



Nectarine core-derived magnetite biochar for ultrasound-assisted preconcentration of polycyclic aromatic hydrocarbons (PAHs) in tomato paste: A cost-effective and sustainable approach

Ali Azari^{a,b,*}, Hossein Kamani^c, Maryam Sarkhosh^d, Neda Vatankhah^e, Mahmood Yousefi^f, Hadi Mahmoudi-Moghaddam^g, Seyed Ali Razavinasab^a, Mahmood Reza Masoudi^a, Reza Sadeghi^a, Nafiseh Sharifi^a, Kamyar Yaghmaeain^{h,**}

^a Sirjan School of Medical Sciences, Sirjan, Iran

^b National Elites Foundation, Tehran, Iran

^c Infectious Diseases and Tropical Medicine Research Center, Research Institute of Cellular and Molecular Sciences in Infectious Diseases, Zahedan University of Medical Sciences, Zahedan, Iran

^d Department of Environmental Health Engineering, Mashhad University of Medical Sciences, Mashhad, Iran

^e Department of Pharmaceutical, School of Pharmacy, Mashhad University of Medical Sciences, Mashhad, Iran

^f Department of Environmental Health Engineering, School of Health, Khoy University of Medical Sciences, Khoy, Iran

^g Pharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, Iran

^h Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

ARTICLE INFO

Keywords:

Magnetite biochar
Nectarine cores
Tomato paste
Polycyclic aromatic hydrocarbons
Ultrasound-assisted solid-phase extraction

ABSTRACT

A novel ultrasound-assisted magnetic solid-phase extraction coupled with gas chromatography–mass spectrometry (US-MSPE-GC/MS) was developed to detect trace amounts of polycyclic aromatic hydrocarbons (PAHs) in tomato paste, using a magnetic biochar adsorbent derived from nectarine cores. The highest extraction recovery was attained under 10 mg adsorbent mass, 30 min extraction time, 9 % (w/v) sodium chloride, and elution with 200 μ L of dichloromethane. Under optimum conditions, the method demonstrated excellent linearity ($R^2 > 0.992$) across a wide concentration range (0.01–100 ng g^{-1}) with high sensitivity (LODs: 0.028–0.053 ng g^{-1} , LOQs: 0.094–0.176 ng g^{-1}) and good repeatability (RSDs < 5.96 %). The application of the US-MSPE-GC/MS method was tested on four brands of real tomato paste and no PAHs were detected in unspiked samples, indicating no background contamination. This method showed high relative recoveries 88.03–98.52 % and good reproducibility (< 9.19 %) at two concentration levels, confirming its effectiveness for PAH analysis in real samples.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent an extensive group of environmental and food contaminants that are principally formed through the incomplete combustion of organic matter (Ofori et al., 2020). Due to their stability, carcinogenicity, mutagenicity and teratogenicity, PAHs are identified as priority pollutants by regulatory agencies like the United States Environmental Protection Agency (EPA) and the International Agency for Research on Cancer (IARC) (Tavoosidana et al., 2024; Zungum & Imam, 2021). Several studies have highlighted the presence of PAHs in a wide variety of foods including

fish, grains, vegetables, rice, as well as various beverages such as tea, coffee, milk, and alcoholic drinks (Akbari-Adergani et al., 2021; Sampao et al., 2021; Sun et al., 2019). In Iranian cooking, tomato paste is widely used as a basic ingredient for flavoring and increasing the seasoning of various foods during the cooking process. Tomato paste is used to add flavor, color, and thickness to various dishes, such as stews, soups, rice, and meatballs. The production of tomato paste involves a meticulous process wherein tomatoes are subjected to prolonged cooking until they attain a condensed consistency, resulting in a viscous paste. Hence, raw materials, cooking/drying in high temperature processes, flavorings and essential oils used, contaminated water/washing

* Corresponding author at: Sirjan School of Medical Sciences, Sirjan, Iran.

** Corresponding author.

E-mail addresses: azari.hjh@gmail.com, azari.resrach@gmail.com (A. Azari), k_yaghmaeain@yahoo.com (K. Yaghmaeain).

water and packaging/storage step can be considered as possible sources of PAH in tomato paste (Das et al., 2023; Sampaio et al., 2021). Consequently, monitoring of PAH concentration levels within tomato paste assumes paramount significance in safeguarding human health and well-being. PAHs are usually found at very low levels in real samples, necessitating the use of pre-concentration techniques to extract and enrich the levels of analytes prior to their quantification by instrumental methods (such as gas chromatography and high-performance liquid chromatography combined) (Agus et al., 2023; Raza et al., 2018). Some of the commonly used pre-concentration methods for PAHs are liquid-liquid extraction, solid-phase extraction, solid-phase microextraction, and dispersive liquid-liquid microextraction (Jinadasa et al., 2020). Liquid-Liquid Extraction (LLE) is a traditional method known for its simplicity and effectiveness in separating PAHs from aqueous samples. However, it requires large volumes of organic solvents and is time-consuming, which can limit its efficiency and environmental sustainability (Manousi & Zachariadis, 2020; Temerdashev et al., 2021). Solid-Phase Extraction (SPE) offers greater efficiency (high recovery and cleaner extracts) and lower solvent consumption compared to LLE, and it can be easily automated. Nevertheless, SPE can be costly, and the choice of sorbent material significantly impacts its effectiveness, which may require optimization for different PAH profiles (Andrade-Eiroa et al., 2016). Solid-Phase Microextraction (SPME) is a solvent-free technique that integrates sampling, extraction, and concentration in a single step, making it highly efficient and environmentally friendly. Its main drawbacks are the limited capacity of the fiber, which can affect sensitivity/reproducibility, and the need for careful handling to prevent damage to the fiber (Zhang et al., 1994). Dispersive Liquid-Liquid Microextraction (DLLME) is another method that offers rapid and efficient extraction with minimal solvent use and high enrichment factors. However, DLLME can be less effective in complex matrices and may suffer from issues related to emulsification, which can complicate phase separation. In addition, the selection of suitable dispersing solvents is very important to achieve a high recovery rate in this process (Rezaee et al., 2010; Rykowska et al., 2018). Among these methods, magnetic solid-phase extraction (MSPE) has gained attention from researchers in recent years as an efficient technique for sample preparation. MSPE involves the use of a magnetic adsorbent that can be directly separated by an external magnet without the need for centrifugation and filtration steps, which simplifies the procedure and reduces the cost and energy consumption (Sajid et al., 2021; Yu et al., 2019). So far, various materials have been used to develop magnetic adsorbents (Manousi & Zachariadis, 2020; Wu et al., 2021; Yu et al., 2019). In this among, carbon-based adsorbents have garnered escalating interest due to their outstanding performance, high extraction capacity, good dispersion in the sample, affordable price, and availability (Thakur & Kumar, 2023). Biochar, a carbonaceous material derived from biomass pyrolysis, seems to be a promising candidate for the MSPE process because of its substantial porosity, surface area and active site (functional groups), superior dispersibility, simple preparation procedure, and high selectivity (Di et al., 2020). In this context, the use of agricultural waste as a precursor for biochar synthesis has attracted the attention of researchers due to the dual benefits of waste valorization and environmental remediation (Barasikina, 2021; Yaashikaa et al., 2019). Among the wide variety of agricultural wastes, nectarine cores present themselves as a convincing candidate for biochar production due to their abundance, high carbon content, suitable physicochemical properties, and economic and environmental benefits. Accordingly, it is expected that the development biochar from nectarine cores (NBC) as a novel adsorbent in PAHs extraction/preconcentration will bring hopeful results. However, efficient and affordable separation and reuse of post-extraction NBC remains a major barrier to cost reduction and pollution prevention in this promising technology. Researchers have proposed incorporating magnetite nanoparticles (Fe_3O_4 NPs) into the biochar matrix as a rapid and cost-effective method for separating adsorbents from samples. This approach utilizes the magnetic properties of Fe_3O_4 NPs for efficient

separation under external magnetic fields, offering significant improvements (e.g., reduction in separation time and cost) compared to conventional filtration methods (Prajapati & Mondal, 2022). In addition to material modification, the acoustic cavitation is highlighted as a mechanism to accelerate chemical processes through the application of ultrasound irradiation (US). This phenomenon involves the generation, growth, and subsequent implosion of micro-sized bubbles as pressure waves propagate through the liquid medium. This cavitation-induced process notably enhances the mass transfer and affinity between adsorbate (PAHs) to the adsorbent (MNBC) in extraction systems (Savun-hekimoglu, 2020). Some studies have also reported that ultrasound-assisted extraction system has resulted in improved equilibration and shorter contact time during the extraction process (Dalmat et al., 2020). Considering the significant advantages offered by the hybrid the US-MSPE-GC/MS method, the potential toxicity and carcinogenic nature of PAHs, and the existing research gap concerning the application of magnetite biochar derived from nectarine core as an adsorbent under ultrasound irradiation for PAHs extraction from tomato paste, the current study was undertaken with the following main objectives: (i) The synthesis and characterization of the MNBC adsorbent derived from nectarine core, (ii) Investigation of the influence of key variables (i.e. adsorbent dose, extraction time, NaCl addition, eluent type, and volumes) on the efficacy of PAHs extraction from samples, (iii) Investigating the influence of stirrer and ultrasound irradiation in the extraction process and (iv) Determination of the PAHs concentration in tomato paste (as real samples).

2. Materials and methods

2.1. Chemicals, instruments, and analytical methods

The following solvents were purchased from Sigma-Aldrich (St. Louis, MO; United States): n-Hexane, dichloromethane, acetonitrile and acetone. A standard mixture of PAHs (QTM PAH-Mix, 2000 $\mu\text{g mL}^{-1}$) was procured from Supelco (Bellefonte, PA, USA). The NBC adsorbent was prepared from the core of nectarine, which was bought from a fruit market in Sirjan, Iran. The chemicals used for the magnetization of the adsorbent, including $\text{FeNO}_3 \cdot 9\text{H}_2\text{O}$ ($\geq 99.99\%$), melamine ($\text{C}_3\text{H}_6\text{N}_6$), anhydrous ethanol ($\text{CD}_3\text{CD}_2\text{OD}$, $\geq 99.5\%$) and NaOH (93 %) were purchased from Sigma Aldrich (St. Louis, MO, USA). H_2SO_4 ($> 99.0\%$) and HCl (35-37 %) were obtained from Merck Co. (Darmstadt, Germany). All the other chemicals were of analytical grade and used as received without any further purification. A stock solution of PAHs was prepared by dissolving predetermined quantities of PAHs in methanol. For other required concentrations, appropriate portions of the standard stock solution were diluted daily with DI- water. The stock solutions were stored in a dark place at 4 °C. In this study, PAHs, comprising benzo(a)pyrene [BaP], benzo(a)anthracene [BaA], benzo(b) fluoranthene [BbFL], chrysene [Chr], benzo(k)fluoranthene [BkFL], dibenzo[a,h] anthracene [DBA], indeno[1,2,3-cd] pyrene [Ind] and benzo[g,h,i] perylene [BP], was selected as a representative of PAHs (Carcinogenic one) for the extraction process by the US-MSPE hybrid system. An Agilent-fused silica HP-5MS capillary column (30 m \times 0.25mm.i.d., coated with 5 % diphenyl, 95 % dimethyl polysiloxane, film thickness 0.25 μm) was used for chromatographic separation in splitless mode. High-purity helium ($> 99.999\%$) was employed as carrier gas at a flow rate of 1 mL min^{-1} . Injector and GC-MS interface temperatures were set at 280 °C and 150 °C, respectively. The column temperature program followed this sequence: held at 60 °C for 1 min, then ramped to 290 °C at 5 °C min^{-1} , and finally maintained at the target temperature for 2 min. The injection volume was 1 μL and the analytes were quantified by normalizing the area under the curve (AUC) value between 0 and 1 according to Eq. 1:

$$\text{Normalized value of AUC} = \frac{\text{AUC value} - \text{Min value of AUCs}}{\text{Max value of AUCs} - \text{Min value of AUCs}} \quad (1)$$

Where AUC value represents the specific AUC value for a given sample, Min value of AUCs is the smallest AUC value among all the samples, and Max value of AUCs is the largest AUC value among all the samples.

2.2. Preparation and characterization of MNBC adsorbent

The pyrolysis method (Chen et al., 2022) was considered to prepare the NBC adsorbent. Initially, nectarine cores were thoroughly cleaned with ultrapure water and dried in an oven at 120 °C for 12 h until a constant weight was attained. Next, the dried cores were ground using a ball mill (QM-3SP04, China) and sieved (100-mesh) to achieve a fine powder. Afterwards, 1.5 g of the obtained powdered was mixed with 70 mL of ferric iron solution ($\text{FeNO}_3 \cdot 9\text{H}_2\text{O} = 0.5 \text{ g}$) and stirred for 3 h. Subsequently, 5 g of melamine and anhydrous ethanol were added to the mixture and stirred. The resulting solution was heated in a water bath at 80 °C until all the water evaporated. The dried precursor was pyrolyzed in two stages under a N_2 atmosphere. First, it was heated to 600 °C at a rate of 5 °C min^{-1} and held for 2.5 h. Then, the temperature was increased to 850 °C at the same rate and held for another 1.5 h. Finally, the pyrolyzed powder was treated with 1.5 M HCl for 7 h to remove unwanted components. The product (MNBC) was then separated using a neodymium magnet, washed with deionized water and ethanol until the wash solution remained neutral, and finally dried under vacuum at 90 °C for 5 h. The synthesized adsorbent characterizations are given in Supplementary Information, Text 1.

2.3. Optimization of extraction processes

The current study has focused on the systematically investigation and optimization of five key parameters including contact time, adsorbent mass, NaCl addition, solvents type and its volume on PAHs extraction efficiency using US-MSPE hybrid system based on the one factor at a time (OFAT) approach. For extraction times, the vial containing 5 mg adsorbent in 20 mL model solution (initial PAHs: 25 ng mL^{-1}), was placed on an ultrasonic bath (frequency: 45 kHz) at room temperature ($25 \pm 5 \text{ }^\circ\text{C}$) and sonicated for 5 to 60 min. The effect of varying quantities of MNBC (e.g., 1 to 30 mg) were used to evaluate the best amount of PAHs extraction from the samples, while other parameters held constant and contact time fixed at optimized amount. The effect of different NaCl concentrations in the range of 0 to 18 % w/v was examined under the optimized conditions established in the previous steps to determine the optimal NaCl level. For elution, n-hexane, acetone, acetonitrile and dichloromethane were employed to identify the most efficient solvent for the PAHs desorption process. Moreover, the influence of different eluent volumes (50-300 μL) on quantitative recovery of the target analyte was investigated under the defined experimental conditions. It should be noted that after each experimental step, the MNBC adsorbents were separated from samples using a strong magnet (dimensions: 10 × 5 cm × 4 cm, magnetic field strength: 1.4 T) and their supernatant was collected and injected (1 μL) into the GC/MS system to determine the final PAHs concentration (area under the curve: AUC). All experimental procedures were conducted in triplicate, and the reported values represent the average of three measurements. The schematic of PAHs extraction procedures by US-MSPE hybrid system summarized in Fig. S1.

2.4. Method validation

The study of Farrokhzadeh et al. with some modifications was used to validate the US-MSPE-GC/MS method in the present study (Farrokhzadeh & Razmi, 2018). The proposed method was validated for linearity (LR), limits of detection (LODs), limits of quantification

(LOQs), coefficient of determination (R^2), and relative standard deviation (RSDs). The relationship between the peak area and the concentration of the analyte was assessed by plotting calibration curves at four standard solutions (0.01, 5, 25, 50, and 100 ng g^{-1}). Each solution was analyzed in five replicates ($n = 5$), and the slope, intercept, and coefficient of determination (R^2) were calculated by the least squares linear regression analysis. LODs and LOQs were determined based on signal-to-noise ratios (S/N) of 3 and 10, respectively. In order to measure the accuracy of the method, the extraction recovery of the analytes was calculated by spiking a known amount of PAH concentration into a sample matrix. The repeatability and precision of the method was assessed by performing five replicate extractions of a spiked sample and calculating the RSDs of the measured concentrations. A lower RSD value confirms the high precision of the proposed method for PAHs extraction.

2.5. Real samples

The applicability of the optimized US-MSPE-GC/MS method for PAHs extraction in real samples was assessed using four commercially available tomato paste brands with high consumption rates in Iran (named S.1 to S.4, $n = 5$ per brand). These samples were purchased from various local markets across Sirjan (Iran) and stored at 4 °C. For sample preparation, 5.0 g of tomato paste from each sample were accurately weighed and transferred to 50 mL centrifuge tubes. The samples were then vigorously shaken and homogenized for 15 min after the addition of 10 mL of deionized water. The prepared samples were then centrifuged at 4000 rpm for 10 min. Finally, the resulting supernatant was collected and subjected to further analysis (determination of PAHs) using the optimized procedures described in section 2-3 and Fig. S1. The relative recovery percentage (RR%) for analytes spiked in the real samples was calculated using the following equation:

$$\text{RR (\%)} = \frac{(C_f - C_i)}{C_s} \times 100 \quad (2)$$

where C_f is the concentration of target PAHs measured in a spiked sample, C_i is the initial concentration of analyte in the sample (background concentration before spiking), and C_s is the spiked concentration of target analyte.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the SEM analysis of the synthesized adsorbent before and after its modification with Fe_3O_4 NPs. It can be observed that the original biochar derived from nectarine core (NBC) exhibited a relatively smoother surface (Fig. 1a). Conversely, the surface of MNBC displayed a markedly roughened texture characterized by the numerous presences of granular/spherical particles on the biochar surface, which attributed to the presence of iron oxide species (Fig. 1b). The structure of MNBC appears to be non-uniform (non-monodisperse) and a slight agglomeration was observed in it, which can be attributed to the incorporation of Fe_3O_4 NPs into the composite structure. The TEM image (Fig. 1c) reveals that the Fe_3O_4 NPs with a diameter of 20 to 40 nm and a spherical shape are heterogeneously distributed on the NBC surface (NBC diameter = 30 to 80 nm). Additionally, TEM analysis confirmed the partial aggregation of Fe_3O_4 NPs, which was earlier observed using the SEM analysis. This phenomenon can be attributed to the inherent magnetic properties of Fe_3O_4 NPs, which makes the nanoparticles tend to aggregate or accumulate in certain areas. The average particle size of the MNBC was analyzed using dynamic light scattering (DLS) analysis and its results can be seen in Fig. 1d. The evidence indicates that the average particle size of the prepared nanocomposite is $74.05 \pm 4.38 \text{ nm}$. The EDS spectrum (Fig. 1e) verified the existence of carbon, iron, and oxygen in the MNBC structure, with atomic percentages of 53, 26 and

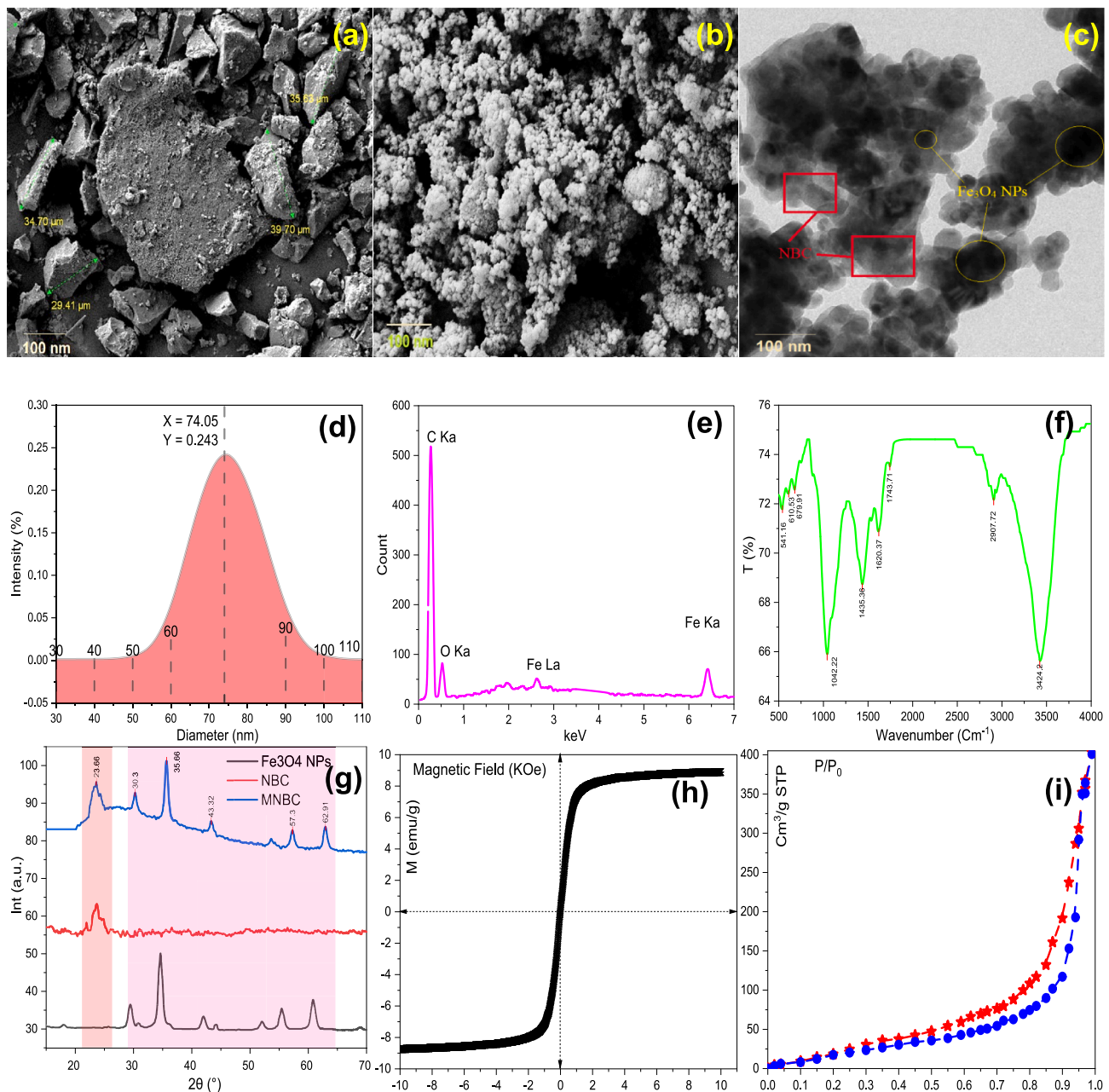


Fig. 1. SEM images of NBC (a) and MNBC (b), TEM image (c), DLS size (d), EDS pattern (e), FTIR spectrum (f), XRD pattern (g), VSM characterization (h), and BET measurement (i) of MNBC adsorbent.

21 %, respectively. The demonstration of these elemental peaks affirms the successful synthesis of Fe_3O_4 NPs and their successful stabilization within the NBC structure. The FTIR spectra of the as-synthesized MNBC were examined in the wavelength range of $500\text{--}4000\text{ cm}^{-1}$ (Fig. 1f). The peak at 1743.71 cm^{-1} can be attributed to the $\text{C}=\text{O}$ stretching vibrations arising from carbonyl and carboxyl groups present in the adsorbent. The peak at 1620.37 cm^{-1} represents $\text{C}=\text{C}$ aromatic stretching vibrations, while those at 1042.22 cm^{-1} correspond to $\text{C}-\text{O}$ alkoxy stretching vibrations. These observations suggest successful oxidation of nectarine core to biochar (NBC). The broad peaks around 3424.2 cm^{-1} are associated with $-\text{OH}$ stretching vibrations, which are characteristic of hydroxyl groups on the surface of the adsorbent. A distinctive peak at 2907.72 cm^{-1} is indicative of $\text{C}-\text{H}$ (carbon-hydrogen) bond stretching vibrations commonly found in organic compounds. Peaks observed at 1435.36 cm^{-1} represent symmetric and asymmetric stretching vibrations related to $-\text{COOH}$ and COO^- groups, indicating melamine ligand

presence in MNBC. The appearance of a peaks at 541.16 cm^{-1} to 679.91 cm^{-1} denoted the presence of $\text{Fe}-\text{O}$ in the MNBC structure, indicating that iron has been oxidized into Fe_3O_4 nanoparticles (NPs). These findings are in good agreement with the literature reported in previous studies (Ilyas et al., 2020). The crystal phase and structure of the synthetic NBC before and after modification with Fe_3O_4 NPs were characterized by XRD method in the range of $2\theta = 15^\circ$ to 70° and their obtained patterns are presented in Fig. 1g. For NBC, a distinctive diffraction peak was observed around $2\theta = 23.66^\circ$, corresponding to the (002) planes of carbon (Wang et al., 2023). XRD analysis of the Fe_3O_4 NPs revealed characteristic peaks at 30.3° (220), 35.66° (311), 43.32° (400), 52.5° (422), 57.3° (511), and 62.91° (440), consistent with the reference pattern for magnetite (JCPDS file no. 19-0629). These results provide strong evidence for the successful synthesis of crystalline Fe_3O_4 NPs. The XRD pattern of the MNBC composite retained all the characteristic peaks observed in the individual XRD profiles of Fe_3O_4 NPs and NBC. This

observation suggests the successful preservation of both components during the synthesis of the magnetic biochar. VSM analysis revealed a saturation magnetization value of ± 8.4 emu/g for the MNBC, as shown in Fig. 1h. The hysteresis loop exhibited minimal (near zero) coercivity and remanence, which is characteristic of superparamagnetic behavior of MNBC. This feature enables easy, fast and efficient separation of MNBC from mixtures using an external magnetic field without leaving impurities and secondary contamination. Nitrogen gas adsorption-desorption analysis using the BET method was employed to assess the surface characteristics of the MNBC adsorbent (Fig. 1i). The obtained isotherm corresponds to type IV with an H3 hysteresis loop according to IUPAC classification. This observation signifies the mesoporous nature

of MNBC (pore size 2-50 nm) with a non-uniform pore size distribution and interconnected network porosity. The BET surface area of the MNBC was determined to be $371 \text{ m}^2 \text{ g}^{-1}$. Furthermore, BJH desorption analysis revealed a pore size of 3.4 nm and a pore volume of $0.33 \text{ cm}^3 \text{ g}^{-1}$ for the synthesized adsorbent. These results collectively demonstrate that MNBC possesses a high surface area and a mesoporous structure, both of which are highly desirable properties for an efficient adsorbent material.

3.2. Optimization of the extraction process

3.2.1. Extraction time

The effect of extraction time on PAHs recovery was investigated

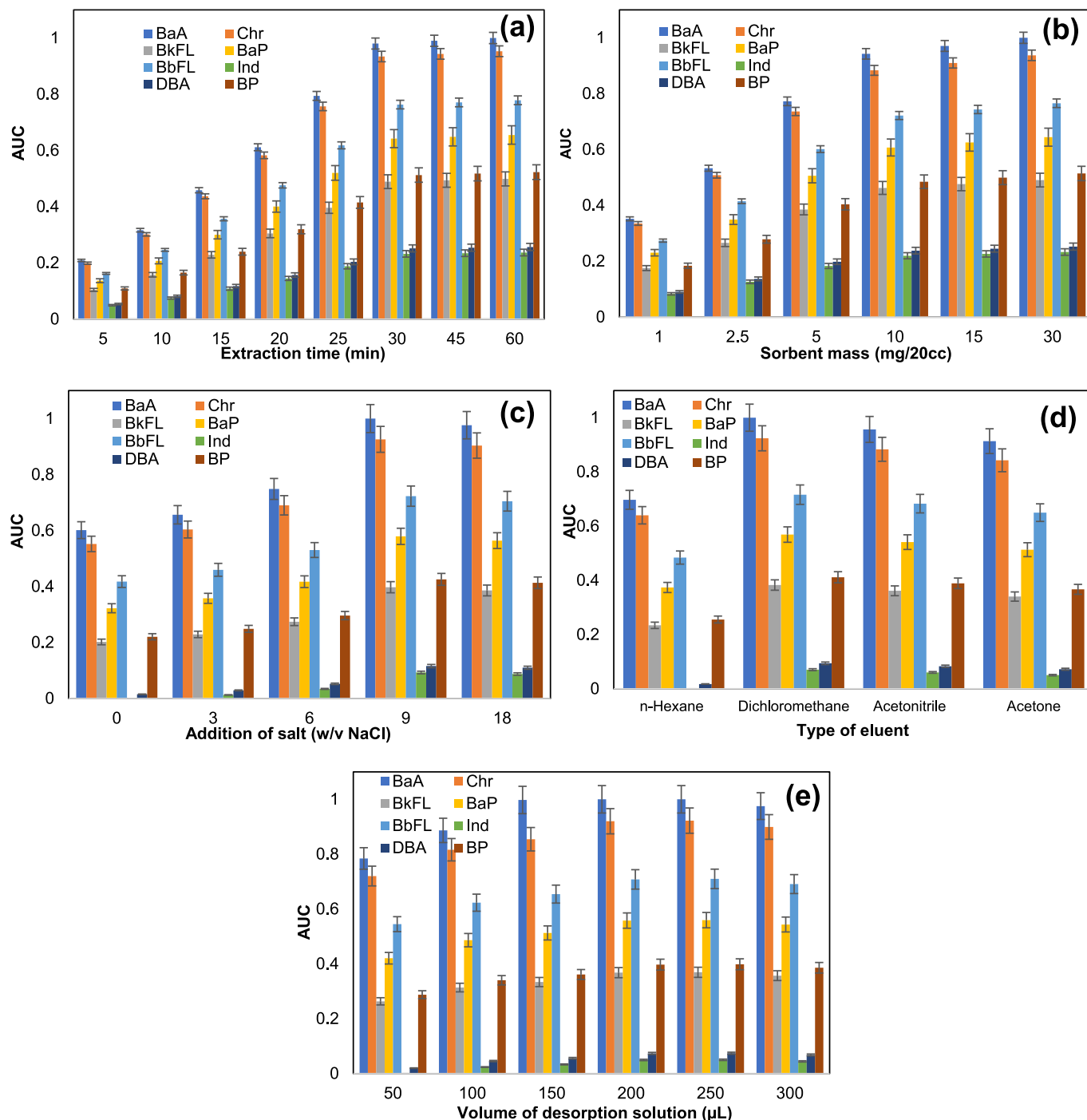


Fig. 2. Effect of extraction time (a), adsorbent mass (b), additional NaCl (c), eluent type (d), and elution volume (e) on the extraction efficiency of PAHs.

within a range of 5 to 60 min. As shown in Fig. 2a, the area under the curve (AUC) increases with increasing extraction time and reaches the equilibrium point at approximately 30 min. Thereafter, the extraction efficiency remained relatively constant. The initial rapid increase in peak area can be attributed to enhanced mass transfer of PAHs from the solution to the MNBC adsorbent due to greater contact time between the two phases. During this initial stage (within the first 30 min), the abundance of unoccupied sites and functional groups on the adsorbent surface facilitates efficient PAHs interaction, leading to high extraction efficiency. However, as the extraction time extends beyond 30 min, these active sites become progressively saturated with PAHs, resulting in a decline in further uptake. Therefore, based on the observed trend, 30 min was selected as the optimal extraction time for subsequent experiments.

3.2.2. Adsorbent mass

The impact of varying adsorbent mass (ranging from 1 to 30 mg) on the extraction efficiency process was investigated, and their results are presented in Fig. 2b. The results revealed a significant enhancement in extraction performance for all eight PAHs with increasing adsorbent mass. The most improvement was observed at 10 mg MNBC adsorbent, where the area under the curve reached the highest point ($\Sigma AUC_s = 1.25E+07$). Further increases in adsorbent mass resulted in negligible changes in extraction efficiency ($\Sigma AUC_s = 1.33E+07$ at 30 mg), hence adsorbent dosages greater than 10 mg were not explored further. The observed enhancement in extraction performance can be attributed to the greater availability of active sites on the MNBC surface with a higher adsorbent dose. These sites, along with functional groups, play a critical role in trapping and binding PAH molecules, leading to improved extraction efficiency (Jebli et al., 2023). Therefore, to balance economic considerations with effective performance, an adsorbent dose of 10 mg was recommended for further experiments.

3.2.3. NaCl addition

To investigate the impact of ionic strength on extraction efficiency, a series of experiments were conducted using NaCl concentrations ranging from 0 to 18 % w/v. As depicted in Fig. 2(c), the area under the curve of PAHs increased by 1.51-fold as the NaCl concentration rose from 0 to 9 %. This enhancement can be ascribed to two primary mechanisms. Firstly, NaCl disrupts the hydrogen bonding interactions/ bonding between solvents and the nonpolar PAH molecules. This reduces the affinity of PAHs for the solvent and consequently promotes their migration towards the MNBC adsorbent for enhanced extraction. Secondly, the increasing ionic strength associated with NaCl addition leads to a decrease in the aqueous solubility of PAHs. This phenomenon minimizes the formation of emulsions during extraction process. This facilitates cleaner separation of the target analytes from the aqueous phase, ultimately improving the efficiency of PAH recovery (Manousi & Zachariadis, 2020; Zeger et al., 2023). While a 9 % w/v NaCl concentration demonstrably enhances extraction efficiency, exceeding this limit can be counterproductive. Saturation of the aqueous phase with Na^+ and Cl^- ions, coupled with increased solution viscosity, can hinder the extraction process. Furthermore, excessively high ionic strength might lead to competition between PAHs and NaCl for binding sites on the MNBC adsorbent and potentially interfere with subsequent analytical methods employed for PAH quantification (Sajid et al., 2021; Zhang et al., 2020). Therefore, 9 % w/v NaCl was chosen for optimal efficiency and minimal drawbacks.

3.2.4. Elution solvents

Four solvents including n-Hexane, dichloromethane, acetonitrile and acetone were comprehensively investigated to determine the most efficient solvent for the extraction process. As illustrated in Fig. 2(d), dichloromethane (DCM) yielded the highest peak area (AUC), indicating its superior ability to extract PAHs from the samples. This can be attributed to the moderate polarity of DCM that effectively solvates a

broad range of PAHs with varying polarities (low and high polarity PAHs). Additionally, DCM benefits from both high solubility and good volatility (Szulejko et al., 2014). In contrast, n-hexane demonstrated the lowest AUC, reflecting its limited extraction efficiency. Acetone and acetonitrile displayed similar performances, and were ranked second and third, respectively. Based on these findings, dichloromethane (DCM) was selected as the most effective and reliable solvent for the extraction and analysis of PAHs from the samples for subsequent analysis.

3.2.5. Eluent volume

As shown in Fig. 2(e), increasing the elution volume from 50 μ L to 200 μ L led to a corresponding rise in the ΣAUC_s level from $2.06E+07$ to $2.49E+07$. The enhancement can be attributed to the greater availability of solvent molecules for PAHs solubilization with increasing volume. This facilitates the desorption of PAHs from the solid phase (MNBC adsorbent) and significantly enhances the extraction efficiency (Ameer et al., 2017). Interestingly, further increasing the volume to 250 μ L showed slight changes in the process (ΣAUC_s change to $2.50E+07$) and more than this volume even resulted in a decrease in extraction efficiency ($\Sigma AUC_s = 2.45E+07$). Several factors can contribute to the negative impact of excessive eluent volume on the efficiency of the extraction process. One key concern is the dilution effect, where unnecessary eluent volume diluted the concentration of PAHs in the final extract. This can significantly compromise the sensitivity of subsequent analyses (Truffelli et al., 2011). On the other hand, a larger elution volume can increase the co-elution of matrix components that may interfere with PAHs detection, especially those with similar chromatographic properties (Cortese et al., 2020). Additionally, an increased eluent volume also raises the risk of carryover, a phenomenon where residual analytes or interfering compounds are washed off or carried over from the sorbent into the collected fraction, potentially contaminating subsequent samples (Russo et al., 2024). Finally, handling larger volumes can introduce variability through pipetting errors or evaporation losses, ultimately compromising the precision and accuracy of the final analytical results (Greer et al., 2021). Therefore, 200 μ L was identified as the optimal elution volume for MNBC-based PAH extraction and adopted for subsequent experiments.

3.3. PAHs extraction efficiency comparison: US + MSPE vs. stirrer + MSPE

Following the optimization of key parameters on PAH extraction process, a comparative investigation was conducted to evaluate the efficacy of ultrasound-assisted magnetic solid-phase extraction (US + MSPE) versus stirrer-assisted magnetic solid-phase extraction (Stirrer + MSPE). As detailed in the supporting information (Fig. S2 and Table S1), under same conditions, the US + MSPE system exhibited a significantly higher extraction efficiency (2.61-fold) compared to the Stirrer + MSPE system. This statistically significant difference was further confirmed by ANOVA analysis (p -value = $3.1E-05$). Acoustic cavitation and microscopic disturbances generated by ultrasound waves in the vicinity of the adsorbent surface can explain the superior performance of the US + MSPE system. Due to these phenomena, mass transfer boundary layers are reduced and PAHs can be more effectively transferred from the sample matrix to the adsorbent (Azam et al., 2020; Liu et al., 2020). Interestingly, increasing the stirrer speed from 150 to 200 rpm had minimal impact on extraction efficiency. Conversely, increasing the ultrasound frequency from 45 kHz to 55 kHz resulted in a decrease in PAHs extraction. This observation suggests the possibility of partial degradation or destruction of PAH molecules at frequencies exceeding 45 kHz, potentially due to sonochemical effects or free radical generation induced by the ultrasound.

3.4. Method validation

To ensure the accuracy and reliability of the developed method, the performance of the US-MSPE-GC/MS for PAH extraction validated under optimum conditions and their results are presented Table 1. A correlation determination (R^2) over 0.992 was obtained for all calibration curves (concentration range = 0.01–100 ng g⁻¹), indicating a strong and good linear relationship between the analytical signal and the PAH concentrations. The limit of detection (LODs) based on a signal-to-noise ratio (S/N) of 3 ranged from 0.028 to 0.053 ng g⁻¹, and the limit of quantification (LOQs) calculated at an S/N of 10 were between 0.094 and 0.176 ng g⁻¹. The obtained values confirm that the method has sufficient sensitivity for the detection and quantification of PAHs, which allows a robust assessment of PAHs in tomato paste samples. To evaluate the consistency of the US-MSPE-GC/MS method within a lab setting, tomato paste samples spiked with known amounts of PAHs (25 ng g⁻¹ PAHs) were analyzed. These analyses were performed on the same day (intraday) and across three consecutive days (interday) to assess both repeatability and reproducibility. The method's precision was confirmed by calculating the relative standard deviations (RSDs) of peak areas, which are detailed in Table 1. The RSDs were found to be below 4.035 % for intraday analysis and within 5.96 % for interday analysis, indicating acceptable precision. These findings suggest that the US-MSPE-GC/MS method is a promising candidate for the accurate, reliable, and sensitive analysis of PAHs in real tomato paste samples.

3.5. Analysis of real samples

To assess the applicability of the proposed US-MSPE-GC/MS method for real sample analysis, four high consumed brands of tomato paste (labeled S₁ to S₄) were investigated under optimized conditions. Based on the results presented in Table 2, no PAHs were detected (denoted as ND) in the unspiked samples. This absence of target PAHs in any of the unspiked samples suggests that the samples were free from background contamination. The relative recovery (RR%) of the proposed method for PAHs was evaluated by analyzing the specified target analytes at two concentration levels of 25 and 50 ng g⁻¹ in tomato paste samples. Five replicate experiments were performed at each concentration level. The results indicated that relative recoveries for the PAHs in real samples were in the range from 88.03 to 98.52 % with RSDs of 1.50–9.19 % (see Table 2). The acceptable recovery values and good reproducibility at two concentration levels indicates the suitability of the developed method for PAHs quantification in tomato paste samples. Fig. S3 (a–c) presents the typical chromatograms of the PAHs in standard solution, unspiked tomato paste sample (S₁) and its corresponding spiked sample (concentration: 50 ng g⁻¹) after extraction process, respectively. As evident in the chromatogram of sample S₁, no distinct peaks corresponding to PAHs are observed, suggesting their absence concentration in the original sample. The chromatogram of the spiked sample displayed clear and distinct peaks at the expected retention times for the targeted PAHs. This verifies the successful extraction, enrichment, and detection of PAHs by the US-MSPE-GC/MS method, demonstrating its applicability for the analysis of these compounds in tomato paste samples.

Table 1
Analytical merits of the proposed method.

Analyte	Linearity (ng g ⁻¹)	Slope	Intercept	R ²	LOD (ng g ⁻¹)	LOQ (ng g ⁻¹)	Intraday RSDs (% , n = 5)	Interday RSDs (% , n = 5)
BaA	0.01–100	4.26E+05	6.42E+06	0.997	0.033	0.109	1.899	2.867
Chr	0.01–100	4.52E+05	5.28E+06	0.994	0.045	0.150	1.587	2.560
BkFL	0.01–100	2.50E+05	2.47E+06	0.992	0.053	0.176	4.035	5.960
BaP	0.01–100	2.92E+05	3.75E+06	0.998	0.029	0.097	1.082	2.069
DBA	0.01–100	1.17E+05	1.39E+06	0.998	0.028	0.094	2.521	3.476
Ind	0.01–100	1.00E+05	1.52E+06	0.997	0.032	0.108	3.507	4.482
BP	0.01–100	2.37E+05	2.98E+06	0.996	0.037	0.123	1.507	2.484
BbFL	0.01–100	3.60E+05	4.22E+06	0.996	0.036	0.120	3.294	4.240

3.6. Comparison of US-MSPE-GC/MS with other reported MSPE methods

The analytical efficiency and reliability of the US-MSPE-GC/MS method, using nectarine core-derived biochar (NBC) as adsorbent, was evaluated in comparison with previously reported methods for the PAHs determination. As can be seen from Table 3 and Table S4, MNBCs as a sorbent offer ease of separation and cost-effectiveness compared to other sorbents. Furthermore, the magnetic solid phase extraction (MSPE) method employed here, simplifies handling procedures compared to traditional extraction techniques. The developed method uses a very small amount (10 mg) of MNBC adsorbent. This minimum adsorbent requirement has led to a significant economic savings in reagent consumption compared to previous studies. Besides, the low optimal adsorbent dose of MNBC suggests an intrinsic advantage for this adsorbent. This observation implies potentially superior inherent capabilities of MNBC for PAHs extraction compared to conventional adsorbents employed in previous studies. The lower RSDs value (<5.96 %) in comparison to the average RSDs of 8.96 % reported in other studies highlights the higher precision and reproducibility of the current method. The best extraction time (30 min) is within a reasonable range compared to previous studies reported using a mechanical stirrer (e.g., 15–45 min). However, the use of ultrasound irradiation did not significantly speed up the extraction process or shorten the overall duration of the procedure. This observation contradicts our initial expectations and suggests a limited impact of ultrasound irradiation on the PAHs extraction process using MNBCs as a sorbent. The present investigation achieved a remarkably low LODs (0.0405 ng g⁻¹, range: 0.028–0.053 ng g⁻¹), representing a near nine-fold improvement over established methods (average LODs: 0.3631 ng g⁻¹). This enhanced sensitivity facilitates detection of trace concentrations of PAH analytes. The mean of extraction recovery (ER) of 93.28 %, slightly lower than the mean ER of 94.62 % in other studies. Despite the small difference, the high ER indicates that US-MSPE-GC/MS method is efficient in extracting of PAHs from tomato paste. A key limitation of this study is related to the utilization of dichloromethane as the extraction eluent. Dichloromethane undeniably offers exceptional efficiency in PAHs extraction, but its environmental impact compared to alternative eluents has raised significant concerns. Therefore, it can be proposed to use a solvent with competitive extraction performance and less adverse effects on the environment in the future studies.

4. Conclusion

This study presents an ultrasound-assisted magnetic solid phase extraction (US-MSPE) method coupled with gas chromatography–mass spectrometry (GC–MS) for the efficient extraction and pre-concentration of polycyclic aromatic hydrocarbons (PAHs) from tomato paste samples. A novel magnetic nanocomposite adsorbent (MNBC) was synthesized and successfully integrated into the US-MSPE process. Under optimized extraction conditions, the developed method demonstrated exceptional performance with a total area under the curve (ΣAUC_s) of 2.50E+07 and relative standard deviations (RSDs) below 5.96 %. The method exhibited low limits of detection (LODs) and limits of quantification (LOQs), indicating its high sensitivity for PAHs analysis. Moreover, excellent

Table 2
Recovery and precision of PAHs in various tomato paste samples using US-MSPE-GC/MS method.

Sample	Analyte	Mean(ng g^{-1})	Spiked amount				Sample	Mean(ng g^{-1})	Spiked amount			
			(ng g^{-1})						(ng g^{-1})			
			25		50				25		50	
RR(%)	RSD(%)	RR(%)	RSD(%)	RR(%)	RSD(%)	RR(%)	RSD(%)	RR(%)	RSD(%)			
S1	BaA	ND	95.87	3.52	96.89	2.25	ND	93.78	2.08	96.57	1.69	
	Chr	ND	93.30	3.10	95.21	3.46	ND	93.96	3.51	95.62	2.44	
	BkFL	ND	96.56	2.44	98.52	1.59	ND	92.03	6.53	95.66	5.15	
	BaP	ND	90.15	5.49	92.24	3.10	ND	88.03	3.34	93.67	5.83	
	DBA	ND	93.73	2.59	95.81	4.48	S2	ND	91.64	3.16	94.08	2.50
	Ind	ND	92.99	1.50	96.26	3.26	ND	92.07	4.78	97.22	5.58	
	BP	ND	95.70	4.14	97.94	1.52	ND	93.74	5.84	98.90	5.27	
	BbFL	ND	92.58	3.90	96.29	4.72	ND	91.30	4.81	94.72	4.20	
	BaA	ND	92.78	3.11	95.98	3.45	ND	91.40	4.99	96.42	5.31	
	Chr	ND	91.43	1.66	94.96	5.61	ND	95.37	5.66	97.08	4.93	
S3	BkFL	ND	93.02	4.68	97.27	5.32	ND	93.87	3.78	96.23	8.86	
	BaP	ND	89.90	2.38	94.29	3.69	S4	ND	91.19	6.82	92.29	1.95
	DBA	ND	90.43	5.32	95.32	4.72	ND	93.00	9.19	93.57	7.57	
	Ind	ND	91.53	4.51	94.82	5.30	ND	90.07	4.41	95.24	5.90	
	BP	ND	94.37	3.34	95.59	5.88	ND	89.59	5.49	93.39	7.88	
	BbFL	ND	93.91	2.85	97.96	6.06	ND	94.75	4.20	97.39	8.91	

Table 3
Comparison of other reported analytical methods with the current proposed MSPE for PAHs extraction.

	Study 1	Study 2	Study 3	Study 4	Study 5
Sorbent	modified fiber	Neutral Si/basic Si/acidic	β -CD@GO/SiO ₂	Silica-alumina	mMWCNTs
Methods	SPME	SPE	SPE	SPE	MSPE
Instrument	HS-GC-FID	GC-FID	HPLC-DAD	HPLC-UV	GC-MS
Sorbent mass (mg)	N.D.	400	200	8	5
Type of eluent.	methanol	dichloromethane	Acetone	acetonitrile	toluene
extraction time (min)	40	15	N.D.	45	10
LODs (ng g^{-1})	0.04–2.32	0.1–0.3	0.1–0.3	0.26–1.15	0.10 – 0.88
RSD (%)	< 11.6	< 15.6	< 5.5	< 7.4	< 9.6
ER%	81.07–97.5	83.69–94.25	75.1–102.6	80–104	87.8–122.3
Samples	Vegetables	meat products	Fried Food	barbecued food	Edible oils
Reference	(Lei et al., 2011)	(Olatunji et al., 2014)	(Wang et al., 2021)	(Dost & Ideli, 2012)	(Zhao et al., 2011)
	Study 6	Study 7	Study 8	Study 9	Study 10
Sorbent	3D-IL@mGO	Spent tea leaves	Fe ₃ O ₄ /Cu: CuO/GO-NC	CP-Sil 19CB	MNBC
Methods	MSPE	μ -SPE	MD- μ -SPE	SPME	MSPE
Instrument	GC-MS	GC-FID	HPLC-UV	HPLC-FLD	GC-MS
Sorbent mass (mg)	50	5	14	N.D.	10
Type of eluent.	toluene	hexane	acetonitrile	methanol	dichloromethane
extraction time (min)	10	12	12	15	30
LODs (ng g^{-1})	0.05–0.30	0.05–0.4	0.015–0.061	0.01–0.1	0.028 to 0.053
RSD (%)	< 7.9	< 9.8	< 5.62	< 7.6	< 4.96
ER (%)	80.2–115	88–111.4	95.1–106.8	70.1–98.24	88.03 to 98.52
Samples	vegetable oil	Rice	Vegetables, fruits	food samples	tomato paste
Reference	(Zhang et al., 2017)	(Nazir et al., 2020)	(Asfaram et al., 2020)	(Ishizaki et al., 2010)	This Study

linearity was observed with high R-squared values, confirming the method's reliability. The incorporation of ultrasound irradiation into the US-MSPE system significantly enhanced the extraction efficiency of PAHs compared to a conventional stirrer-based MSPE system. ANOVA analysis revealed a statistically significant difference (p -value = 3.1×10^{-5}) between the two methods, with US-MSPE achieving a 2.61-fold increase in extraction efficiency. The US-MSPE-GC/MS method demonstrated effective detection of PAHs in real tomato paste samples with satisfactory relative recoveries ranging from 88.03 % to 98.52 % and low RSDs (RSD < 9.19 %). However, no PAHs were detected in the tested samples. Overall, the US-MSPE-GC/MS method offers a compelling combination of simplicity, ease of separation, and high efficiency, making it a promising alternative for PAHs analysis in environmental monitoring and other sensitive applications.

Ethical approval

IR.SIRUMS.REC.1402.012.

Consent to participate

Not applicable.

Consent to publish

Not applicable.

Funding/Acknowledgment

This work was supported by Sirjan School of Medical Sciences, Sirjan, Iran [grant number: 40100010, Ethical code: IR.SIRUMS.REC.1402.012] and Dr. Kazemi Ashtiani Grant (given to selected young researcher and assistant professor) from Iran's National Elites Foundation.

Authors Contributions

This research is a collaborative effort by a team of authors with expertise in various areas relevant to the investigation. **Ali Azari** and **Seyed Ali Razavi Nasab** were involved in visualization, writing, reviewing, editing, and supervision. **Hossein Kamani** and **Kamyar Yaghmaein** were involved in conceptualization, methodology, software, and writing-reviewing and editing. **Neda Vatankhah**; **Mahmood Yousefi** and **Maryam Sarkhosh** were involved in formal analysis, methodology, investigation, and writing original draft preparation. **Hadi Mahmoudi-Moghaddam** and **Mahmood Reza Masoudi** contributed to investigation, writing original draft, formal analysis, data collection, and methodology. **Reza Sadeghi** was involved in investigation, software, and validation.

Declaration of competing interest

The authors have declared no conflict of interest.

Data availability

The data that has been used is confidential.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fochx.2024.101810>.

References

- Agus, B. A. P., Rajentran, K., Selamat, J., Lestari, S. D., Umar, N. B., & Hussain, N. (2023). Determination of 16 EPA PAHs in food using gas and liquid chromatography. *Journal of Food Composition and Analysis*, 116, Article 105038.
- Akbari-Adergani, B., Mahmood-Babooi, K., Salehi, A., Khaniki, G. J., Shariatifar, N., Sadighara, P., & Zeinali, T. (2021). GC-MS determination of the content of polycyclic aromatic hydrocarbons in bread and potato tahdig prepared with the common edible oil. *Environmental Monitoring and Assessment*, 193, 540.
- Ameer, K., Shahbaz, H. M., & Kwon, J. H. (2017). Green extraction methods for polyphenols from plant matrices and their byproducts: A review. *Comprehensive Reviews in Food Science and Food Safety*, 16, 295–315.
- Andrade-Eiroa, A., Canle, M., Leroy-Cancellieri, V., & Cerdà, V. (2016). Solid-phase extraction of organic compounds: A critical review. Part ii. *TrAC Trends in Analytical Chemistry*, 80, 655–667.
- Asfaram, A., DIL, E. A., Arabkhani, P., Sadeghfard, F., & Ghaedi, M. (2020). Magnetic CuO-GO nanocomposite for efficient dispersive micro-solid phase extraction of polycyclic aromatic hydrocarbons from vegetable, fruit, and environmental water samples by liquid chromatographic determination. *Talanta*, 218, Article 121131.
- Azam, S. R., MA, H., XU, B., Devi, S., Siddique, M. A. B., Stanley, S. L., ... Zhu, J. (2020). Efficacy of ultrasound treatment in the removal of pesticide residues from fresh vegetables: A review. *Trends in Food Science & Technology*, 97, 417–432.
- Baraskina, J. D. A. (2021). *Evaluation of the efficiency of okra adsorbent for heavy metals removal from wastewater in natural gas production*.
- Chen, W., He, H., Lei, L., Zhu, K., He, D., Huang, J., & Ai, Y. (2022). Green synthesis of novel Fe nanoparticles embedded in N-doped biochar composites derived from bagasse for sulfadiazine degradation via peroxymonosulfate activator: Mechanism insight and performance assessment. *Journal of Water Process Engineering*, 49, Article 103131.
- Cortese, M., Gigliobianco, M. R., Magnoni, F., Censi, R., Martino, D. I., & P. (2020). Compensate for or minimize matrix effects? Strategies for overcoming matrix effects in liquid chromatography-mass spectrometry technique: A tutorial review. *Molecules*, 25, 3047.
- Dalmau, E., Rosselló, C., Eim, V., Ratti, C., & Simal, S. (2020). Ultrasound-assisted aqueous extraction of biocompounds from orange byproduct: Experimental kinetics and modeling. *Antioxidants*, 9, 352.
- Das, A. K., Bhattacharya, D., Das, A., Nath, S., Bandyopadhyay, S., Nanda, P. K., & Gargaoua, M. (2023). Current innovative approaches in reducing polycyclic aromatic hydrocarbons (PAHs) in processed meat and meat products. *Chemical and Biological Technologies in Agriculture*, 10, 109.
- Di, S., Ning, T., Yu, J., Chen, P., Yu, H., Wang, J., Yang, H., & Zhu, S. (2020). Recent advances and applications of magnetic nanomaterials in environmental sample analysis. *TrAC Trends in Analytical Chemistry*, 126, Article 115864.
- Dost, K., & Ideli, C. (2012). Determination of polycyclic aromatic hydrocarbons in edible oils and barbecued food by HPLC/UV-vis detection. *Food Chemistry*, 133, 193–199.
- Farrokhzadeh, S., & Razmi, H. (2018). Use of chicken feet yellow membrane as a biosorbent in miniaturized solid phase extraction for determination of polycyclic aromatic hydrocarbons in several real samples. *Microchemical Journal*, 142, 403–410.
- Greer, B., Chevallier, O., Quinn, B., Botana, L. M., & Elliott, C. T. (2021). Redefining dilute and shoot: The evolution of the technique and its application in the analysis of foods and biological matrices by liquid chromatography mass spectrometry. *TrAC Trends in Analytical Chemistry*, 141, Article 116284.
- Ilyas, S., Abdullah, B., & Tahir, D. (2020). Enhancement of absorbing frequency and photo-catalytic performance by temperature treatment of composites Fe3O4-AC nanoparticle. *Advanced Powder Technology*, 31, 905–913.
- Ishizaki, A., Saito, K., Hanioka, N., Narimatsu, S., & Kataoka, H. (2010). Determination of polycyclic aromatic hydrocarbons in food samples by automated on-line in-tube solid-phase microextraction coupled with high-performance liquid chromatography-fluorescence detection. *Journal of Chromatography A*, 1217, 5555–5563.
- Jebli, A., El Amri, A., Hsissou, R., Lebki, A., Zarrik, B., Bouhassane, F. Z., ... Lebki, A. (2023). Synthesis of a chitosan@ hydroxyapatite composite hybrid using a new approach for high-performance removal of crystal violet dye in aqueous solution, equilibrium isotherms and process optimization. *Journal of the Taiwan Institute of Chemical Engineers*, 149, Article 105006.
- Jinadasa, B., Monteau, F., & Morais, S. (2020). Critical review of micro-extraction techniques used in the determination of polycyclic aromatic hydrocarbons in biological, environmental and food samples. *Food Additives & Contaminants: Part A*, 37, 1004–1026.
- Lei, F.-F., Huang, J.-Y., Zhang, X.-N., Liu, X.-J., & Li, X.-J. (2011). Determination of polycyclic aromatic hydrocarbons in vegetables by headspace SPME-GC. *Chromatographia*, 74, 99–107.
- Liu, S., Huang, Y., Qian, C., Xiang, Z., & Ouyang, G. (2020). Physical assistive technologies of solid-phase microextraction: Recent trends and future perspectives. *TrAC Trends in Analytical Chemistry*, 128, Article 115916.
- Manousi, N., & Zachariadis, G. A. (2020). Recent advances in the extraction of polycyclic aromatic hydrocarbons from environmental samples. *Molecules*, 25, 2182.
- Nazir, N. A. M., Raoov, M., & Mohamad, S. (2020). Spent tea leaves as an adsorbent for micro-solid-phase extraction of polycyclic aromatic hydrocarbons (PAHs) from water and food samples prior to GC-FID analysis. *Microchemical Journal*, 159, Article 105581.
- Ofori, S. A., Cobbina, S. J., & Doko, D. A. (2020). The occurrence and levels of polycyclic aromatic hydrocarbons (PAHs) in African environments—a systematic review. *Environmental Science and Pollution Research*, 27, 32389–32431.
- Olatunji, O. S., Fatoki, O. S., Opeolu, B. O., & Kimba, B. J. (2014). Determination of polycyclic aromatic hydrocarbons [PAHs] in processed meat products using gas chromatography-flame ionization detector. *Food Chemistry*, 156, 296–300.
- Prajapati, A. K., & Mondal, M. K. (2022). Green synthesis of Fe3O4-onion peel biochar nanocomposites for adsorption of Cr (VI), methylene blue and Congo red dye from aqueous solutions. *Journal of Molecular Liquids*, 349, Article 118161.
- Raza, N., Hashemi, B., Kim, K.-H., Lee, S.-H., & Deep, A. (2018). Aromatic hydrocarbons in air, water, and soil: Sampling and pretreatment techniques. *TrAC Trends in Analytical Chemistry*, 103, 56–73.
- Rezaee, M., Yamini, Y., & Faraji, M. (2010). Evolution of dispersive liquid-liquid microextraction method. *Journal of Chromatography A*, 1217, 2342–2357.
- Russo, M., Camillo, M. R. T., La Tella, R., Rigano, F., Donato, P., Mondello, L., & Dugo, P. (2024). Principles and applications of porous graphitic carbon stationary phase in liquid chromatography: An update. *Journal of Chromatography A*, 1719, 464728.
- Rykowska, I., Ziemlińska, J., & Nowak, I. (2018). Modern approaches in dispersive liquid-liquid microextraction (DLLME) based on ionic liquids: A review. *Journal of Molecular Liquids*, 259, 319–339.
- Sajid, M., Nazal, M. K., & Ihsanullah, I. (2021). Novel materials for dispersive (micro) solid-phase extraction of polycyclic aromatic hydrocarbons in environmental water samples: A review. *Analytica Chimica Acta*, 1141, 246–262.
- Sampaio, G. R., Guizzellini, G. M., da Silva, S. A., de Almeida, A. P., Pinaffi-Langley, A. C. C., Rogero, M. M., ... Torres, E. A. (2021). Polycyclic aromatic hydrocarbons in foods: Biological effects, legislation, occurrence, analytical methods, and strategies to reduce their formation. *International Journal of Molecular Sciences*, 22, 6010.
- Savun-hekimoglu, B. (2020). A review on sonochemistry and its environmental applications. *Acoustics*, 2(6), 766–775.
- Sun, Y., Wu, S., & Gong, G. (2019). Trends of research on polycyclic aromatic hydrocarbons in food: A 20-year perspective from 1997 to 2017. *Trends in Food Science & Technology*, 83, 86–98.
- Szulejko, J. E., Kim, K.-H., Brown, R. J., & Bae, M.-S. (2014). Review of progress in solvent-extraction techniques for the determination of polyaromatic hydrocarbons as airborne pollutants. *TrAC Trends in Analytical Chemistry*, 61, 40–48.
- Tavoosidana, G., Abdolhosseini, M., Mazaheri, Y., Basaran, B., Shavali-GILANI, P., & Sadighara, P. (2024). *The carcinogenic PAHs in breads, amount, analytical method and mitigation strategy, a systematic review study* (p. 24). BMC Public Health.
- Temerdashev, Z., Musorina, T., Chervonnaya, T., & Arutyunyan, Z. V. (2021). Possibilities and limitations of solid-phase and liquid extraction for the determination of polycyclic aromatic hydrocarbons in environmental samples. *Journal of Analytical Chemistry*, 76, 1357–1370.
- Thakur, A., & Kumar, A. (2023). Unraveling the multifaceted mechanisms and untapped potential of activated carbon in remediation of emerging pollutants: A comprehensive review and critical appraisal of advanced techniques. *Chemosphere*, 346, 140608.
- Trufelli, H., Palma, P., Famigliani, G., & Cappiello, A. (2011). An overview of matrix effects in liquid chromatography-mass spectrometry. *Mass Spectrometry Reviews*, 30, 491–509.
- Wang, N., Lu, Y., & Cui, B. (2021). Preparation and application of β -Cyclodextrin functionalised graphene oxide-grafted silica sorbents for solid-phase extraction (SPE) of polycyclic aromatic hydrocarbons from fried food using a box-behnken design. *Food Analytical Methods*, 14, 1577–1589.

- Wang, Q., Fagbohun, E. O., Zhu, H., Hussain, A., Wang, F., & Cui, Y. (2023). One-step synthesis of magnetic asphalt-based activated carbon with high specific surface area and adsorption performance for methylene blue. *Separation and Purification Technology*, 321, Article 124205.
- Wu, A., Zhao, X., Wang, J., Tang, Z., Zhao, T., Niu, L., Yu, W., Yang, C., Fang, M., & Lv, H. (2021). Application of solid-phase extraction based on magnetic nanoparticle adsorbents for the analysis of selected persistent organic pollutants in environmental water: A review of recent advances. *Critical Reviews in Environmental Science and Technology*, 51, 44–112.
- Yaashikaa, P., Kumar, P. S., Varjani, S. J., & Saravanan, A. (2019). Advances in production and application of biochar from lignocellulosic feedstocks for remediation of environmental pollutants. *Bioresource Technology*, 292, Article 122030.
- Yu, M., Wang, L., Hu, L., Li, Y., Luo, D., & Mei, S. (2019). Recent applications of magnetic composites as extraction adsorbents for determination of environmental pollutants. *TrAC Trends in Analytical Chemistry*, 119, Article 115611.
- Zeger, V. R., Bell, D. S., & Anderson, J. L. (2023). Understanding the influence of polymeric ionic liquid sorbent coating substituents on cannabinoid and pesticide affinity in solid-phase microextraction. *Journal of Chromatography A*, 1706, Article 464222.
- Zhang, W., Zhou, P., Liu, W., Wang, H., & Wang, X. (2020). Enhanced adsorption/ extraction of five typical polycyclic aromatic hydrocarbons from meat samples using magnetic effervescent tablets composed of dicationic ionic liquids and NiFe₂O₄ nanoparticles. *Journal of Molecular Liquids*, 315, Article 113682.
- Zhang, Y., Zhou, H., Zhang, Z.-H., Wu, X.-L., Chen, W.-G., Zhu, Y., Fang, C.-F., & Zhao, Y.-G. (2017). Three-dimensional ionic liquid functionalized magnetic graphene oxide nanocomposite for the magnetic dispersive solid phase extraction of 16 polycyclic aromatic hydrocarbons in vegetable oils. *Journal of Chromatography A*, 1489, 29–38.
- Zhang, Z., Yang, M. J., & Pawliszyn, J. (1994). Solid-phase microextraction. A solvent-free alternative for sample preparation. *Analytical Chemistry*, 66, 844A–853A.
- Zhao, Q., Wei, F., Luo, Y.-B., Ding, J., Xiao, N., & Feng, Y.-Q. (2011). Rapid magnetic solid-phase extraction based on magnetic multiwalled carbon nanotubes for the determination of polycyclic aromatic hydrocarbons in edible oils. *Journal of Agricultural and Food Chemistry*, 59, 12794–12800.
- Zungum, I. U., & Imam, T. S. (2021). *Ecotoxicity and associated threat of polycyclic aromatic hydrocarbons (PAHs) to biodiversity: A review*. <https://doi.org/10.20944/preprints202109.0377.v1>. Preprints, Article 2021090377.