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Application of nanomaterials for determination and removal of polycyclic aromatic hydrocarbons in food products: A review

Ehsan Shamloo [a], Samira Shokri [b], Parisa Sadighara [b], Saeid Fallahizadeh [c,d], Ahmad Ghasemi [e], Zohreh Abdi-Moghadam [e], Alieh Rezagholizade-shirvan [a,*], Yeganeh Mazaheri [b,*]

[a] Department of Food Science and Technology, Neyshabur University of Medical Sciences, Neyshabur, Iran
[b] Department of Environmental Health, Food Safety Division, Faculty of Public Health, Tehran University of Medical Sciences, Tehran, Iran
[c] School of Public Health, Yasuj University of Medical Sciences, Yasuj, Iran
[d] Social Determinants of Health Research Center, Yasuj University of Medical Sciences, Yasuj, Iran.
[e] Department of Biochemistry, Nutrition and Food Sciences, School of Medicine, Gonabad University of Medical Sciences, Gonabad, Iran

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs), toxic persistent pollutants, result in adverse impacts to human being health. Among the variety contaminant remediation approaches, nanotechnology was found promising in terms of its efficiency and exceptional size-dependent properties. Nanomaterials also possess high particular surface area, rapid dissolution characteristics, high sorption, magnetic -properties and quantum confinement. Nanoparticles (NPs) have been employed as sorbents in the assessment of PAHs, including carbon NPs, mesoporous silica NPs, metallic species, metal oxides, as well as magnetic and magnetized NPs. Magnetic nanocomposites have demonstrated high efficiency (>99 %) in removing PAHs from food products. Similarly, a magnetic chitosan/molybdenum disulfide nanocomposite exhibited excellent adsorption capacities for PAHs in milk samples. Present research was conducted on multiple academic platforms, including Google Scholar, Science Direct, Elsevier, Springer, Scopus, and PubMed from 2017 to 2024. Various combinations of keywords, such as "PAHs," "extraction," "removal," and "nanomaterials," were used in the search. The aim of this manuscript is to reviews the application of nanotechnologies for the elimination and extraction of PAHs from contaminated food products. The findings of this study offer novel insights into efficient and cost-saving approach and suggest the potential of NPs as promising agents for preconcentration and remediation of PAHs from variety food samples. Also, the obtained results will pave the way for future explorations that will lead to the achievement of maximum efficiency for the analysis and extraction of materials in more diverse matrices. Therefore, it is suggested to investigate the potential of various nanomaterials regarding various matrices in future.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are classified as a diverse group of persistent organic environmental contaminant recognized by the presence of two or more fused benzene rings within their molecular composition. The formation of these substances occurs via the pyrolysis process of organic materials or during inadequate industrial combustion activities (Abbas et al., 2018; Li, Yn, et al., 2018). The classification of PAHs is determined by variables including their relative molecular weight and the quantity of benzene rings they possess, leading to the differentiation between low molecular PAHs (LPAHs, 2–4 rings) and high molecular weight PAHs (HPAHs, > 4 rings). A considerable number of PAHs have been scientifically linked to teratogenic, carcinogenic, and mutagenic characteristics, thus presenting a notable hazard to human health (Abbas et al., 2018; Li, Yn, et al., 2018). Seven of these, namely benzo (a)anthracene (BaA), benzo(*a*)pyrene (BaP), benzo(*b*)fluoranthene (BbF), benzo(k) fluoranthene (BkF), dibenzo(*a*)anthracene (DBA), chrysene (Chry), and indeno (1,2,3-c,d) pyrene (IP), have been identified as potential human carcinogens. BaP is frequently utilized as a surrogate for the entire group of PAHs due to its known carcinogenic properties. Due to the ecological risks, toxic nature, and negative impacts on human health, the assessment, identification, and removal of PAHs have emerged as a matter of global concern. Therefore, it is critical to remove PAHs, and their derivatives using efficient and novel methods

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* Corresponding authors.
E-mail addresses: alie.gholizade@gmail.com (A. Rezagholizade-shirvan), y.m.mazaheri20@gmail.com (Y. Mazaheri).

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(Bacosa et al., 2020).

Several remediation technologies have been investigated for their effectiveness either independently or in combination with physical, chemical, biological, and thermal approaches (Farhadi et al., 2022; Khosravi-Darani et al., 2019; Mohtashami et al., 2024; Rezagholizade-shirvan, Masrournia, et al., 2023; Shokri et al., 2023; Shokri et al., 2024). Traditional physicochemical approaches, such as micro flocculation and absorption, have been commonly employed for the remediation of hazardous pollutants (Rezagholizade-Shirvan, Kalantarmahdavi, & Amiryousefi, 2023). However, these methods are known to be time-consuming and can sometimes lead to the conversion of PAHs into other harmful substances (Kim et al., 2022; Rotondo et al., 2023). In recent times, nanomaterials (NMs) have garnered significant attention owing to their nanometer size-related properties. From this perspective, the use of NMs has the potential to offer a quicker and more efficient method for the removal of PAHs. In addition, nanomaterials possess characteristics such as rapid dissolution, high absorption, super magnetic properties, and quantum confinement (Azari et al., 2024; Borji et al., 2020).

The most recent ten years of research activity have shown a focus on the application of NPs for the elimination of harmful PAHs. This review provides valuable information about the significant role of various NPs in determination and remediation of PAHs. The objective of this study was to deliver a comprehensive synthesis of contemporary understanding and data to evaluate the necessity for additional investigation that may facilitate effective and optimal extraction and detection techniques of PAHs using NPs.

2. Toxicity of PAHs on human health

Benzene, its derivates, and PAHs have gained significant acknowledgement as environmental contaminants due to their association with various diseases. PAHs constitute a group of chemicals composed of multiple benzene rings. Numerous PAHs and their derivates have been identified as carcinogenic, teratogenic, and genotoxic agents (Mallah et al., 2022). The association between the carcinogenic properties of PAHs and the quantity of benzenoid rings is well established. PAHs have been categorized into four distinct groups by the International Agency for Research on Cancer (IARC). Group 1 involves of constituents known to be carcinogenic to humans, while group 2 A and 2B encompass compounds suspected of being human carcinogens. In contrast, group 3 does not fall under the classification of human carcinogens (Das & Ravi, 2022). The IARC has identified certain PAHs as either carcinogen for human or potential carcinogens. The classification of PAHs is primarily determined by their capacity to promote cancer development within specific groups BaP is considered carcinogenic to human beings (Group1).

Cytochrome P450 (CYP450) and epoxide hydrolase enzymes metabolize BaP into various metabolites, including reactive epoxide 7,8-dihydroxy-9,10-oxy-7,8,9,10-tetrahydrobenzo[a] pyrene (BPDE). Although BaP is not considered as carcinogenic or even mutagenic by itself, its derivatives like BPDE change the function of cell and organs. Long-term PAH exposure leads to tumor development in numerous organs such as lung, skin, pancreas, bladder, esophagus, female breast, and colon (Barbosa Jr et al., 2023). In addition, PAH contact may raise the risk of lung cancer and cardiovascular disease (CVD), as well as atherosclerosis, hypertension, thrombosis, and myocardial infarction (MI) (Holme et al., 2019). The serious impacts of PAHs on human being health will be mainly depends on the amount of exposure (Length of time), the content of PAHs, the toxicity property of the PAHs, and the routes of exposure, over ingestion, skin connection and inhalation (Fig. 1). PAHs are one of the most prevalent organic persistent environmental pollutants that contain a hazard risk to human health. (See Table 1.)

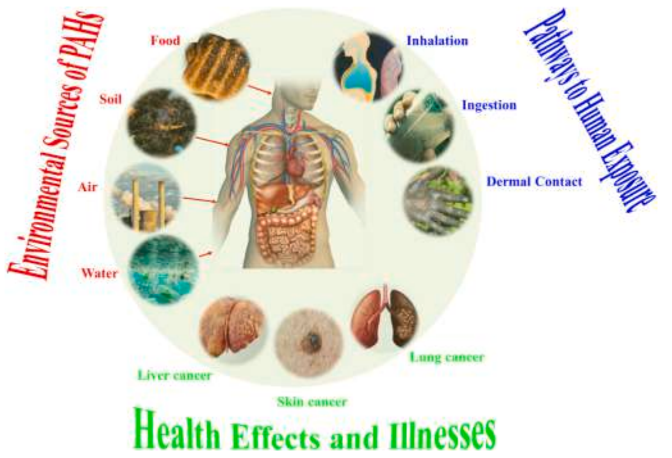

Fig. 1. Schematic diagram of resources of PAHs.

3. PAHs in food products

PAHs are generated from the partial combustion of organic materials, such as burning wood, grilling, smoking, frying, roasting, toasting and barbecuing foods, especially fish and meat, where contact between dripping lipids and flames leads to PAH deposition on the food surfaces (Fig. 2). The PAHs accumulation in the food chain is because of their lipophilic and hydrophobic properties (Adeyeye & Ashaolu, 2022; Luper Tsenum & Yarkwan, 2020). PAHs residues have been identified in a range of food items such as vegetable oils, seafood, milk, fruits, grilled meat, tea, and coffee. Despite the relatively low levels of PAHs in food products, their existence has been associated with the increase of cancer in humans (Mahgoub, 2019). Regarding vegetable oils, coconut oil may demonstrate heightened concentrations of PAH4 in comparison to oils and fats obtained from other origins due to the relatively higher amount of BaA and Chr in coconuts, which are challenging to remove through the refining processes of coconut oil. After a recent evaluation carried out in 2018, it was determined by the European Commission that enhancements in smoking were inadequate in lowering the levels of PAHs to permissible thresholds. Consequently, an unspecified prolongation was sanctioned for the domestic manufacture and utilization of smoked commodities from these particular Member States, permitting BaP and 4 PAH concentrations exceeding 5.0 and 30.0 μg/kg, respectively. Moreover, the recent regulation set threshold of 10.0 for BaP and 50.0 μg/kg for4PAH in plant-drived powders employed for the preparation of beverages (Regulation, 2020). In the United States, a permissible limit of 0.2 was set by the Environmental Protection Agency (EPA) for drinking water (Anonymous, Atabati et al., 2020).

Factors influencing PAH formation include environmental contamination in raw samples, cooking procedures and temperature and time duration of processing in processed samples, which further enhance PAH levels in the final products (Onopiuk et al., 2021; Sailer et al., 2023).

In study conducted by Min et al. (Onopiuk et al., 2021) finding showed that PAHs generation in meat and their products exposed to heat is more influenced by temperature changes comparing to exposure time period (Yousefi et al., 2022).

Ciecierska et al. (Ciecierska et al., 2019) observed that roasted coffee beans posed considerably lower amount of contamination in comparison to green coffee beans, demonstrating that the f roasting result in reducing PAHs content in the coffee. This is related to the maximum volatility of light PAHs.

The processes of food production, particularly those involving elevated temperatures comprising smoking, roasting, baking, and frying are more prone to the production and accumulate of substantial quantities of PAHs. The generation of PAHs at high temperatures is predominantly attributed to the processes of pyrolysis reaction of fat and oxidation, protein, and carbohydrates. Moreover, pyrolysis reaction of

Table 1
Nanothechnology application in PAHs detect.

Nanocomposite	Food products	PAHs compounds	Technique	Analytical Methods	Limit of detection	Result	Reference
Fe_3O_4/CNS/ppy Fe_3O_4@ppyMWCN	Environmental water samples	NAP, 2-methylnaphthalene, 2-bromonaphthalene, FLU, and ANTH	MSPE		0.01–0.05 ng·mL^{-1}	The percentage of recovery of the applied approach ranged from 88.9 to 99 % Condition: sorbent amount, 20 mg; extraction time, 10 min.	(Abbasi et al., 2018)
Fe_3O_4@COF	Sausage and barbecue	NAP,ACY (acenaphthylene) PHEANT PYRCHR (chrysene), perylene (Pery), BaA, benzo [b] fluoranthene BbF FLU BkF BaP	MSPE	High performance liquid chromatography diode array detection (HPLC-DAD)	1.84–8.35 ng/kg	The recoveries of the method ranged between 83.2 and 119.3 sorbent amount, 6 mg; extraction time, 9 min.	(Chen, Li, et al., 2020)
(Poly(βCD-IL)@Fe_3O_4 in 1-octanol)	Water, rice and tea beverage	ACE, FLU, PHE, FLA, PYR, BaA, and BaP	Dispersive liquid phase microextraction	GC-FID	0.02–0.14	The recoveries of the method ranged between 84 and 110. Dosage Amount (10 mg), Sample Volume (15 mL), Extraction Time (5 min)	(Hui et al., 2020)
(Fe_3O_4@βCD-Vinyl-TDI) Ferrofluid	Rice	ACE (acenaphthene), PHE, FLA (Fluoranthene), FLU, and PYR	MSPE	Gas chromatography–mass spectrometry (GC/MS)	0.01–0.18	The recoveries of the method ranged between 0.01 and 0.18 Dosage Amount 20 mg, Sample Volume25 Ml, Extraction Time 30 min	(Boon et al., 2019)
GCA-SPE	Water and milk	NAP, ACY ACE FLU PHE ACE FLA PYR benzo[*a*]anthracene CHR benzo[*b*]fluoranthene benzo[*k*]fluoranthene BaP indeno[1,2,3-c,d]pyrene dibenzo [*a*,*h*]anthracene benzo[*g*,*h*,*i*]perylene	SPE	GC/MS	1.7–8.8 **pg** mL^{-1})	The recoveries of the method ranged beetween 85.9–113. Sorbent mass (100 mg), Samplevolume (100 mL), Solventvolume (20 mL), Extraction elution time (45 min).	(Gao et al., 2020)
RP-C18	Alcoholic and non-alcoholic drinks	NAP ACE FLU PHE ANTH FLA PYR, CHR benzo[*a*]anthracene benzo(*b*) fluoranthene benzo(*k*) fluoranthene benzo(*a*)pyrene benzo[*ghi*]perylene dibenz[*a*,*h*] anthracene indeno[1,2,3-*cd*] pyrene	SPE	GC/MS	0.02–0.6 pg mL^{-1})	The recoveries of the method ranged between 90 and 103 %.	(Rascón et al., 2019)

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Table 1 (*continued*)

Nanocomposite	Food products	PAHs compounds	Technique	Analytical Methods	Limit of detection	Result	Reference
Three-dimensional ionic liquid functionalized magnetic graphene oxide nanocomposite (3D-IL@mGO)	Edible oils	16 PAHs	MSPE	GC–MS	0.05–0.30 g/kg	BaP level in 3 out of 11 oil samples were determined above the permissible limit (2.0 g/kg, Commission Regulation 835/2011a), also the sum of 8PAHs (BaA, CHR, BaP, BbF,, BgP BkF, IcP, DaA) in 11 samples ranged from 3.03 g/kg to 229.5 g/kg.	(Zhang et al., 2017)
Magnetic multiwalled carbon nanotube-octadecylphosphonic acid modified zirconia (mMWCNT–ZrO_2–C18)	Edible oils	NAPPHEACEPYRANTand Benzo [*b*]fluoranthene	MSPE	HPLCHigh Performance Liquid Chromatography	0.06–0.55 ng/g	mMWCNT–ZrO2–C18 hybrid nanomaterial showed the highest adsorption capability and considerable impact on the enrichment and extraction of PAHs. Recovery percent of PAHs enhanced from 95.19 to 110.93 %, 95.24 to 109.94 %, 95.48 to 108.93 %, 93.14 to 106.72 %, 97.12 to 106.55 %, and 93.99 to 102.93 %, for NAP, PHE, ACE, ANT, PYR, and B(*b*)F, respectively	(Wang et al., 2018)
β-cyclodextrin functionalised graphene oxide-grafted silica (β-CD@GO/SiO_2)	Fried food	16 PAHs	SPE	HPLC	0.1–0.3 μg L	The intra-day and inter-day precisions were found to be below 3.9 % and 5.5 %, respectively. Furthermore, the analytical approach was effectively utilized for the amount of PAHs in fried food samples, revealing satisfactory recovery rates following spike experiments.	(Wang et al., 2021)
The multi-walled carbon nanotubes modified with iron oxide and silver nanoparticles (MWCNTs-Fe_3O_4)	Baby food	16 PAHs	MSPE	GC–MS	0.06–1.12 μg/kg	mixed five cereal-derivate baby food revealed the highest mean of ΣPAHs (5.06 ± 0.68 μg/kg) and mixed wheat and date-based baby food showed the lowest mean of ΣPAHs (3.03 ± 0.41 μg/kg)	(Moazzen et al., 2022)
Poly(methyl methacrylate-vinyl imidazole bromide) (poly-MMA-IL)-grafted magnetic nanoparticles	Tea fried food grilled food samples	16 PAHs	MSPE	GC-FID	0.06μg/L – 0.32μg /L	Satisfactory level of reproducibility was achieved, demonstrating intra-day and inter-day precisions with RSD ranges spanning from 3.6 % to 11.1 %. The percentage of spiked recovery values of 16 PAHs in grilled food, fried food, and tea samples varied between 80 and 12, respectively.	(Muhammad Yunus et al., 2024)
The nanohybrids utilized $NiFe_2O_4$ as magnetic cores, and NH_2-MIL-101(Al), β-cyclodextrin and graphene oxide as functional compounds cooperated with magnetic core	Roasted meat: Lamb sausagePork Chicken and Beef	PAHs	MSPE	HPLC fluorescence detector (FLD)	0.07–0.30 μg/kg	This technique simultaneous assessment of pollutants in various roasted meat samples with suitable recovery percent ranged from 86.9 to 103.9 along with high precision (relative standard deviations of 1.9–6.7 %). The effervescent reaction-enhanced nanohybrids-based microextraction technique proved to be effective in extracting	(Liu, AgyeKum, et al., 2021)

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Table 1 (*continued*)

Nanocomposite	Food products	PAHs compounds	Technique	Analytical Methods	Limit of detection	Result	Reference
						a wide range of organic pollutants from roasted meat samples.	
Magnetic nanomaterial	Barbecue smoked pork belly	16PAHs	MSPE	GC/MSS	1.2–5.4 ng·L	The method that has been developed has the potential to be employed for the evaluation of profiles of PAHs with recovery percent of 73.4 % to 90.7 %	(Pan et al., 2020)
Multiwall carbon nanotube/ zirconium oxide nanocomposite (MWCNT/ ZrO_2)	Water Coffee and tea	NAP ACY ACP (acenaphthelene) 4-Hcyclopenta[*def*]phenanthrene (CPP) FLU and carbazole	Hollow fiber solid-phase microextraction (HF-SPME)	HPLC-UV	0.033–0.16 μg L	The obtained relative recoveries from spiking PAHs into water, coffee, and tea samples ranged from 92.0 % to 106.0 %. In comparison to alternative approaches, the utilization of MWCNT/ZrO2 hollow fiber solid phase microextraction exhibited a favorable efficacy in the analysis of PAHs in intricate coffee and tea.	(Yazdi et al., 2018)
Phenyl functionalized $NiFe_2O_4@Ti_3C_2T_X$ nanocomposites	Tea and coffee	16 PAHs	MSPE	GC–MS/MS	0.1 to 0.3 ng/L	Under optimal circumstances, the method displayed exceptional linear associations for 16 PAHs falling within the intervals of 0.001–25 and 0.0005–25 μg.L^{-1}, with correlation coefficients surpassing 0.9979. An evaluation of the efficiency of the approach was undertaken by evaluating samples of tea and coffee, leading to acceptable spiked recovery percent of PAHs ranging from 84.5 to 112.6.	(Yazdi et al., 2018)
nanocomposite containing of hydroxyapatite nanomaterials (nHA) and modified carbon nanotubes (hydrogel/mCNTs (Hy/ mCNTs)	roasted and ground coffee (including Indonesian, Turkish, and Java coffee), bread (including local, baguette, toast, and sangak), kebab (chicken, hot dog, and pounded), hookah water (peach, mint gum tobacco and nectarine)	NAPFLU AndANTH	Headspace solid phase microextraction HS-SPME	GC–MS	0.0026–0.0029 μg/ml	Nanocomposite showed good adhesion on the steel surface with maximum thermal stability and long life. The sorbent could be effectively utilized to extract and detect PAHs. The relative recoveries obtained by spiking the final analytes in samples were ranged from 58.9 to 92.4 %.	(Ghorbani et al., 2023)
Chitosan-dicationic ionic liquid modified clay (bionanocomposite MMT/ CH/DIL)	Coffee and tea	16 PAHs	SPME	Gas chromatography/ mass spectrometry(GC/ MS)	0.0001 and 0.05 μg/ L	The utilization of the HS-SPME technique for the lighter PAHs alongside the DISPME approach for the heavier PAHs proved to be more suitable and discerning. The MMT/ CH/O-DIL fiber demonstrated superior extraction efficiency for PAHs in comparison to the parents substances (MMT, MMT/CH, and MMT/DIL) fibers.	(Erdem et al., 2021)
Poly(*o*-phenylenediamine)-Zn composite	Coffee	BaA Chry BbF and BaP	MSPE	GC (FID detector)	-	Concentrations of PAHs in coffee beverage samples were quantified as follows: BaA ranged from 1.4 to 16.5 μg L − 1; Chry ranged from 0.5 to 2.1 μg L − 1; Benzo[*b*]	(Khanaaekwichaporn et al., 2023)

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Table 1 (*continued*)

Nanocomposite	Food products	PAHs compounds	Technique	Analytical Methods	Limit of detection	Result	Reference
						fluoranthene (BbF) was measured at 2.2 μg L − 1; and BaPwas reported to be 6.2 μg L − 1. The analysis resulted in satisfactory recovery rates, ranging from 82.7 % to 99.0 %.	

organic constituents such as fat, carbohydrates, and protein of foods at temperature of 200 °C and higher improves the creation of low molecular weight PAHs and also free radicals which result in both cyclization and recombination reactions to generate HMW PAHs. The HMW PAHs transferred to hydrophobic and high fat parts of foods (Singh et al., 2020).This circumstance is favorable for the formation of PAHs. Alongside originating from environmental contamination and food processing, the presence of PAHs in food may result from interactions with contaminated packaging components. It is noteworthy that food consumption significantly influences the exposure to PAHs outside of the occupational setting. Individuals who do not smoke can attribute over 70 % of their PAH exposure to dietary sources (Sun et al., 2019).

Alomirah et al. (Anonymous) determined the levels of 16 PAHs in different grilled and smoked food products. Among eight detected genotoxic PAHs, Chr with level of 4.88 μg/kg and BaA with level of 2.27 μg/kg showed the maximum mean concentration. Morever, numerous reasons that have a major impact on the PAHs formation are the type of heat source, grilling time, grill geometry and marinades consumed, and fat level.

Rascón et al. (Rascón et al., 2018) detected 16 PAHs in several cereal-derived foods ($n = 22$), containing flour, cookies, breakfast cereal, pasta, rice, and bread. Anthracene and naphthalene were detected as the most common PAHs, with levels ranged between 13 and 5500 ng/kg. The concentration of 4PAH in cereals including granola, chocolate granola, milk-filled cereal and also flatbreads were reported higher than the maximum limit stablished by the European Commission.

Khalili et al., 2023 determined the level of PAHs in meat, poultry, fish and other meat products in Iran. The maximum mean concentration of 16 PAH was evaluated in smoked fish (222.7 μg/kg) and the lowest mean amount of 16 PAH was observed in chicken kebab (112.9 μg/kg). The highest mean of 4PAHs was determined in tuna fish (23.7 ± 2.4 μg/kg) and the lowest mean of 4PAHs was detected in grilled chicken and sausages (non-detected). The 4PAHs and BaP were below the EU (European Union) standard (standard limits were 30 and 5 μg/kg, respectively) (Khalili et al., 2023).

4. *Carbon-based nanoparticle* (CNMs)

Carbon-based nanomaterials (CNMs) have been applied for the reduction of PAHs in several foods. These nanomaterials can be used as bio-sorbents in solid-phase extraction (SPE) cartridges for both extraction and pre-concentration of PAHs in food samples before their examination using high-performance liquid chromatography with ultraviolet detection (HPLC-UV) (Gulia et al., 2023). Carbon-based nanomaterials including fullerenes, graphene, carbon nanotubes, and graphene derivatives incorporated with several functional groups, have unique physicochemical features that make them appropriate for the elimination of hydrocarbons from the environment (Singh et al., 2021). Unique physical and chemical features of CNMs including large surface area, high mechanical strength, good electrical conductivity, and also stability (Boopalan et al., 2024). Therefore, Nano bioremediation, which involves the use of biosynthetic nanomaterials, is known as an emerging approach for the elimination of contaminants, including PAHs, in a sustainable and eco-friendly manner (Singh et al., 2021). Various types of carbon-based NPs have been established for the degradation of PAH from water and food products.

The monomer structure of fullerene consists of a closed graphite sphere, whereas carbon nanotubes are cylindrical structures made of rolled-up graphite layers that create a concentric tube. A single rolled graphite layer gives rise to the structure of single-walled carbon nanotubes, whereas multiple rolled graphite layers contribute to the formation of multi-walled carbon nanotubes (Singh et al., 2021**).** According Zouh et al., 2018 investigation, Fullerene combined with magnetic nanomaterials ($Fe_3O_4@SiO_2@C_{60}$) were developed to the analysis of 16 PAHs by the magnetic solid-phase extraction (MSPE) technique in tea. $Fe_3O_4@SiO_2@C_{60}$ showed the detection limits ranging from 0.8 to

Table 2
Nanothechnology application in PAHs reduction.

Nanomaterial	Target pollutant	Means of removal	Percentage of removal	Matrics	Ref
Multiwalled-carbon nanotube (MWCNTs)	PAH	Extraction	99	Tap and river water	(Paszkiewicz et al., 2018)
Magnetic chitosan/molybdenum disulfide CS/MoS_2/Fe_3O_4))	PYR, ANTH, and PHE	Adsorption	90<	Milk and dairy	(Rezagholizade-Shirvan et al., 2024)
TiO_2/SiO_2–carbon nanotubes	PAH	Adsorption	> 90	Wastewater	(Rasheed et al., 2019)
Nano-reduced graphene oxide-hybridized polymeric high-inter- nal phase emulsions(RGO/polyHIPEs)	PAH	Adsorption	50–90	Water	(Huang et al., 2018)
Fe_3O_4–FeOOH	ANTH	Photodegradation	–	Water	(Gupta et al., 2017)
Graphitic carbon nitride (g-C_3N_4/Fe_3O_4)	PAH	Adsorption	100	Water	(Nian et al., 2019)
Fe_3O_4–chitosan	PAH	Sorption	96	Water	(Nisticò et al., 2017)
Fe_3O_4–wood biochar	PAH	Adsorption	90	–	(Dong et al., 2018)
Magnetic graphene oxide	PAH	Adsorption(Hussain et al., 2019)	100	–	(Hussain et al., 2019)

Fig. 2. Polycyclic aromatic hydrocarbons in various food products.

14.3 ng/L, recovery percent of 92.4 % to 106.9 % for 16 PAHs in tea (Zhou et al., 2018). The Du research team recently published findings on the production of Fe_3O_4@3-(trimethoxysilyl)propyl methacrylate@ionic liquid magnetic nanoparticles (Fe_3O_4@MPS@ILNPs), which were subsequently utilized for the magnetic extraction of seven HMW PAHs from samples of tea. Various types of functionalized Fe_3O_4 nanoparticles, such as C18 functionalized, diphenyl functionalized, fluorenyl functionalized, and grapheme functionalized, along with carbon–ferromagnetic nanocomposites, n-octadecylphosphonic acid modified mesoporous magnetic nanoparticles polydopamine-functionalized magnetic graphene and carbon nanotubes hybrid nanocomposites, (Chen et al., 2018) and porphyrin-based magnetic nanocomposites (Yu et al., 2018) have also been employed for the PAHs extraction in water. Fullerene (C60), Because of three-dimensional conjugate system, revealed strong π-π conjugative influence on aromatic components (Yu et al., 2018).

5. Graphene and graphene oxide nanocomposite

Graphene represents a carbon nanomaterial with a two-dimensional structure, consisting of single coating layer of carbon atoms densely arranged in a benzene-ring structure. Its considerable specific surface area, mechanical robustness, and notable electric and thermal attributes render graphene well-suited for various emerging applications. Through chemical functionalization, the two-dimensional carbon layer can give rise to derivatives like graphene oxide (GO) and reduced graphene oxide (rGO). The functionalization of graphene nanomaterials imparts distinct features, including enhanced dispersibility and versatility, thereby expanding their range of potential applications. Some properties including huge surface area (2630 m^2/g), high heat conductivity (3000 W/mK), as well as surface functionality have made graphene a valuable material in the food field through the world (Martínez-Álvarez et al., 2021).

Li, Yn, et al., 2018 investigated the sorption of PAHs such as NAP, FLUO, PHE, and PYR using carbon nanotubes. It was found the PAHs behavior in column leaching within the nearness of 5 mg/g CNTs appeared that the PAHs mobility could considerably be held. On the other hand, the mobility of PAHs was represented via micropore volume, surface area, and also hydrophobic characteristics. In spite of the great properties of graphene, it has a few disadvantages such stacking and agglomeration amid utilization, which can ruin its adequacy in certain applications. Thus, graphene has been commonly adjusted to upgrade its viability in numerous applications. Among the graphene subordinates, graphene oxide, a decreased form of graphene, has gotten intrigued as an amazing adsorbent owing to its abundant surface functional groups including hydroxyl, carboxyl, and epoxy groups (Huang et al., 2019). Graphene oxide nanoparticles had drown high attention for the reason of their ability to eliminate several pollutants specially PAHs.03 GO showed a high sorption potential for PAHs that was driven predominantly by the hydrophobicity of each PAH (Martínez-Álvarez et al., 2021). The mechanism of adsorption was due to the π–π interaction between PAH and magnetic GO, and the maximum adsorption potential was associated to the vast surface area and also pore volume of the nanomaterial (Huang et al., 2019).

According to Gao et al., 2020 study, the graphene/chitosan composite aerogels was utilized as solid-phase extraction sorbents to extract PAHs from water and milk. Aerogels showed the high adsorption potential for well-known 16 PAH compounds with LOD of 1.7 to 8.8 pg/mL, recovery percent of 85.9–113 % (Gao et al., 2020).

6. Metal dioxide-based nanoparticle

6.1. Iron and iron dioxide nanocomposite

Iron-based nanomaterials are employed for a variety of purposes in the mitigation of PAHs found in food (Góral et al., 2023). The synthesis of iron oxide nanoparticles through plants, bacteria, algae, and fungi has proven to be useful in the decomposition of hydrocarbons and other pollutants. Furthermore, the potential of iron carbon-based nanomaterials as adsorbents for pollutant elimination, including PAHs, has been investigated due to their durable nature, extensive surface area, and magnetic attributes. These various applications underscore the promising role of iron-based nanomaterials in reducing the presence of PAHs in food (Gabalda, 2022). Nanoscale magnetic particles can be produced through various techniques, including chemical methods like coprecipitation of hydrothermal synthesis, hydroxides, ball milling, and sol-gel transformation (Góral et al., 2023).

Iron oxide nanoparticles synthesized using green approaches, such as employing plant extracts or microorganisms, have demonstrated efficacy in the elimination of PAHs (Gulia et al., 2023). These nanoparticles possess the ability to establish robust reducing conditions that expedite the elimination of PAHs, rendering them a propitious technology for remediation of PAHs-contaminated food (Rani & Shanker, 2020b). The utilization of iron dioxide nanomaterials has shown promise in the reduction of PAHs in food due to their distinctive physicochemical attributes, characterized by heightened reactivity and increased surface area (Góral et al., 2023). Magnetic nanomaterial demonstrated simple preparation, easy use, high reusability, low cost and good potential applicability for deletion of polyaromatic hydrocarbons (Zhou et al., 2019).

Rani & Shanker, 2020a, 2020b studied the iron-oxide based chitosan-nanocomposites impact on toxic PAHs including anthracene (ANTH) and phenanthrene (PHEN) degradation. Results showed the highest degradation determined for $ZnFe_2O_4$-CS (ANTH: 95 %; PHE: 92 %) (Rani & Shanker, 2020b).

Fe_3O_4 magnetic NPs altered with polyaniline (Fe_3O_4@polyaniline) was introduced as a good alternative adsorbent for the MSPE of particular PAHs including fluoranthene, PYR and BaP in water(Zhou et al., 2019). It can be for the reason of the good affinities of polyaromatic hydrocarbons to polyaniline by $\pi - \pi$ and van der Waals interactions.

6.2. Titanium dioxide-based nanomaterials

TiO_2-based nanomaterials exhibit various applications in the reduction of PAHs in food products. Such nanomaterials are applicable in food processing for functions such as preservatives, colorants, antioxidants, and thickening agents. They possess antimicrobial characteristics and demonstrate efficacy in the prevention of food spoilage (Jawad et al., 2022). Nonetheless, it is imperative to acknowledge that prolonged or excessive utilization of TiO2 in food processing may result in allergic responses and food poisoning. Hence, it is advisable to minimize the combination of TiO_2 with other substances as much as possible. TiO_2 NPs have recently been revealed to adsorb a number of PAHs from soil and water (Rani & Shanker, 2020a). The nanoparticles scavenge activity for PAH and other toxicants can be explained by their increased affinity towards the xenobiotics as a result of surface chemistry, extensive surface area, and other inherent properties of nanoparticles. Furthermore, the synthesis of TiO_2 nanoparticles can be achieved through eco-friendly methods, including the utilization of plants and microorganisms, to yield sustainable and environmentally benign nanomaterials. These TiO_2-based nanomaterials can be applied in sensor platforms for the surveillance of environmental contamination and the formulation of advanced approaches to remediate hazardous pollutants, ultimately to a cleaner environment (Albinsson, 2018). Rani & Shanker, 2019 showed that synthesized TiO_2 incorporating ZnHCF nanocomposites (TiO2@ZnHCF) can effectively reduce 96 % PAHs from water (Rani & Shanker, 2019).

Results showed that the coupling of Fe_3O_4 with TiO_2 in the Chitosan structure have considerably effective in absorption of Naphthalene molecule through Donor (D)-π-acceptor interactions from aqueous water (Solano et al., 2021).

6.3. Silver-based nanomaterials

Silver-based nanomaterials, particularly silver nanoparticles (AgNPs), are utilized for various purposes in the mitigation of PAHs present in food. The utilization of garlic extract as a green route process in synthesizing AgNPs has demonstrated optimal efficacy in the elimination of PAHs, achieving removal efficiencies exceeding 80 % (Sengar et al., 2021).

Furthermore, nanomaterials, which encompass silver-based variants, have found application in agriculture and food-related sensing tasks for the identification and surveillance of PAHs and other contaminants. The amalgamation of AgNPs with reoxidized graphene oxide (rGO) has been proven effective in facilitating the simultaneous detection of multiple PAHs, offering low detection limits and a high degree of identification accuracy (Wang et al., 2020). Overall, silver-based nanomaterials exhibit considerable potential in the reduction of PAHs in food owing to their antimicrobial attributes, enhanced physicochemical characteristics in packaging materials, as well as their integration in sensing and detection systems

6.4. Gold-based nanomaterials

Gold nanoparticles (AuNPs) coupled with 3-mercaptopropyltrimethoxysilane and different other thiolating agents have been utilized in the detection of 16 PAHs, displaying a LODs between 0.8 and 60 mg/L and relative recovery percent of 44.6–90.5 (Bernardo et al., 2022).

Subsequently, Wang et al. employed an Ag NPs/graphene hybrid for the evaluation of ANTH, PHEN, and PYR, with exposure limits of 1.1 ppb, 0.73 ppb, and 0.57 ppb, respectively. It was observed that the immobilization of PAHs on graphene, providing an additional benefit for the analysis and quantification of above analytes, thus facilitating the designing, improvement, and enhancement of sensors with significant effectiveness (Dutta et al., 2022).

6.5. Elimination of polycyclic aromatic hydrocarbons by other nanocomposites

Polymeric nanocomposites have revealed high potential in the removal of PAHs (Table 2). Various kinds of polymeric nanocomposites, including iron-oxide based chitosan-nanocomposites (Rani & Shanker, 2020b), graphene oxide (GO) nanoparticle and titanium dioxide (TiO_2) nanoparticle composites (Öztekin & DAT, 2022), and polymer nanocomposite materials (chitosan) incorporating metal oxide nanoparticles (Munyengabe et al., 2023), have been employed for the remediation of PAHs. Polymeric nanomaterials offer a suitable platform for the immobilization of metal oxide nanoparticles, improving their catalytic activity for PAH elimination in numerous matrices. These nanocomposites displayed excellent photocatalytic effectiveness, resulting in the degradation of PAHs such as anthracene and phenanthrene under variety conditions, including sunlight irradiation and different levels of nanomaterials. The incorporation of active catalyst particles into polymers offers a facile separation and reuse option, decreasing post-treatment processes and overall costs, while also displaying benefits such as mechanical stability, chemical inertness, and easy to use, making them promising candidates for the efficient removal of PAH contaminants (Munyengabe et al., 2023). Polymeric nanocomposites formed with maltodextrin have shown effectiveness in the elimination of PAHs from water. These nanocomposites, particularly those incorporating cyclodextrin polymers, metal nanoparticles and, carbon nanomaterials, have been found as hopeful approaches for water treatment by adsorption and also catalytic degradation methods (Kumari et al., 2020).

In study conducted by Dai et al., 2020 organic montmorillonite sodium alginate nanocomposites was employed as new and high efficient and biocompatibility adsorbents for elimination of PAHs including acenaphthene, fluorene, and phenanthrene in aqueous medium (Dai et al., 2020).

Rezagholizade-shirvan et al.,(Rezagholizade-Shirvan et al., 2024) 2024 showed notable capability of nanocomposite made of magnetic chitosan/molybdenum disulfide ($CS/MoS_2/Fe_3O_4$) for elimination of PAHs from milk and other dairies. Results indicate that the highest absorption potential for PHEN, PYR, and ANTH on the sorbent (chitosan) was evaluated as 217 mg/g, 222 mg/g and, 204 mg/g, respectively (Table 2).

Solano et al., 2021 developed Thiourea-Fe3O4-TiO2 modified chitosan beads (Chitosan beads functionalized with Titanium Dioxide (TiO_2), Thiourea and Magnetite (Fe_3O_4) nanomaterials for Naphthalene adsorption from water. The high adsorption potential of 133.690 mg/g was reported. Fe_3O_4 and TiO_2 incorporation in the Chitosan structure promote its textural charestrictics (Solano et al., 2021**).** Incorporation of Fe3O4 and TiO2 into the Chitosan framework enhances its textural properties. Furthermore, chitosan beads modified with thiourea-Fe_3O_4-TiO_2 exhibited high attraction towards Naphthalene due to Donor (D)- π -acceptor interactions. On the other hand, the extraction of polycyclic aromatic hydrocarbons (PAHs) using nanomaterials involves several key mechanisms that enhance the efficiency and selectivity of the process. These mechanisms primarily include adsorption, π-π stacking, and magnetic separation, which are influenced by the properties of the nanomaterials and the matrix from which PAHs are extracted. Nanomaterials like TiO2 nanotubes and carbonaceous materials exhibit strong adsorption capabilities due to their high surface area and functional groups, facilitating effective PAH capture from aqueous matrices (Bejaoui et al., 2023). The interaction between the aromatic structures of PAHs and the π-electron-rich surfaces of nanomaterials, such as carbon nanotubes and graphene, significantly enhances adsorption efficiency (Chen, Zhang, et al., 2020).

6.6. MOFs and COFs

Metal-organic frameworks (MOFs), a category of crystalline substances resulting from the self-assembly of metal ions and organic ligands, have found widespread utilization in the realms of enrichment as well as separation (Bag et al., 2020; Yousefi et al., 2024). Nevertheless, constraints persist in the practical use of MOFs primarily due to their inadequate stability. A significant drawback of many MOFs lies in their chemical instability upon exposure to solvents, notably moisture, owing to the coordination bonds serving as the linkage mode between organic ligands and metal constituents of MOFs. A more recent addition to the domain of advanced materials is covalent organic frameworks (COFs), characterized as a fresh variety of porous substances formed reversibly over robust covalent bonds such as Si—C, C—C, C—O, and B—C (Alhumaimess, 2020). In comparison to MOFs, COFs exhibit distinct advantages including enhanced specific surface area, superior structural stability, and also π - π stacking interaction. Owing to these attributes, the utilization of COFs in the realm of separation knowledge has garnered escalating interest **(**Gong et al., 2022**).**

Li, Wu, et al., 2018 (Li, Wu, et al., 2018) developed a facile approach for producing of core-shell construction magnetic COFs (Fe_3O_4@COF (TpBD) to enrich the trace PAHs from wild fish, smoked pork, smoked bacon, grilled fish, coffee and water. The LODs and LOQs for 15 PAHs ranged between 0.83 and 11.7 ngL^{-1} and 2.76 to 39.0 47 ngL^{-1}, respectively. Within the coffee, only PHEN was identified, while the smoked bacon sample showed detection of six PAHs at levels between 0.001 and 0.006 μg/kg. Moreover, the smoked pork sample exhibited the presence of fluorine (FLU) and benzoapyrene, with concentrations of 5.24 and 2.82 μg/kg, respectively. Additionally, the presence of FLU, PHEN, and ANTH in wild fish, with a higher concentration of PAHs found in grilled fish samples compared to other food samples. Moreover, five PAHs were also identified in water samples, with concentrations of 0.02–1.43 μgL^{-1}.

Fe_3O_4@COFs nanocomposites were employed for extraction and determination of 11 PAHs in sausage and roasted duck meets. PAHs are capable of undergoing enrichment by covalent organic frameworks (COFs) via robust π-π interactions and hydrophobic interactions. However, scant attention has been paid to the examination of the adsorption capabilities of such nanocomposites. In this study high linearity (R^2 ranged from 0.9954 to 0.9988), satisfactory recoveries between 83.2 and 119.3 %, and the relative standard deviations (RSD) was below the 5.8 % was attained (Chen, Li, et al., 2020).

Strengths and limitations of application of NPs in determination of PAHs Carbon-based nanomaterials, metal oxides, and magnetic nanoparticles have been employed as sorbents for the extraction and analysis of PAHs. These materials present significant advantages in dispersive solid-phase extraction methodologies, such as enhanced sample purification and analyte concentration (Singh et al., 2021). Their unique properties, stemming from nanoscale sizes, enhance extraction efficiency and detection sensitivity (Liu, Wu, et al., 2021).

A significant subject that demands further analysis relates to the methods for the proper disposal of NPs. The consequences of extended exposure to NPs on both human health and environmental systems require a thorough evaluation prior to their large-scale production. The minuscule size of NPs enables their infiltration into the dermal layers, respiratory system, and neurological tissues, leading to harmful outcomes. The advancement of environmentally friendly synthesis techniques for NPs offers a feasible alternative for the creation of nanoparticles that are more environmentally sustainable (Radhika et al., 2016). The development of green synthesis methodologies for NPs presents a viable alternative for the production of more ecologically benign nanoparticles. Additionally, green-synthesized nanomaterials are emerging as cost-effective, rapid, and environmentally friendly adsorbents and photocatalysts for PAH degradation (Rani & Shanker, 2018).

7. Challenges and future perspectives

Over the past decade, green nanoremediation represents a promising and noteworthy strategy for remediating contaminants specially PAHs. The inherent characteristics of nanoparticles, including their small size (1–100 nm), effective surface-coating capabilities, and expansive surface area, render them a preferred choice for on-site applications when compared to larger-scale materials. Therefore, it is imperative to conduct a thorough investigation on the utilization of green nanoremediation and its functional integration with well-established remedial techniques such as chemical oxidation or the fenton process. This integration can be achieved through the synthesis of nano-oxidizers to facilitate the oxidation of PAHs, as well as the exploration of novel, efficient, and sustainable nano-adsorbents for adsorption processes. It is crucial to further delve into the potential of these green nanoadsorbents. By efficiently combining established remediation methods with green nano remediation, there is a promising opportunity to enhance effectiveness and enable swift degradation or elimination of PAHs in real-world scenarios, whether in the field or in industrial settings.

The large-scale deployment of nanomaterials for PAHs elimination cop with several main challenges, including the demand for modifications of nanomaterials to improve efficacy (Gulia et al., 2023), potential issues related to the adaptation of nanomaterials to varying matrics (Dutta et al., 2022). Additionally, advancements in nano bioremediation techniques using biosynthetic nanomaterials are highlighted as a sustainable and eco-friendly approach for PAHs elimination, emphasizing the need for continued study and advance in this field to enhance the deployment of nanomaterials for effective remediation on a large scale (Borah et al., 2022). Green nanotechnology is an emerging discipline that is expanding its presence in a multitude of sectors for the purpose of altering or creating robust, groundbreaking, and environmentally friendly remedies. Nevertheless, there are still numerous aspects that require further clarification.

Furthermore, from a technical perspective, there is a disparity in the documented ideal conditions for attaining maximum removal rates of the specific contaminants. Therefore, it is imperative for future studies to concentrate on: (1) comprehending the relationship between the optimum circumstances of a particular factor and the adsorbent, (2) examining the variations in interactions when various adsorbents are employed, (3) consideration the influence of operational conditions on the adsorption rate, and (4) studying the impact of a combination of pollutants on the anticipated performance of a specific adsorbent and specific characteristics of the type of food matrix (Munyengabe et al., 2022). Overall, the continued research and development in nanotechnology for PAHs remediation hold promise for more effective and sustainable remediation strategies in the future.

8. Conclusion

Nanomaterials have displayed potential in the remediation of PAHs. Various nanomaterials with excellent characteristics are being investigated for application in variety section of food industry. PAHs, toxin environmental contaminant, present in food are derived from environmental accumulations or generated through various food processing methods, including smoking, drying, roasting. The application of nanoparticles is evident in the mechanisms of adsorption, photocatalytic processes, and redox degradation of polycyclic aromatic hydrocarbons (PAHs). The advent of environmentally-friendly synthesized nanomaterials, particularly those comprised of metal oxide-based nanoparticles such as titanium dioxide (TiO_2), zinc oxide (ZnO), and iron oxide (Fe_2O_3), as well as carbon-based nanoparticles, is significant for their efficacy and economic viability as adsorbents and photocatalysts in the remediation of PAHs Graphene based and metal-based NPs showed relatively high performance (>90 %) in PAHs reduction. On the other hand, functionalized nanomaterials, such as carbon nanotubes, graphene oxide, and metal-based materials, have been explored for PAH degradation, with metal oxides demonstrating the ability to oxidize and degrade PAHs through reactive species. Overall, nanomaterials provide an effective, reusable, and environmentally friendly method to PAH degradation in various media. It is clear that nanocomposites are unique and provide several advantages for usage in PAHs remediation in the food sector. Therefore, Future studies should focus on understanding the relationship between factors and adsorbents, examining interactions, operational conditions, and the impact of pollutants on adsorbent performance and food matrix characteristics. To improve the applicability of nanomaterials and composites in large-scale field applications, studies should include applications using naturally contaminated samples, determine the effects of experimental conditions on removal efficiency, quantify the impact of pollutants, and evaluate the technological advantages and cost-effectiveness of nanotechnology.

CRediT authorship contribution statement

Ehsan Shamloo: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation. **Samira Shokri:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Parisa Sadighara:** Writing – review & editing, Writing – original draft, Investigation. **Saeid Fallahizadeh:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Ahmad Ghasemi:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Zohreh Abdi-Moghadam:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Alieh Rezagholizade-shirvan:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Yeganeh Mazaheri:** Writing – review & editing, Writing – original draft, Methodology, Investigation.

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.

Data availability

The data that has been used is confidential.

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No potential conflict of interest was reported by the author(s).

Compliance with ethical standards

This article lacks research involving human or animal subjects.

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