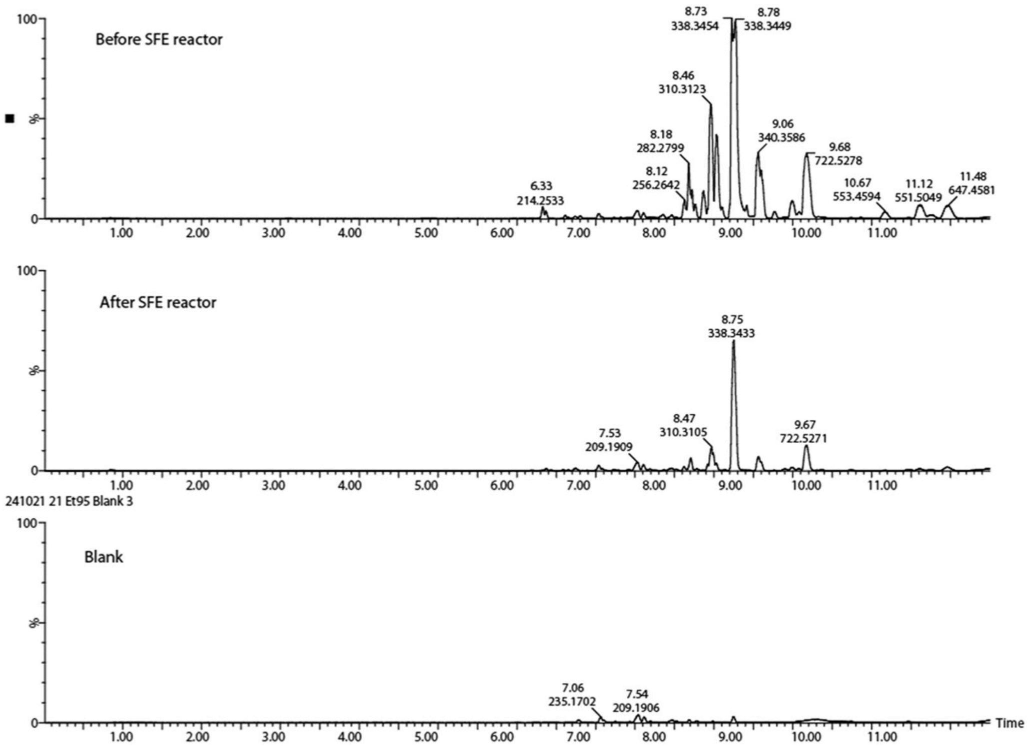


Fig. 5. Chromatogram of Sample 4 (S4) before and after reactor analyzed by UPLC-MS/TOF.

underperformed compared to the other samples.

However, S3 exhibited a heterogeneous decontamination profile. While certain contaminants were efficiently removed (>90 %), others, particularly those with low molecular weight and log P values, persisted (down to ~15 %). The strong variability suggests incomplete decontamination and highlights sensitivity to contaminant characteristics.

S4 demonstrated relatively high and consistent efficiency, with most compounds falling in the range of 70–90 %. Although some lower efficiency regions (<50 %) were still observed, the overall performance was better than S1 and S3, but not as consistent as would be expected in an optimized process.

The observed difficulty in removing higher molecular weight and high logP substances is not unique to the presented technology but represents a fundamental, shared challenge across various commercial and developmental plastic decontamination methods. This predicament is rooted in diffusion limitations (Contaminants with a higher molecular weight exhibit significantly lower diffusion coefficients) and partitioning affinity (Substances with a high log P demonstrate a strong lipophilic affinity for the non-polar polymer matrix) (Palkopoulou et al., 2016).

This limitation is evident even in highly optimized, commercialized processes for melt-phase decontamination. For instance, technologies like the Starlinger viscoZero system, widely used for polyolefin and PET recycling, employ intensive methods such as high-temperature processing and deep vacuum to achieve excellent decontamination efficiency (Lambré et al., 2021).

3.4. Risk assessment

To assess the potential risks associated with the identified migrant compounds, their compliance with the established specific migration limits (SMLs) was evaluated. For compounds not covered by legislation, the Threshold of Toxicological Concern (TTC) approach was applied. Among the identified compounds, thirty-five were included in the positive list of Regulation (EU) No. 10/2011 (see Supplementary Tables S2 and S3), of which eleven were authorized without a specific migration limit. Of the remaining twenty-four, two volatile compounds—1-dodecene and butylated hydroxytoluene—showed migration levels well below their respective regulatory limits of 0.05 and 3 mg/kg. Twelve non-volatile compounds had defined SMLs: triethanolamine (0.05 mg/kg), a group of amides (5 mg/kg), N,N-bis(2-hydroxyethyl)hexylamine (1.2 mg/kg), 2-ethylhexyl adipate (18 mg/kg), and Irganox 1076 (6 mg/kg). Notably, triethanolamine, detected in sample S4 after the decontamination process, exceeded its SML, showing a migration value of 0.15 ± 0.02 mg/kg.

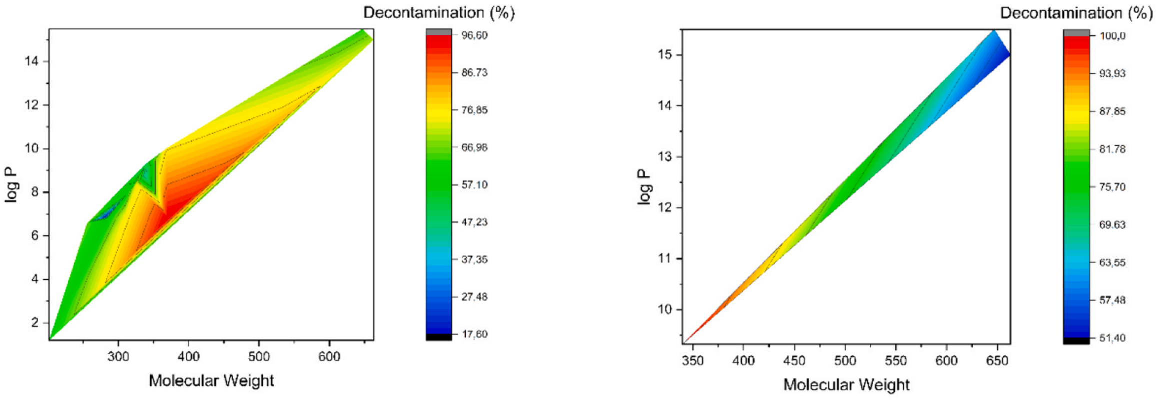
For compounds not covered by legislation, the Cramer classification was applied: most were assigned to Class I, five to Class II, and fourteen to Class III (see Supplementary Tables S2 and S3). When compared to the corresponding Cramer limits, the compound D-limonene exceeded the recommended Class I threshold value (>1.8 mg/kg), with a migration level of 2.35 ± 0.40 mg/kg in sample S2. Furthermore, the compounds 2,6-di-tert-butyl-4-[3,5-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzylidene]-2,5-cyclohexadienone and N,N′-1,2-ethanediylbis[heptadecanamide] exceeded the Class III threshold value of 0.09 mg/kg, with migration levels of 0.09 ± 0.01 and 8.31 ± 0.01 mg/kg, respectively.

Overall, these results indicate that although most identified compounds comply with the established specific migration limits or TTC criteria, some exceed their respective thresholds, underscoring important safety considerations regarding the use of decontaminated recycled PE in food-contact applications.

3.5. Overview of decontamination efficacy

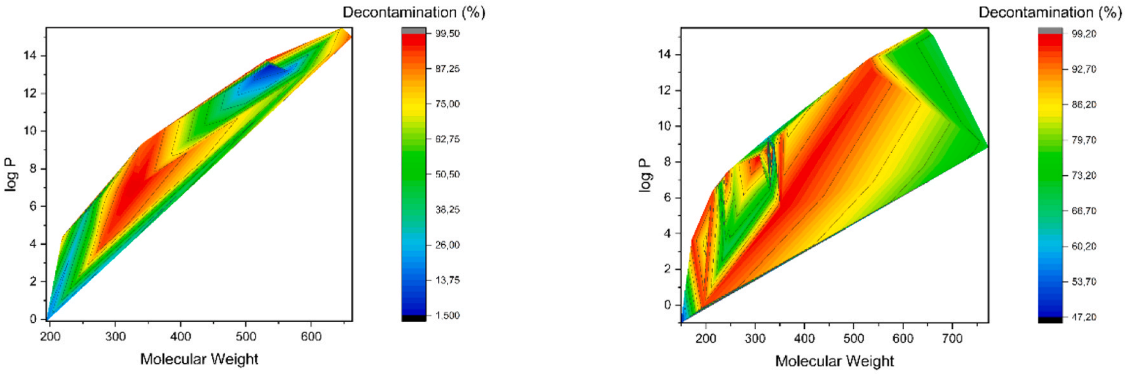
The decontamination efficacy (%) for volatile and non-volatile substances is shown in Fig. 7 for all samples (S1 to S4) under optimized conditions.

The results indicate that the reactor performs better in the removal of volatile compounds, with efficiencies ranging from approximately 45 % to nearly 100 %. Specifically, sample S3 exhibits the highest efficiencies, surpassing 95 %, suggesting that the reactor operates optimally under their conditions. However, a clear issue arises with sample S2, where the decontamination efficiency for volatiles is notably low (approximately



1: Heat map for the S1

2: Heat map for the S2



3: Heat map for the S3

4: Heat map for the S4

Fig. 6. Heat map for each sample showing the decontamination percentage of non-volatile compounds analyzed by UPLC-MS/QTOF plotted against their log P and molecular weight.

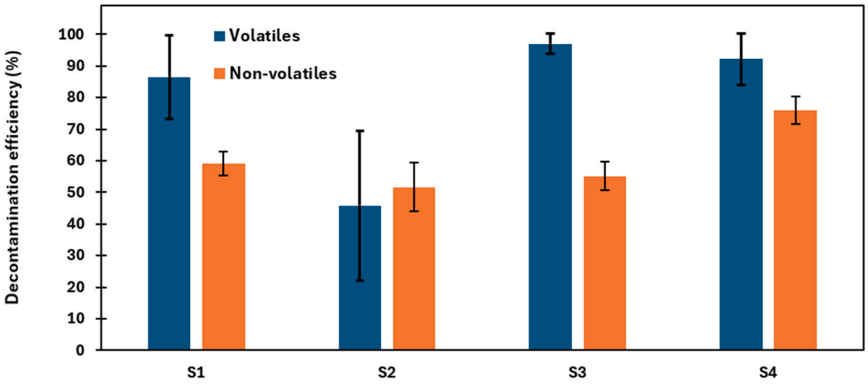


Fig. 7. Decontamination efficacy (%) for volatile and non-volatile substances from sample 1 to sample 4 (S1-S4) in the optimized conditions.

45 %) and displays significant variability. This reduction in performance can be attributed to the large particle size introduced into the reactor for this sample, which likely hindered the efficiency of the extraction process.

For non-volatile compounds, the efficiencies are consistently lower compared to volatiles, ranging between approximately 50 % and 75 %. Sample S4 stands out as achieving the closest balance between the two contaminant types, with volatile and non-volatile removal efficiencies reaching approximately 92 % and 75 %, respectively.

While the SFE reactor demonstrates a higher decontamination efficiency for volatiles, the results for sample S2 underscore the importance of controlling particle size to optimize reactor performance.

4. Conclusions

Supercritical fluid extraction (SFE) with CO2 has demonstrated a significant reduction of contaminants in polyolefins, achieving removal efficiencies of up to 99 % for volatile compounds and 75 % for non-volatile compounds. Among the various sample treatments, particle size emerged as the most critical factor in attaining high decontamination efficacy. Furthermore, it was observed that decontamination efficiency could be enhanced by optimizing reactor conditions tailored to each type of polyolefin, probably using a modifier to adapt the polarity of CO_2 to the target contaminants, if any, particularly when processing industrial quantities. From an environmental perspective, SFE as technology for decontamination of polyolefins is very promising, as SFE, once filtered to eliminate the contaminants, is recirculated in the process. However, challenges were encountered in reducing the particle size of the HDPE rigid containers, primarily due to the constraints imposed by available mechanical tools. The established use of this technology in existing industrial applications significantly reduces the barrier to adoption and ensures immediate scalability within current recycling plant infrastructure.

A critical consideration in validating this decontamination process, which leverages the high-solvency power of supercritical CO_2, is the inherent trade-off between chemical purity and material functionality. While high efficiency was demonstrated for both volatile and non-volatile contaminants, the potential for simultaneous co-extraction of essential polymer additives, such as antioxidants, UV stabilizers, and processing aids, is a significant concern for the material's fitness-for-use. Loss of these components can detrimentally compromise the material's thermal stability, mechanical integrity, and long-term performance, all of which are non-negotiable requirements for high-value applications, particularly food-contact packaging applications.

In addition, migration analysis revealed that four identified compounds did not comply with the established specific migration limits or the Threshold of Toxicological Concern (TTC) criteria, exceeding the regulatory or recommended thresholds. This finding highlights that, although the SFE process substantially reduces contamination levels, certain residual compounds may still pose safety concerns. Therefore, further optimization of the decontamination process is required to ensure complete compliance with food-contact safety regulations

Overall, the practical feasibility of the supercritical CO_2 process hinges upon future work addressing both post-treatment material property restoration and residual contaminant control, necessitating a comprehensive assessment of the resulting material performance and the development of strategic re-stabilization or polymer blending approaches to guarantee compliance, safety, and market viability.

Associated content

Quantification standards list /Tables S1, S2, S3 and S4 for GC and LC and decontamination results for volatile and non-volatile compounds

CRediT authorship contribution statement

Fallah Belgharbi: Software, Methodology. **Lobez Silvia:** Methodology, Conceptualization. **Cristina Nerín:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **Ana M. Mainar:** Supervision, Resources, Funding acquisition, Conceptualization. **Paula Vera:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization. **Carlos Estremera:** Writing – original draft, Software, Methodology, Investigation, Data curation, Conceptualization.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fpsl.2025.101682.

Data availability

Data will be made available on request.

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