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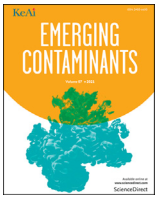

Emerging contaminants in biosolids: Presence, fate and analytical techniques

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ABSTRACT

Emerging contaminants (ECs) represent a small fraction of the large chemical pollution puzzle where a wide variety of potentially hazardous chemicals reach the environment, and new compounds are continuously synthesized and released in wastewater treatment plants and ultimately in effluent and biosolids. ECs have been classified into various categories; however, this article focuses on the fate of major categories, namely pharmaceutical and personal care products (PPCPs), per-and poly-fluoroalkyl substances (PFAS), flame retardants, surfactants, endocrine-disrupting chemicals (EDCs), and microplastics (MPs). These ECs when discharged to sewer and downstream wastewater treatment plants can undergo further transformations and either degrade, persist or convert into by-products which have the potential in some cases to be more hazardous. Because of potential dangerous impacts of the availability of these contaminants in the environment, information on the fate and behavior of these pollutants is highly important to develop new strategies, such as the regulation of chemicals imported into Australia and Australian consumer goods and environmental policies to mitigate them in a sustainable way. Moreover, advanced technologies are required for the detection and identification of novel contaminants emerging in the environment at ultra low levels. The application of chromatographic techniques coupled with mass spectroscopy has provided attractive breakthroughs to detect new emerging contaminants. However, it is crucially important to understand the sensitivity and robustness of these analytical techniques when dealing with complex matrices such as biosolids. In addition, most of the literature was focused on selected compounds or a family of compounds and the existing reviews have paid less attention to examine the formation of metabolites during the wastewater treatment process and their impacts on the ecosystem. This review presents an overview of the presence of different classes of ECs around the world, their quantification from different sources like wastewater (influents or effluents), sludge and biosolids. In addition, the transformation of ECs during the treatment process, the formation of intermediate products and their impacts on the environment are also critically discussed. Three major steps of ECs analysis include sample preparation, extraction and clean-up, and analysis; hence, different methods employed for extraction and clean-up, and analytical techniques for identification are thoroughly discussed, their advantages and limitations are also highlighted. This comprehensive review article is believed to enhance the understanding of ECs in sewage sludge and would be useful to the readers of the relevant communities and various stakeholders to investigate potential technologies to maximize destruction of ECs.

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1. Introduction

Irrespective of the economic status of a nation, known and unidentified contaminants represent a noticeable threat, with little known risk to human health and environment. In the recent past, a wide variety of new chemicals continue to be developed as a result of industrial development and associated anthropogenic activities. Noticeably, more than 80,000 synthetic chemicals are released into the environment every year, either as industrial wastes or as a part of manufacturing processes [1]. The lack of information on the fate and transportation of these new synthetic chemicals in the environment makes it difficult for the policymakers to develop policies that assist in environmental management. For instance, chemicals like perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) were not recognized as potentially toxic until recently [2].

Emerging contaminants (ECs) represent a recently detected wide group of families of synthetic or naturally occurring compounds, such as endocrine-disrupting chemicals (EDCs), pharmaceuticals and personal care products (PPCPs), flame retardants, nanoparticles, etc. [3]. These compounds are omnipresent and pose risks to human health and the environment. For instance, prolonged exposure to EDCs such as alkylphenols (APs), bisphenol A (BPA), parabens (PBs) or phthalates can impact the reproductive system in humans and wild life [4,5]. Flame retardants and PPCPs can cause neurotoxicity and impact the normal routine of the endocrine system [6]. Nanoparticles, commonly used in industrial and consumer products can cause cytotoxicity and cell damage [7,8]. More information is needed regarding their environmental risks [9,10]. These concerns have led the scientific community across the globe to shift its focus from conventional “priority” pollutants to “emerging” or “new generation” contaminants.

ECs enter into the environment via a number of routes, which include municipal [11], hospitals [12], wastewater treatment plants (WWTPs) [13], sewer leakage/overflow [14], and runoff from agricultural and urban areas [15], the application of biosolids and treated effluent to land. From the above-mentioned sources of ECs, WWTPs are regarded as a major concentrator of ECs since they receive wastewater from different sources like domestic waste, sewage and industrial trade waste, infiltration of groundwaters. The range of concentrations of ECs in the effluents of wastewater vary from a few ng/L to μg/L [16,17], and their types and concentrations depend on the socioeconomic status of the community feeding the WWTPs. However, current WWTPs are traditionally not equipped with advanced technologies to remove ECs at such low concentrations. Treatment plants were traditionally designed with the removal of nutrients and organic material in mind. The insufficient removal of ECs leads to their accumulation either in effluent or sludges, resulting in either the contamination through release of effluent to the receiving aquatic habitat or sorption onto biosolids/sludge [18]. The biosolids or the sludge may contain microorganisms that are separated from the liquid phase as well as a variety of organic and inorganic compounds [19].

In the past, several methods have been used for the disposal of biosolids, which include incineration, landfilling, composting, etc., and most of them result in the disposal of sludge or biosolids in the environment [20]. Since sludge or biosolids are employed in agricultural applications, ECs can further leach into the soil, groundwater and even taken up by the surrounding flora and fauna [18].

In addition, many medical drugs used for human disease treatment, such as chemotherapy drugs, antibiotics, NSAID's, endocrine disruptors are excreted within the domestic catchment and discharged into sewers reaching WWTPs. Some of these pharmaceutical compounds that have strong sorption characteristics and low solubility and are likely to be concentrated in biosolids. When such biosolids are used for land application, it can take years for the ECs to get removed from the environment and they can eventually end up in the food chain [21].

Moreover, the microbial contaminants in the environment, more precisely, antibiotic-resistant genes/bacteria produced as a result of mutation due to antibacterial drugs, are also considered ECs and specifically called emerging microbial contaminants (EMCs) [11,22]. A few examples of EMCs are sapoviruses [23], *Waddlia chondrophila* [24] and *Streptococcus parauberis* [25]. In addition, horizontal gene transfer phenomena allow the transfer of genetic material between microorganisms, implying that antibiotic-resistant genes can be further transferred between microbial populations [13].

During the wastewater treatment process, the parent contaminants may undergo various transformations and generate more metabolites and intermediate compounds, which pose similar environmental risks. For example, Carbamazepine (CBZ) and Oxcarbazepine (OXC) are pharmaceuticals detected in drinking water, wastewater and treated water [26]. The major content of CBZ and OXC is generally metabolized to several metabolites, including 10-hydroxy-CBZ and 10,11-dihydro-10,11-dihydroxy-CBZ, which have been found in influents and effluents of WWTPs at various concentrations up to 4 μg/L [26]. During the biological treatment process, these metabolites can be further transformed into various intermediators, such as 1-(2-benzoic acid) -(1H, 3H)-quinazoline-2,4-dione (BaQD), 1-(2-benzoic acid)-(1H, 3H)-quinazoline-2-one (BaQM), 9-aldehyde-acridine, 9-carboxylic acid-acridine (9-CA-ADIN), hydroxyl 9-CA-ADIN, acridone (ADON), 11-keto-OXC, and 2,2′ -(carbamoylazanediyl) dibenzoic acid [26]. Some of the intermediate compounds are more persistent compared to the parent compound, thus, pose a higher environmental risk. For instance, metabolites of tetracyclines, such as 5a,6-anhydrotetracycline and 5a, 6-anhydrochlortetracycline show different modes of structure-activity relations compared to the parent compounds and exhibit potency against tetracycline-resistant bacteria [27].

Sludge/biosolids are a complex matrix that may contain contaminants at trace levels and below detection limits. Therefore, analyzing emerging contaminants in sludge or biosolids is often considered a challenging task. The real concentrations are often underestimated as different matrix components co-elute at the interface of the system leading to suppression of the signal intensity from the analytical instrument [28]. In addition, the availability of these compounds at such low concentrations makes it extremely difficult to develop an efficient pre-treatment step and extract the target compounds [29]. Thus, it is pivotal to develop robust and sensitive methods for the determination of a variety of ECs in sludge/biosolids. In the recent decade, a plethora of review papers have been published, focusing on the availability and fate of ECs in sludge [30–35]. For example, Clarke and Smith published a review article on emerging organic contaminants in biosolids and assessed their toxicity impact on human and ecological food chains [36]. In 2018, Martin-Pozo et al. published a review paper detailing the analytical methods for the detection of emerging contaminants in sewage sludge samples [37]. Another review paper was published by Naidu et al., Per- and poly-fluoroalkyl substances (PFAS): Current status and research needs; however, this article was focused mainly on the outcomes from an expert workshop held in Adelaide, South Australia, Australia in September 2019 [38]. It was noticed that most of the literature was focused on selected compounds or a family of compounds. Also, the existing reviews have paid less attention to examining the formation of metabolites during the wastewater treatment process and their impacts on the ecosystem. In the recent decade, several studies have been conducted in various parts of the world on emerging organic contaminants in sewage sludge/biosolids, consequently, published in different journals and media outlets [39–41].

Table 1
Different types of emerging contaminants in sewage sludge/biosolids.

Category of EC	Contaminant Name	Location	LOD/LOQ	Sample treatment	Analytical technique	Amount detected	Reference
1. PPCPs	Ciprofloxacin Diclofenac Enrofloxacin	Brazil (2021)	No data	- Centrifugation at 14000 rpm - Extraction with methanol and n-hexane, methanol in formic acid - Filtration at 0.45 μm	UPLC-ESI-MS/MS	10.9-158.4 μg/kg 13.3 μg/kg 45 μg/kg	[57]
	^{1}Pharmaceutical compounds (24)	Portugal (2021)	LOD-1.66-10.5 ng/g LOQ-5.49-34.5 ng/g	- Dried samples were treated by accelerated solvent extraction - Solid-phase extraction was performed - Extract evaporation under nitrogen stream	LC-MS/MS	Each compound has a mean concentration in the range of 0-70.8 ng/g	[58]
	Triclosan	USA (2012)	No data	- Biosolid sample was homogenized with sodium sulfate and spiked with the standard, fluid extraction with DCM: hexane (50:50) - Solid phase extraction (preconditioned with 10 mL of 50:50 DCM: hexane) - Further elution with DCM: hexane - Extracts reconcentrated and solvent-switched to methanol under a gentle N_2 stream - Samples spiked with the recovery standard	GC/ECNI—MS	490-13,866 ng/g	[59]
	Pharmaceutical compounds (42)	Czech Republic (2021)	LOD-0.3-5.4 ng/g LOQ-1-12 ng/g	- Sonication extraction of sample with 6 ml of methanol-water solution (0.5% HCOOH and 0.1% Na_2EDTA) - Supernatant centrifugation at 13000g for 10 min - Added 200 μL of 5-sulfosalicylic acid, vortexed, and centrifuged at 2 °C at 16,000 g for 10 min	UPLC-ESI-MS/MS	Each compound has a mean concentration in the range of 2.2 to 3.8 μg/g	[60]
	^{2}Pharmaceutical compounds (35)	South Korea (2021)	LOD-0.1-10 ng/L LOQ-0.5-20 ng/L	- Filtered samples spiked with 80 μL of citric acid buffer and 100 μL of internal standard solution - Solid phase extraction - 5 mL of methanol and 10 mL of DI water and samples loaded into the cartridge for approximately 1 h - Eluted with alkaline and acidic solutions	GC-MS/MS	Mean concentration of all compounds- 12000 ng/L	[61]
	Pharmaceutical compounds (35)	Italy (2021)	LOQ- 0.21-47.92 ng/g LOD-0.11-14.38	- Sample was homogenized and spiked with the standard - Accelerated solvent extraction was performed with water: methanol (1:1) - Solid-phase extraction for purification	HPLC-MS/MS	Mean concentration of each compound was in the range of <LOQ- 4889 ng/g	[62]
	Bisphenol A Estradiol Triclosan Pharmaceutical compounds (27)	Czech Republic (2021)	No data	- Samples were extracted with ethyl acetate and purified - Evaporated in the presence of dimethylformamide and trimethylasilylated - Reconstituted in 800 ml of ethyl acetate and 100 ml of internal standard stock solution - Extraction of PPCPs was performed with methanol ASE (80 °C and 10.3 MPa),	GC-MS LC-MS/MS	1023 ng/g 29 ng/g 2236 ng/g Mean concentration of each compound was in the range of 0.1 to 50 ng/g	[63]
	4-Aminoacetophenone 2,3-Dimethylnaphthalene-1,4-dione	China (2021)	No data	- Extraction using acetone, acetone/n-hexane 1:1 (v/v) n-hexane 100 °C and 10.35 MPa) - Eluted mixtures of n-pentane, dichloromethane and methanol - Spiked with 50 μL surrogate standard solution	GC-MS	0.3 mg/kg dw 0.1 mg/kg dw	[64]
2. Flame retardants	Polybrominated diphenyl ethers	USA (2012)	No data	- Biosolid sample was homogenized with sodium sulfate and spiked with the standard, fluid extraction with DCM: hexane (50:50) - Solid phase extraction (preconditioned with 10 mL of 50:50 DCM: hexane) - The elute was treated with 1 mL of concentrated sulfuric acid - The mixture was extracted in triplicate with 3 mL aliquots of hexane - Samples spiked with the recovery standard	GC/ECNI—MS	1750-6358 ng/g	[59]

	2,4,6-tribromophenyl allyl ether (ATE)	China (2020)	No data	- Samples were filtered through a GF/C 1.2 μm glass microfiber filter - Filtered water sample spiked with 5 ng of the surrogate standards and extracted with 3 ×200 mL DCM - Sulfur-containing compounds were removed by adding activated copper powder - Extract was cleaned and fractionated on a 5% H_2O deactivated active Al_2O_3 column - The column packed with 2 g of anhydrous sodium sulfate, 8 g of 5% H_2O-deactivated active Al_2O_3 and an additional 2 g of anhydrous sodium sulfate - The sample eluted with 30 mL *n*- hexane and a 30 mL mixture of *n*- hexane and DCM (3:1, v/v)	GC/ECNI−MS	0.17 ng/g	[65]
	2,3-dibromopropyl tribromophenyl ether (DPTE)					0.47 ng/g	
	1,2- bis(2,4,6-tribromophenoxy) ethane (BTBPE)					0.65 ng/g	
	bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (TBPH)					8.9 ng/g	
	decabromodiphenyl ethane (DBDPE)					184 ng/g	
	2,4,6-tribromophenyl allyl ether (ATE)	China (2020)				0.05-0.07 ng/L	
	1,2- bis(2,4,6-tribromophenoxy) ethane (BTBPE)					0.11-0.14 ng/L	
	bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (TBPH)					0.68-1.0 ng/L	
	decabromodiphenyl ethane (DBDPE)					9.9-18.0 ng/L	
	Polybrominated diphenyl ethers	China (2016)	No data	- Wastewater was filtered through glass fiber filters (0.45 μm, Millipore) and spiked surrogate standards - Liquid−liquid-extracted with DCM - Oscillation-extracted with 10 mL hexane/ethyl acetate (1/1, v/v) - Soxhlet-extracted with 120 mL DCM for 24	GC/ECNI−MS	503 ng/g	[66]
	Decabromodiphenyl ethane (DBDPE)					33.86-607.32 ng/g	
	Tris(2-chloro-iso-propyl) phosphate	China (2021)	No data	- Extraction using acetone, acetone/n-hexane 1:1 (v/v) n-hexane 100 °C and 10.35 MPa) - Eluted mixtures of n-pentane, dichloromethane and methanol - Spiked with 50 μL surrogate standard solution	GC-MS	19-70 mg/kg dw	[64]
	Triphenyl phosphate					14 mg/kg dw	
	Triethyl phosphate					39-269 mg/kg dw	
3. PFAS	PFAS compounds (32)	Czech Republic (2020)	LOQ- 0.05-0.7 ng/ml LOD-0.01-0.25 ng/ml	- Dried samples were treated by accelerated solvent extraction - Solid-phase extraction was performed - Extract evaporation under nitrogen stream	LC-MS/MS	Mean concentration in the range of 5.6 to 963.2 ng/g	[67]
	PFBS	Australia (2021)	/	/	/	0.002 mg/kg	[68]
	PFHxS					0.0006 mg/kg	
	PFOS					0.0148 mg/kg	
	PFBA					0.0020 mg/kg	
	PFPeA					0.0023 mg/kg	
	PFHxA					0.0037 mg/kg	
	PFHpA					0.0013 mg/kg	
	PFOA					0.0086 mg/kg	
	Perfluorinated acids (C3−C14 PFAs)	China (2012)	/	- Sample was freeze-dried at 50 °C for 24 h and homogenized by sieving through a stainless steel 60-mesh sieve - Sonication solvent extraction - Solid-phase extraction and dispersive carbon sorbent cleanup	HPLC-MS/MS	Mean concentration in 25 wastewater treatment plants in the range of 126−809 ng/g dw	[69]
	PFAS compounds (44)	Australia (2021)	/	- Samples were homogenized, freeze-dried and finely ground - Spiked with 25 ng of isotopically labelled PFAS and added 4.65 mL of 10 mM NaOH in methanol - Sonication solvent extraction - Added 100 mL of glacial acetic acid and 100 mg of C18 and 50 mg (PSA) added to remove interfering compounds, followed by filtration	LC-MS/MS	Mean concentration of all compounds-260 ng/g dw	[70]
	PFAS compounds (13)	Canada (2020)	LOQ-2.32-38.8 ng/g	- Samples spiked with standards	LC-MS/MS	Median concentration of each compound was in the range of 3.3-15 ng/g dw	[71]

(*continued on next page*)

Table 1 (*continued*)

Category of EC	Contaminant Name	Location	LOD/LOQ	Sample treatment	Analytical technique	Amount detected	Reference
	PFAS compounds (13)		LOQ-2.06-22.9 ng/g	- Extraction with 3% acetic acid, 15 ml 0.3 % methanolic ammonium hydroxide and 5 ml 0.3% methanolic ammonium hydroxide - Solid-phase extraction - Washing with 50% methanol and 50% 0.1 M formic acid in water - Elution with .3% methanolic ammonium hydroxide - Spike with recovery standards		Median concentration of each compound was in the range of 3.8-21 ng/g dw	[71]
	PFOA	Italy (2021)	LOQ- 0.36 ng/g LOD-0.11 ng/g	- Sample was homogenized and spiked with the standard	HPLC-MS/MS	2.5-3.4 ng/g	[62]
	PFOS		LOQ- 1.12 ng/g LOD-0.34 ng/g	- Accelerated solvent extraction was performed with water: methanol (1:1) - Solid-phase extraction for purification		18.9-22.4 ng/g	
4. Surfactants	Linear alkylbenzene sulfonates	South Korea (2021)	No Data	- Samples pelleted by centrifugation at 10,000 rpm for 3 min, and stored at -80 °C.	CHEMets test kits	0.6-4.5 mg/L	[72]
	Linear alkylbenzene sulfonates	Spain (2012)	No Data	- Microwave assisted extraction LAS with 25 mL methanol	HPLC	1.27-8.06 g/kg	[73]
	Linear alkylbenzene sulphonate	Austria (2007)	LOD-500 ng/L LOQ-1000 ng/L	- Filtered by a 0.45 mm glass fibre filter - A surrogate standard was added and eluted with methanol	HPLC-FD	2,166667 ng/L	[74]
	Alkyl benzyl ammonium chlorides compounds		LOD-11-23 ng/L LOQ-6-11 ng/L	- Samples were extracted by liquid-liquid extraction using chloroform and evaporated to dryness, redissolved in $CHCl_3$ and extracted three times with 4ml milli-Q water	LC-MS/MS	55,111 ng/L	
	Dialkyl ammonium chlorides compounds		LOD-11-23 ng/L LOQ-6-21 ng/L	- Evaporated to dryness by nitrogen and filled up to the final volume with methanol		68,444 ng/L	
	Trialkyl ammonium chlorides compounds		LOD-12-46 ng/L LOQ-6-23 ng/L			2400 ng/L	
	Nonylphenol		LOD-10 ng/L LOQ-20 ng/L	- Filtered by a 0.45 mm glass fibre filter - Samples were acidified with sulphuric acid and 25 ml of surrogate standard was added	LC-MS/MS	2933 ng/L	
	Nonylphenol monoethoxylate		LOD-20 ng/L LOQ-40 ng/L	- Eluted by acetone and a mixture of methanol/methyl-tert-butylether (1:9)		9167 ng/L	
	Nonylphenol diethoxylate		LOD-10 ng/L LOQ-20 ng/L	- Extracts were evaporated by nitrogen and filled up to a final volume of 1ml with acetonitrile		2300 ng/L	
	Octylphenol		LOD-10 ng/L LOQ-20 ng/L			302 ng/L	
	Sodium dodecylsulfate	Spain (2020)	LOD-0.03 ng/g LOQ-0.11ng/g	- Samples were freeze-dried, homogenized, crushed with a mortar and sieved (particle size <100 μm)	LC-MS/MS and HPLC	2452 ng/g	[75]
	Sodium tetradecylsulfate		LOD-2.54 ng/g LOQ-8.48 ng/g	- Ultrasound-assisted extraction with 3 mL of methanol: glacial acetic acid and clean-up by dispersive solid-phase extraction		6210 ng/g	
	Sodium hexadecylsulfate		LOD-2.63 ng/g LOQ-8.76 ng/g			4790 ng/g	
	Sodium octadecylsulfate		LOD-0.03 ng/g LOQ-0.09 ng/g			7111 ng/g	
	C10-Linear alkylbenzenes	China (2021)	No data	- Extraction using acetone, acetone/n-hexane 1:1 (v/v) n-hexane 100 °C and 10.35 MPa)	GC-MS	1-8 mg/kg dw	[64]
	C11-Linear alkylbenzenes			- Eluted mixtures of n-pentane, dichloromethane and methanol		1-15 mg/kg dw	
	C12-Linear alkylbenzenes			- Spiked with 50 μL surrogate standard solution		2-15 mg/kg dw	
	C13-Linear alkylbenzenes					2-16 mg/kg dw	
	C14-Linear alkylbenzenes					1 mg/kg dw	

Note: [1]Pharmaceutical active compounds (24): data included for Faro NW UWWTP. [2]Pharmaceutical active compounds (35): data taken for STP1; ASE: Accelerated solvent extraction; Cl-PFCA: Chlorine substituted PFCA; Cl-PFESA: Chlorine substituted perfluoroalkyl ether sulfonate; FTS: Fluorinated telomer sulfonate; GC/ECNI−MS: Gas chromatography/mass spectrometry operated in negative ionization mode; H-PFCA: Hydro substituted PFCA; H-PFSA: Hydro substituted PFSA; HPFESA: Hydro substituted perfluoroalkyl ether sulfonate; HPLC-FD: liquid chromatography (HPLC) coupled with fluorescence detection; LC-MS/MS- liquid chromatography-tandem mass spectrometry; LOD-limit of detection; LOQ-limit of quantification; OBS: P-perfluorous nonenoxybenzenesulfonate; PFAS: Poly & Per fluoroalkyl substances; PFBA: Perfluorobutanoic acid; PFBS: Perfluorobutanesulfonic acid; PFOS: Perfluorobutanesulfonic acid; PFOA: Perfluorooctanoic acid; PFHxS: Perfluoropentanoic acid; PFHxA: Perfluorohexanoicacid; PFHpA: Perfluoroheptanoic acid; Perfluorohexanesulfonic acid; PFPeA:PPCPs-pharmaceutical and personal care products; PFSM: Perfluoroalkyl sulfonamide; PFEA: Perfluoroalkyl ether alcohol; SPE- solid-phase extraction; UPLC-ESI-MS/MS-Ultra Performance Liquid Chromatography coupled to Mass Spectrometry and Positive Electrospray Ionization; UPFCA: Unsaturated PFCA; UPFA: Unsaturated perfluoroalkyl alcohol.

Therefore, considering the alarming concern of ever-rising organic (inorganic) contaminants in WWTPs, we aimed to prepare a comprehensive review article to provide insightful information on ECs reported in recently published articles. The primary objective of this review is to critically analyze the origin and fate of different classes of ECs in WWTPs. Another major objective is to understand the formation of intermediate compounds during the wastewater treatment process and examine their impact on the environment, human and ecological food chains. Furthermore, this paper critically analyzes the current status of analytical strategies for the detection and characterization of ECs in biosolids. Since many review articles have been published on ECs in the past decade, to make the article more up to date, we have considered the majority of the articles from last five years. We believe that this comprehensive review article will enhance the understanding of ECs in sewage sludge and would be helpful to the readers of the relevant communities and various stakeholders to make efficient strategies and policies to mitigate their harmful effects. To understand the occurrence of ECs in influents and effluents of a wastewater treatment plant, we recommend reading review articles published earlier, for instance, Lenka et al. [42] and Rout et al. [43].

2. Classes of emerging contaminants (EC)

In this article, major categories of ECs that are of serious concern from an environmental risk point of view, namely pharmaceutical and personal care products (PPCPs), per-and poly-fluoroalkyl substances (PFAS), flame retardants, surfactants, endocrine-disrupting chemicals (EDCs), and microplastics (MPs), have been thoroughly discussed in further sections. Table 1 summarizes a few studies that detected different types of emerging contaminants in sewage sludge/biosolids.

2.1. Pharmaceuticals and personal Care products (PPCPs)

PPCPs are a diverse group of compounds that includes antibiotics, anti-inflammatory agents, steroidal hormones and active ingredients in soaps, detergents and perfumes [44,45]. Fig. 1 shows chemical structures of some PPCPs found in sewage sludge. Recent decades have witnessed an increased use of PPCPs. Due to their low biodegradability and high persistence, especially in wastewater treatment plants (WWTPs), PPCPs have become a global environmental issue, requiring careful and innovative consideration. For example, the unmonitored discharge of antibiotics is of great ecological concern since it can prompt the development of antibiotic-resistant microorganisms [46,47]. Other PPCPs such as diclofenac, ibuprofen and triclosan are frequently detected in surface waters and have shown to cause toxicological problems [48]. For instance, diclofenac and ibuprofen are often correlated with several diseases in fishes such as renal failure, visceral gout, increase in liver weight, changes in spawning process, and vitellogenin production [49]. Ibuprofen is also known to affect photosynthetic aquatic organisms by either promoting or inhibiting their growth [49]. Caffeine and carbamazepine are considered anthropogenic markers in water streams since they are two of the most frequently detected PPCPs [50]. Rizzo et al. [51] performed a study to examine the presence of caffeine in 100 drinking water samples collected from 61 locations in Brazil. The authors reported that caffeine was detected in 93% of samples at concentrations ranging from 1.8 ng/L to over 2000 ng/L [51]. Similarly, several other PPCPs act as endocrine-disrupting chemicals (EDCs) and have the potential to impact reproductive health and hormonal functions in fish and humans, emphasizing the need for adequate remediation techniques in WWTPs to mitigate the impact of contaminants during wastewater treatment and futuristic applications [52].

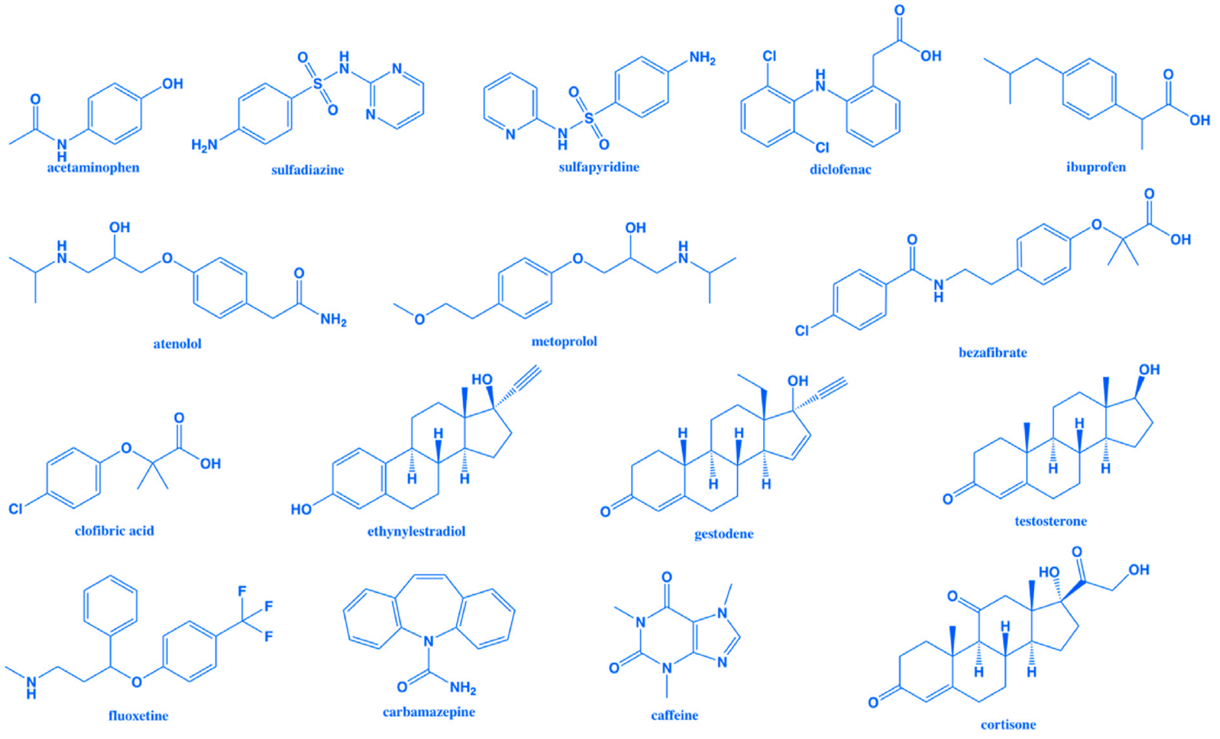

Fig. 1. Chemical structures of some PPPCs found in sewage sludge.

Among various sources, domestic wastewater is considered a major source of PPCPs in the environment. For instance, medicines consumed are metabolized in the human body and later excreted in urine and faeces. Similarly, personal care products like shampoos, toothpaste, soaps, sunscreen lotions are discharged as part of everyday human activities [34]. Furthermore, effluents from manufacturing units of biocides, pharmaceuticals, and other chemicals [53], along with effluents from hospitals [54], are other important sources for PPCPs and discharge to WWTPs. Since biosolids are used for soil amendment applications, adsorbed contaminants can be taken by the surrounding flora and fauna through various known/unknown metabolic mechanisms and eventually enter the food chain [55]. A wide range of PPCPs is taken up by certain species of plants when treated water and manure are used for agricultural activities. The adverse impacts of PPCPs have been already reported in the literature [34,56].

Previous studies reported the presence of various drugs, such as antibacterial [76–78], antifungal drugs [79,80], and antibiotics [81,82], in high quantities in sludge/biosolids. The concentrations of these contaminants were noticed to be available at high concentrations. For instance, Bisognin et al. carried out a study to understand the fate of pharmaceuticals in wastewater effluents and sludge. A total of 13 pharmaceutical compounds, among them paracetamol and caffeine, recorded the highest concentration of 137.98 and 35.29 μg L^{-1}, respectively. The treated effluent contained 11 compounds, and the sludge absorbed seven compounds. The compounds detected in sludge include doxycycline, fenbendazole, norfloxacin [83] and tetracycline, with the concentrations ranging between 0.026 and 5.034 mg/kg [84]. In another study, McClellan and Halden reported the availability of ciprofloxacin, chlortetracycline, triclocarban, and triclosan in biosolids and sludges, indicating that biosolids/sludge can act as a major sink for ECs. Therefore, continuous exposure of agricultural land to biosolids/sludges containing ECs can result in severe problems in the long run. For instance, the use of sludges/biosolids contaminated with pharmaceuticals for agricultural activities can facilitate the development of antibiotic-resistant genes (ARGs) or antibiotic-resistant bacteria (ARBs) [85].

2.2. Surfactants

Surfactants or surface-active agents, are organic chemicals that minimize the surface tension in water or other liquids. Surfactants have a wide range of applications, which include their use in manufacturing soaps and shampoos, dish cleaners and laundry detergents, lubricants, mining flocculates, textile industries, wastewater treatment and petroleum recovery [86]. Depending on the head groups of the surfactant, they are classified into four main categories, which are anionic, cationic, non-ionic and amphoteric [87]. The most commonly used surfactants include alkyl sulfates, alkylethoxylates, alkylethoxy sulfates, alkylphenol ethoxylates, linear alkylbenzene sulfonates and quaternary ammonium-based compounds [87]. Out of the 15 million tons of surfactants produced annually, anionic surfactants account for *ca.*60% [88]. The non-ionic surfactants contribute to *ca.* 30% and, both cationic and amphoteric surfactants together account for the remaining 10% [89]. While the market for surfactants is growing continuously, concerns have been increasing with regard to the negative effects of surfactants on the environment and human health [90]. The length of the alkyl group can influence the hydrophobicity of the surfactant, and an increase in the hydrophobicityincreases the toxicity of the surfactant. Conversely, an increase in the ethylene oxide group can decrease the hydrophobicity and, consequently, the toxicity of the surfactant [91]. In addition, surfactants can increase either the solubility of organic hydrocarbons into water resources or sorption into soils/sediments, resulting in being potentially harmful to crops [92]. While high removal rates are possible for some surfactants (>99% for linear alkylbenzene sulphonates), the remaining surfactants that end up in water bodies can bioaccumulate in a few species. Further, exposure to a few surfactants, such as benzalkonium chlorides can increase resistance to antibiotics in microbes [93].

2.3. Microplastics

Microplastics (MPs) are solid synthetic materials or a polymeric matrix with an irregular size of less than 5 mm. Nanoplastics can display colloidal behaviors with reported sizes varying from 1 to 1000 nm [94,95]. However, no current definition exists for the term “nanoplastics”, and the size range is based on the literature [96]. Nanoplastics may result from the fragmentation of aged-plastic materials, degradation of plastic materials during the manufacturing process or their application [97]. MPs are primarily categorized into two categories depending on the source of generation; primary MPs, which are originally manufactured in the micro-size, and secondary MPs, generated from the decomposition of large-sized plastics [98]. Table 2 presents the distribution and composition of microplastics detected in biosolids/sewage sludge.

The sources of primary MPs are many, which mainly include air-blasting media, baby products, cosmetics, facial-cleansers, drugs production, resin pellets, toothpaste, and virgin plastic production pellets [94,99]. The secondary MPs are the resultant of the breakdown of larger plastic particles into micro-sized particles via physical, chemical and/or biological processes [99]. The sources of secondary MPs are numerous and diverse, which makes it difficult to quantify them [100]. The most important factors that affect the degradation of microplastic include environmental factors, such as temperature and weathering, and properties of plastic material, such as size and density [99]. Additionally, sunlight-induced photodegradation [101], mechanical forces [94] and changes in external environmental conditions can also influence the rate of plastic degradation [102]. Microplastics pose numerous ecological hazards, toxicological effects, ecological imbalances, leaching of chemicals into freshwater and terrestrial environments. Thus, effective measures should be taken to remove microplastic particles during the wastewater treatment process to avoid their translocation into the biosolids.

2.4. Flame retardants

Flame retardant (FR) materials are essential to reduce the number of victims during a fire accident. FRs are increasingly required in many fields such as construction, transportation, electrical and electronics industries and are designed to extend the time-of-escape in fires [120]. Though the use of FRs was found to be lifesaving, they are toxic and have lethal effects on human health and ecosystems [121,122]. To date, there are *ca.* 175 compounds or group of compounds with the properties of a flame retardant [120]. FRs are mostly lipophilic and do not easily dissolve in water [123]. Therefore, in aquatic ecosystems, sediments act as a major sink for FRs [124]. As the most hydrophobic compounds bind to the food and less hydrophobic compounds remain dissolved in water, fauna and flora are generally exposed to FRs via uptake of contaminated water and food [125]. There are many different types of flame retardants; however, they are all grouped into four main categories; (i) halogenated FRs, (ii) phosphorus-containing FRs, (iii) nitrogen-containing FRs and (iv) inorganic FRs [126]. The most commonly used FRs are brominated flame retardants (BFRs) and organophosphate flame retardants (OPFRs). The main pathways of FRs reaching the environment include industries, wastewater

Table 2
Distribution of microplastic particles (MPs) in wastewater/sludge/biosolids.

Country	Source	No. of treatment plants	Analytical techniques	Quantity (MPs/unit weight or quantity in weight)	Microplastic form	Composition	Reference
Turkey (2020)	Wastewater	3	Optical microscope (Olympus SZX16) and FTIR	2584 MPs in influent 1041 MPs in effluent Average 0.9 MPs/L	Fibers, soft plastic, hard plastic, Styrofoam	Polyethylene, polypropylene, polyamide, polyvinyl chloride, polystyrene, polyester, polyethylene terephthalate, polyurethane, and acrylic.	[103]
Finland (2018)	Wastewater and Sludge	1	Optical microscope, FTIR microscope and Raman microscope	170.9 MPs/g dw in sludge 1.1 MPs/L in effluent 57.6 MPs/L in influent	Fibers (round, oval, flat) and particles (flakes, fragments, spheres, flat)	Polyester, polyethylene, polyamide, and polypropylene	[104]
Ireland (2017)	Sludge	7	Optical microscope, ATR-FTIR, SEM	4196 to 15385 MPs/kg dw	Fibers, fragments, films spheres, and others	High density polyethylene, polyethylene, polyester, acrylic, polyethylene terephthalate, polypropylene, and polyamide	[105]
Germany (2017)	Wastewater and Sludge	12	Optical microscope, ATR-FTIR, FTIR microscope with an FPA detector	1×10^3 to 2.4×10^4 MPs/kg dw in sludge 9×10^7 to 4×10^9 MPs in effluents/kg dw	Fibers, fragments	Polyethylene, polypropylene, polystyrene, polyamide, polyester, polyvinyl chloride, polyurethane, polyethylene terephthalate, ethylene vinyl acetate, acrylonitrile butadiene styrene, and polylactide	[106]
Australia (2021)	Sludge and biosolids	3	Optical microscope, micro-FTIR	15.9 to 56.5 MPs/g dw in sludge 864×10^6 to 1020×10^6 MPs/day in biosolids	Fibers, fragments	Polyethylene terephthalate, polyethylene, polypropylene	[107]
USA (2019)	Sludge	60	LC-MS	Polyethylene terephthalate=28-12000 μg/g Polycarbonate= 0.70– 8400 μg/g	Fibers	Polyethylene terephthalate and polycarbonate	[108]
China (2020)	Wastewater (domestic) Wastewater (industrial) Wastewater (industrial)	9 5 10	Optical microscope, micro-Raman spectroscopy	Influent-18-890 MPs/L Effluent-6-26 MPs/L Effluent-6-12 MPs/L Effluent-8-23 MPs/L	Fragments, films, pellets, and fibers	Polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyamide, and polyvinyl chloride	[109]
China (2020)	Wastewater Sludge	1	Optical microscope, micro-Raman spectroscopy	Influent-30.6 MPs/L Effluent-75.7 MPs/L 36.3 MPs/L	Fibers, fragments, films, foams and tubular	Polyesters, polyamide, polyethylene terephthalate, and polyethylene, polypropylene, polystyrene,	[110]
China (2020)	Sludge	1	Optical microscope, FTIR	2933-5533 MPs/kg dw	Pellets/microbeads, fragments, films, and fibers	Poly (11-bromoundecyl acrylate) and poly (11-bromoundecyl methacrylate), rayon, polyethylene, polyethylene terephthalate, polypropylene	[111]
China (2020)	Wastewater	2	Optical microscope, Raman spectroscopy	Influent-23.3-80.5 MPs/L Effluent-7.9-30.3 MPs/L	Fibers, fragments, films, foams, microbead and ellipse	Polyvinylchloride, Polyethylene, polypropylene, Ethylene-vinyl acetate copolymer, polyvinyl acetate, poly acrylonitrile, and polycarbonate	[112]
Spain (2020)	Wastewater Sludge	1	Optical microscope, ATR-FTIR	Influent-11.1 MPs /L Effluent-2.8 MPs /L 112 MPs /g dw	Fibers, fragments	Low density polyethylene, polypropylene, polystyrene, and polyethylene terephthalate	[113]
Denmark (2021)	Sludge Biosolids	1	Optical microscope, micro-FTIR	1.45×10^{-3}g/kg 1.38×10^{-3}g/kg to1.45×10^{-3}g/kg	Fibers, fragments	Polyethylene, polypropylene, polystyrene, polyethylene terephthalate	[114]
Canada (2020)	Biosolids	1	Optical microscope, ATR-FTIR	8.7×10^3 MPs/kg to 1.4×10^4 MPs/kg	Fibers, fragments, microbeads	Polyethylene, polypropylene, polystyrene, polyurethane, polyester	[115]
Spain (2020)	Sludge	1	Optical microscope, micro-FTIR	18000-32070 MPs /kg	Fibers, fragments and film	Polypropylene and polyvinylchloride	[116]
Chile (2019)	Sludge	1	Optical microscope, micro-FTIR	18-40 MPs/g	Fibers, fragments and film	Low density polyethylene, polyvinylchloride, polyester	[117]
Norway (2021)	Drinking water	-	Pyrolysis-gas chromatography-mass spectroscopy	6.1-93.1 μg/m^3	-	Polyethylene, polypropylene, polyvinylchloride, polystyrene, polyamide, polymethyl methacrylate, polycarbonate, polyethylene terephthalate	[118]
Japan (2021)	Standard samples	-	Pyrolysis-gas chromatography-mass spectroscopy	0.1-92.8 μg	-	Polyethylene, polypropylene, polyvinylchloride, polystyrene, polymethyl methacrylate etc.	[119]

Note: ATR: Attenuated total reflectance; FPA: Focal plane array; FTIR: Fourier Transform Infrared; LC-MS: liquid chromatography-mass spectrometry; SEM: Scanning electron microscope treatment plants (WWTPs), incinerators, plastic and e-waste recycling facilities [127].

2.5. Per- and Polyfluoroalkyl Substances (PFAS)

PFAS are a group of synthetic compounds that have been extensively used for over six decades in a variety of applications such as oil-repelling containers, water-proof fabrics, non-stick cookware, paints, aqueous film-forming foams used in firefighting, industrial emulsifiers, and surfactants [128,129]. Polyfluoroalkyls are composed of a hydrophobic carbon chain of varying lengths where at least one hydrogen atom bound to the chain is replaced by fluorine. In contrast, perfluoroalkyls require all hydrogen atoms to to be replaced by fluorine [130]. Both per- and polyfluoroalkyl substances also include a hydrophilic functional group attached at the other end, typically carboxylic or sulfonic acid. Two PFAS, in particular, PFOA and PFOS group contaminants have been extensively studied due to their bioaccumulative, toxic and transport potential in the environment [129,131].

PFAS are known to enter the water cycle through runoff, mainly when fire fighting foams have been in heavy use and WWTPs discharges. They can contaminate drinking water sources due to their low biodegradability [132]. A study published in 2015 analyzed blood serum samples from 1887 individuals using data from the 2011–2012 cycle of the US National Health and Nutrition Examination Survey and found that PFAS were detected in over 97% of samples [131]. Some PFAS exposure has been associated with increased cholesterol and uric acid levels, reproductive and developmental toxicity, endocrine disruption, immunotoxicity and cancer [128,129]. The Australian National Environmental Management Plan (NEMP) guideline values for 99% species protection in fresh and marine water are 0.23 ng/L PFOS and 1900 ng/L PFOA [133]. A 2018 study analyzed the presence of 9 PFAS species in influent, effluent, and biosolid samples taken from 14 Australian WWTPs found that the effluent samples contained on average 25 ng/L PFOS and 22 ng/L PFOA [134]. Hence, the average effluent PFOS concentration of the investigated WWTPs was more than 100 times greater than the NEMP guideline values for receiving waters, and continual discharge into the environment may pose a threat to species due to the tendency of PFOS to bioaccumulate. PFAS were detected in the influent, effluent and biosolids of all 14 WWTPs, with longer chain PFAS being detected at increased concentrations in biosolids compared to liquid streams due to their increased sediment adsorption potential.

2.6. Endocrine-disrupting chemicals

Endocrine disruptors (EDs) are a group of compounds that can have severe negative impacts on human and animal health either by blocking or imitating natural hormones that take care of specific functions [135]. Endocrine-disrupting chemicals (EDCs) are highly heterogeneous and are classified into two categories: (i) natural chemicals and (ii) synthetic chemicals. The natural chemicals are found in food of humans and animals, for example, phytoestrogen: genistein and coumestrol. Synthetic chemicals can be further grouped into industrial solvents, lubricants, plastics, pesticides and some pharmaceutical [136]. The typical human exposure to EDCs occurs with the environmental contamination of food and contaminated dust from households [137]. Other exposure paths include exposure to a myriad of chemical compounds available within household products. Bisphenol A (BPA) has been found in polycarbonate plastics, epoxy resins, the ink used for thermal paper receipts, flame retardants, and medical drugs. Exposure to EDs is virtually unavoidable, and EDs have thus become ubiquitous, leading to a growing concern that such living conditions could result in adverse health effects such as early puberty and infertility [138].

3. Transformation products of ECs during wastewater treatment

3.1. Transformation of pharmaceuticals, PFAS and other contaminants

ECs, such as pharmaceuticals are excreted or released by humans either as free and/or conjugated metabolites. The parent ECs are expected to undergo a set of physicochemical and biological processes (such as photolysis, reactions with oxidants, hydrolysis and microbial metabolism) during the wastewater treatment process to produce a wide variety of transformation products (TPs) [159]. TPs or intermediate products are of particular concern if they are biologically active or offer resistance to biodegradation [160]. Moreover, TPs may act differently in ecotoxicological systems compared with environmental behavior, and consequently, could prove more or less toxic and persistent than the parent compounds, having a different risk to the ecosystem [161]. For instance, degradation products of tetracyclines, such as 5a,6-anhydrotetracycline and 5a, 6-anhydrochlortetracycline show different modes of structure-activity relations compared to the parent compounds and exhibit potency against tetracycline-resistant bacteria [27]. The knowledge on TPs is not only important from the environmental point of view but also for the design and optimization of wastewater treatment plants, providing much-needed information about the formation of unwanted intermediates and assisting in understanding about their toxicity and biodegradability. In addition, information regarding ECs and their TPs could provide valuable insights regarding the reuse of treated wastewater [162]. Table 3 summarizes different transformation products detected in the effluents of wastewater treatment plants/sludge/biosolids after different treatments.

Currently, research on TPs is focused on the degradation products of primary ECs in WWTPs arising through different types of treatment techniques such as oxidation, photolysis, and anaerobic digestion processes. In this regard, several studies have been conducted to determine the potential pathways for the transformation of primary ECs into TPs [26,163,164]. The degradation of some PPCPs into secondary or tertiary metabolites in WWTPs has been well understood. For example, Carbamazepine (CBZ) and Oxcarbazepine (OXC) are popular pharmaceuticals detected in drinking water, wastewater and treated water [26]. The major content of CBZ and OXC is generally humanly metabolized to several metabolites, including 10-hydroxy-CBZ and 10,11-dihydro-10,11-dihydroxy-CBZ, and have been found in influents and effluents of WWTPs at various concentrations up to 4 μg/L [26]. During the biological treatment, these metabolites can be further transformed into various intermediaries, such as 1-(2-benzoic acid) -(1H,3H)-quinazoline-2,4-dione (BaQD), 1-(2-benzoic acid)-(1H,3H)-quinazoline-2-one (BaQM), 9-aldehyde-acridine, 9-carboxylic acid-acridine (9-CA-ADIN), hydroxyl 9-CA-ADIN, acridone (ADON), 11-keto-OXC, and 2,2′ -(carbamoylazanediyl) dibenzoic acid. Fig. 2 shows the possible transformation pathways of DiOHCBZ, 10OHCBZ, and OXC that include oxidation, α-ketol rearrangement, or benzylic acid rearrangement. Another study by Lee et al. [141]. demonstrated the removal and transformation of some PPCPs in WWTPs of South Korea. The results suggested that concentrations of pharmaceutical metabolites increased after the treatment due to the higher structure stability of the metabolites [141]. Evidently, the concentration of 4-hydroxyl-diclofenac (a metabolite of diclofenac) was increased from 396 ng/L (in the influent) to 504.6 ng/L (in the effluent) [141]. Degradation of PFAS during wastewater treatnent is not well

Table 3
Transformation products detected in the effluents of wastewater treatment plants/sludge/biosolids after different treatments.

Category of EC	Parental compound	Source	Analytical technique	Amount in influent	Amount in effluent	Treatment type	Transformation product	Amount in influent	Amount in effluent	Location & Reference
1. PPCPs	4 methyl-1H benzotriazole, 5 methyl-1H benzotriazole	Wastewater	GC-GC-TOFMS	1.48-3.48 μg/L	1.06-1.57 μg/L	Chlorination	4-chloromethyl-2H-benzotriazole, 5-chloromethyl-1H-benzotriazole, 4-chloromethyl-1H-benzotriazole, and 5-chloromethyl-2H-benzotriazole	5.82-18.08 μg/L	5.86-47.17 μg/L	USA (2020) [139]
	Acetaminophen	Sewage sludge	UHPLC-Q Exactive MS	/	1.35–118.02 ng/L	Biodegradation	Hydroquinone	/	/	China (2021) [140]
	Triclosan			/	0.18–1.63 ng/L	Biodegradation	4- Chlorocatechol	/	/	
	Caffeine			/	2.43–518.86 ng/L	Biodegradation	Catechol	/	/	
	N, N-diethyl-m-toluamide			/	0.97–4.10 ng/L	Biodegradation	/	/	/	
	Sulfamethoxazole			/	1.42–55.30 ng/L	Biodegradation	Aminophenolate, Benzenesulfonylazanide	/	/	
	Caffeine	Wastewater	LC-HR-MS/MS	72 471.2 ng/L	< 4.6 ng/L	N & P removal	Paraxanthine	8215.3 ng/L	33.9 ng/L	China (2013) [141]
	Sulfamethoxazole			6048.6 ng/L	88.8 ng/L	N & P removal	N-acetyl-SMZ	5224.8 ng/L	64.5 ng/L	
	Naproxen			1140.5 ng/L	< 10.0 ng/L	N & P removal	O-desmethyl-NPX	191.5 ng/L	31.7 ng/L	
	Diclofenac			2673.5 ng/L	111.7 ng/L	N & P removal	4-OH-DCF	530.6 ng/L	582.1 ng/L	
	Caffeine			45 457.0 ng/L	< 4.6 ng/L	Activated Sludge	Paraxanthine	10 442.1 ng/L	< 27.9 ng/L	
	Sulfamethoxazole			8092.9 ng/L	166.6 ng/L	Activated Sludge	N-acetyl-SMZ	6224.2 ng/L	72.4 ng/L	
	Naproxen			1778.5 ng/L	10.7 ng/L	Activated Sludge	O-desmethyl-NPX	125.0 ng/L	31.1 ng/L	
	Diclofenac			2702.8 ng/L	86.6 ng/L	Activated Sludge	4-OH-DCF	396.0 ng/L	504.6 ng/L	
	Carbamazepine, Oxcarbazepine, 10-hydroxy-CBZ, and 10,11-dihydro-10,11-dihydroxy-CBZ	Sewage sludge	LC-HR-MS/MS	43-4960 ng/L	27-3380 ng/L	Biodegradation	9-aldehyde-acridine, 9-carboxylic acid-acridine, 1-(2-benzoic acid)-(1H ,3H)-quinazoline-2,4-dione, and acridone	<LOQ-700 ng/L	<LOQ-920 ng/L	Germany (2014) [26]
	Benzodiazepines (diazepam, lorazepam, prazepam, oxazepam, alprazolam, nordiazepam, bromazepam, temazepam, chlordiazepoxide, clonazepam, flurazepam, nitrazepam, flunitrazepam, clobazam, midazolam, clozapine and estazolam)	Sewage sludge	MS-HPLC	0.01-45 ng/L	0.37-22 ng/L	Biodegradation	(6-chloro-4-phenyl-2(1H)-quinazolinone; 2-amino-5-chlorobenzophenone and 5-chloro-2-(methylamino) benzophenone	/	/	China (2021) [142]
2. Flame Retardant	Tris(2-butoxyethyl) phosphate	Sewage sludge	UHPLC-HRMS/MS	2.55 μg/L	1.09 μg/L	Biodegradation (Oxidation, Hydrolysis)	TB_88, TB_198, TB_298, TB_412, TB_414	/	/	South Korea (2021) [143]
	Tris(1-chloro-2-propyl) phosphate)	Sewage sludge	UHPLC-HRMS/MS	0.13 μg/L	0.27 μg/L	Biodegradation (Oxidative dichlorination, Hydrolysis, Oxidation)	TC_90, TC_249, TC_290, TC_304	/	/	South Korea (2021) [143]
	Triphenyl phosphate	Sewage sludge	UHPLC-HRMS/MS	0.021 μg/L	0.017 μg/L	Biodegradation (Carboxylation, Oxidation, Hydrolysis, Reduction)	TP_110, TP_138, TP_140, TP_188, TP_250, TP_342	/	/	South Korea (2021) [143]
	TDBP-TAZTO	Sewage sludge	LC–ESI–QTOF–HRMS	10000 ng/L	2100 ng/L	Dehydrobromination, Hydroxylation, and Decarbonylation reactions	TP_1, TP_2, TP_3, TP_4, TP_5, TP_6, TP_7, TP_8, TP_9, TP_10, TP_11	/	/	Japan (2021) [144]
	TDBP-TAZTO	Sewage sludge	LC–ESI–QTOF–HRMS	18000 ng/L	/	Dehydrobromination, Hydroxylation, and	TP_1, TP_2, TP_3, TP_4, TP_5, TP_6, TP_7, TP_8, TP_9, TP_10, TP_11	/	/	Japan (2021) [144]

(*continued on next page*)

Table 3 (*continued*)

Category of EC	Parental compound	Source	Analytical technique	Amount in influent	Amount in effluent	Treatment type	Transformation product	Amount in influent	Amount in effluent	Location & Reference
						Decarbonylation reactions				
	Tetrabromobisphenol A	Sewage sludge	LC-MS/MS	43.7-89.6 μg/L	1.7-4.5 μg/L	Anaerobic Biodegradation (decomposition, dehydrogenation, hydrogenation, deprotonation, and substitutions)	Phenol and Benzoyl-CoA	/	/	Brazil (2021) [145]
	Polybrominated diphenyl ethers	Sewage sludge	GC-MS (Selective Ion Monitoring)	/	19.0-49.1 ng/g	Biodegradation (debromination)	BDEs	/	/	China (2017) [146]
	Decabromodiphenyl ether (BDE 209)	Sewage sludge	GC-MS (Selective Ion Monitoring)	/	200-2150 ng/g	Biodegradation (debromination)	TetraBDEs, PentaBDEs	/	/	China (2017) [146]
	Decabromodiphenyl ethane	Sewage sludge	GC-MS (Selective Ion Monitoring)	/	680-27,400 ng/g	Biodegradation (Bond cleavage at CH_2-CH_2)	Pentabromotoluene, pentabromoethylbenzene, and pentabromobenzene	/	/	China (2017) [146]
	2,3-dibromopropyl tribromophenyl ether (DPTE)	Wastewater	GC/ECNI−MS	1.27 ng/g	1.09 ng/g	Biodegradation (debromination)	2,4,6-tribromophenyl allyl ether	0.13 ng/g	0.08 ng/g	China (2020) [65]
	2,3-dibromopropyl tribromophenyl ether (DPTE)	Biosolids	GC/ECNI−MS	/	0.47 ng/g	Biodegradation (debromination)	2,4,6-tribromophenyl allyl ether	/	0.17 ng/g	China (2020) [65]
	Tetrabromobisphenol A	Sewage sludge	LC−Q-TOF-MS	/	/	Abiotic nitration	Nitrotribromobisphenol A, Dinitrodibromobisphenol A, 2,6-dibromo-4-nitrophenol, 2,6-dibromo-4-(2-(2-hydroxy)- propyl) phenol	/	/	China (2015) [147]
	Tetrabromobisphenol A	Sewage sludge	LC−Q-TOF-MS	/	/	Nitric anaerobic sludge	2,6-dibromo-4-(2-propyl)-phenol, 2,6-dibromo-4-(2-(2 hydroxy)-propyl)- phenol, 2,6-dibromo-4-(1-hydroxy-ethyl)-methoxybenzene, 2-nitro-4-(1-methoxy-ethyl)-6-bromophenol	/	/	China (2015) [147]
3. Surfactants	Linear alkylbenzene sulfonates	Sewage sludge	UHPLC-ESI-QTOF-MS	2600-3500 μg/L	0-47.7 μg/L	Activated sludge	Sulfophenyl alkyl carboxylic acids and Sulfo-tetralin alkyl carboxylic acids		657-5533 ng/L and 757-17142 ng/L	Germany (2019) [148]
	Alkyl ethoxysulfates	Sewage sludge	UHPLC-ESI-QTOF-MS	400-1000 μg/L	0-1.9 μg/L	Activated sludge	/	/	/	Germany (2019) [148]
	Linear alkylbenzene sulfonates	Sewage sludge	UHPLC-ESI-QTOF-MS	2600-3500 μg/L	0-47.7 μg/L	Activated sludge	Di-alkyl tetralin sulfonates	/	843-18951 ng/L	Germany (2019) [148]
	Linear alkylbenzene sulfonates	Sewage sludge	UPLC-MS/MS	1150 μg/L	/	Anaerobic-oxic treatment process		/	/	China (2018) [149]
	Linear alkylbenzene sulfonates			1740 μg/L	27.1 μg/L	Anaerobic-oxic treatment process	/	/	/	
	Linear alkylbenzene sulfonates			1830 μg/L	1.32 μg/L	Cyclic activated sludge technology	Mono- and dicarboxylic sulfophenyl acids	/	/	
	Linear alkylbenzene sulfonates			1280 μg/L	13.7 μg/L	Cyclic activated sludge technology	Mono- and dicarboxylic sulfophenyl acids	/	/	
	Benzalkonium chlorides			0.64 μg/L	0.07 μg/L	Anaerobic-oxic treatment process	/	/	/	
	Benzalkonium chlorides			0.87 μg/L	0.01 μg/L	Cyclic activated sludge technology	/	/	/	
	Nonylphenol diethoxylate (NP2EO)	Sewage sludge	GC-MS/MS	3000 μg/L	269 μg/L	Anaerobic digestion	Nonylphenol monoethoxylate (NP1EO),	/	/	Turkey (2016) [150]

							nonylphenol (NP), nonylphenoxy acetic acid (NP1EC)			
	Nonylphenol polyethoxylates, alcohol polyethoxylates	Sewage sludge	LC-MS-APCI	26.7-438.4 μg/L	12.5-300 μg/L	Anaerobic digestion	Polyethylene glycol, polyethoxylated nonylphenol carboxylates and polyethoxylated alcohol carboxylates	11.9-1031 μg/L	6.4-225 μg/L	Spain (2000) [151]
4. PFAS	8:2 fluorotelomer alcohol	Sewage sludge	HPLC-MS/MS	~ 73.5 mg/L	/	Anaerobic digestion	2H-perfluoro-2-decenoic acid (8:2 FTUA) and PFOA, PFPeA and PFBA	/	/	China (2018) [152]
	PFOA	/	MS	/	/	Photocatalytic degradation	PFHpA, PFHxA, PFPeA, PFBA, PFPrA and TFA	/	/	Finland (2017) [153]
	Short-chain fluorinated carboxylic acids (C3-C5)	Sewage sludge	UHPLC-HRMS/MS	/	/	Aerobic microbial defluorination	Malonyl-CoA and Monofluoromalonyl-CoA	/	/	USA (2021) [154]
	PFOA	/ /	LC-HRMS/MS LC-HRMS/MS	25 μM	/	UV/Sulfite treatment	Defluorinated compounds of PFOA, PFHxA, PFPeA		<LOQ-9.66 μM	USA (2019) [155]
	PFOS						PFHpS, PFHxS, PFBS, PFOA, PFHpA, PFHxA, PFPeA, PFBA		<LOQ-9.81 μM	
	PFNA						Defluorinated compounds of PFNAPFOA, PFHpA, PFHxA, PFPeA, PFBA		<LOQ-9.78 μM	
	PFDA						Defluorinated compounds of PFDA, PFNA, PFOA, PFHpA, PFHxA, PFPeA, PFBA		<LOQ-8.64 μM	
	PFHxS	/	LC-HRMS/MS	25 μM	/	UV/Sulfite treatment	PFPeS, PFBS, PFPrS, PFHxA, PFPeA, PFBA		0-9.08 μM	USA (2019) [155]
	8:2 fluorotelomer alcohol						PFOA, PFHpA, PFHxA, PFPeA, PFBA		1.05-9.88 μM	
	PFPrA	/	LC-HRMS/MS	265.3 μM	/	UV/Sulfite treatment	Defluorinated compounds of PFPrA, TFA		2.8-162.3 μM	USA (2020) [156]
	PFDA	/	LC-HRMS/MS	25 μM	/	UV/Sulfite treatment	Defluorinated compounds of PFDA, PFNA		0.014-9.59 μM	
	PFNA	/	LC-HRMS/MS	25 μM	/	UV/Sulfite treatment	Defluorinated compounds of PFNA, PFOA		0.014-8.74 μM	
	PFOA	/	LC-HRMS/MS	25 μM	/	UV/Sulfite treatment	Defluorinated compounds of PFOA, PFHpA		<LOQ-9.36 μM	
	PFOA PFdiMeOA PFMeUPA FTMeUPA FTMePA	/	LC-HRMS/MS	/	/	Microbial reductive defluorination	TP 256 ($C_6H_2F_8O_2$) TP 276 ($C_6H_3F_9O_2$) TP 259 ($C_6H_4F_8O_2$) TP 241 ($C_6H_5F_7O_2$) (confirmed as FTMePA) TP 221 ($C_6H_4F_6O_2$)	/	/	USA (2020) [157]
	FtTP	Wastewater	LC-QTOF	/	/	Aerobic biodegradation, dechlorination (Hydrolysis, Oxidation)	FtSOPA	/	/	USA (2018) [158]
	FtSOPA			/	/		$FtSO_2PA$	/	/	
	FTSHC			/	/		FTSOHC	/	/	
	FTSOHC			/	/		$FTSO_2HC$	/	/	
	FTSAHC			/	/		FTSOAHC	/	/	

Note: BDE- Decabromodiphenyl ether; CBZ: Carbamazepine; FtTP: Fluorotelomer thioether propanoic acid; FtSOPA: Fluorotelomer sulfinyl propanoic acid; $FtSO_2PA$: Fluorotelomer Sulfonyl propanoic acid; FTSHC: fluorotelomer thioether hydroxyl carboxylate; FTSOHC: fluorotelomer sulfinyl hydroxyl carboxylate; $FTSO_2HC$: fluorotelomer sulfonyl hydroxyl carboxylate; FTSAHC: fluorotelomer thioether alkylamido hydroxyl carboxylate; FTSOAHC: fluorotelomer sulfinyl alkylamido hydroxyl carboxylate; FTMeUPA: 4,5,5,5-tetrafluoro-4-(trifluoromethyl)-2-pentenoic acid; FTMePA: 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentanoic acid; GC-MS: Gas chromatography-mass spectroscopy; GCxGC-TOFMS: Two-dimensional gas chromatography coupled to time of flight mass spectrometry; GC/ECNI–MS: Gas chromatography/mass spectrometry operated in negative ionization mode; LC–ESI–QTOF–HRMS: Electrospray ionization–quadrupole time-of-flight–high-resolution mass spectrometry with liquid chromatography; LC-MS-APCI: Liquid chromatography-mass spectrometry using atmospheric pressure chemical ionization; LC-HR-MS/MS: Liquid chromatography high-resolution mass spectrometry; LC-MS/MS: Liquid chromatography-tandem mass spectrometry; LOQ-Limit of quantification; LOD: Limit of detection; PFBA: Perfluorobutyric acid; PFBS: Perfluorobutanesulfonate/sulfonic acid; PFDA: Perfluorodecanoic acid; PFdiMeOA: Perfluoro-3,7-dimethyloctanoic acid; PFHpA: Perfluoroheptanoic acid; PFHxA: Perfluorohexanoic acid; PFHpS: Perfluoroheptanesulfonate/sulfonic acid; PFHxS: Perfluorohexanesulfonate/sulfonic acid; PFMeUPA: (E)-perfluoro (4-methylpent-2-enoic acid); PFNA: Perfluorononanoic acid; PFOA: Perfluorooctanoic acid; PFOS: Perfluorooctane sulfonate/sulfonic acid; PFPeA: Perfluoropentanoic acid; PFPrA: Perfluoropropionic acid; PFPeS: Perfluoropentanesulfonate/sulfonic acid; PFPrS: Perfluoropropanesulfonate/sulfonic acid; TDBP: TAZTO- 1,3,5-tris-(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-trione;TFA: Trifluoro acetic acid; UHPLC-HRMS/MS: Ultra-high-performance liquid chromatography-electrospray ionization-quadrupole orbitrap mass spectrometer; UPLC-MS/MS: Ultra performance liquid chromatography-tandem mass spectrometry.

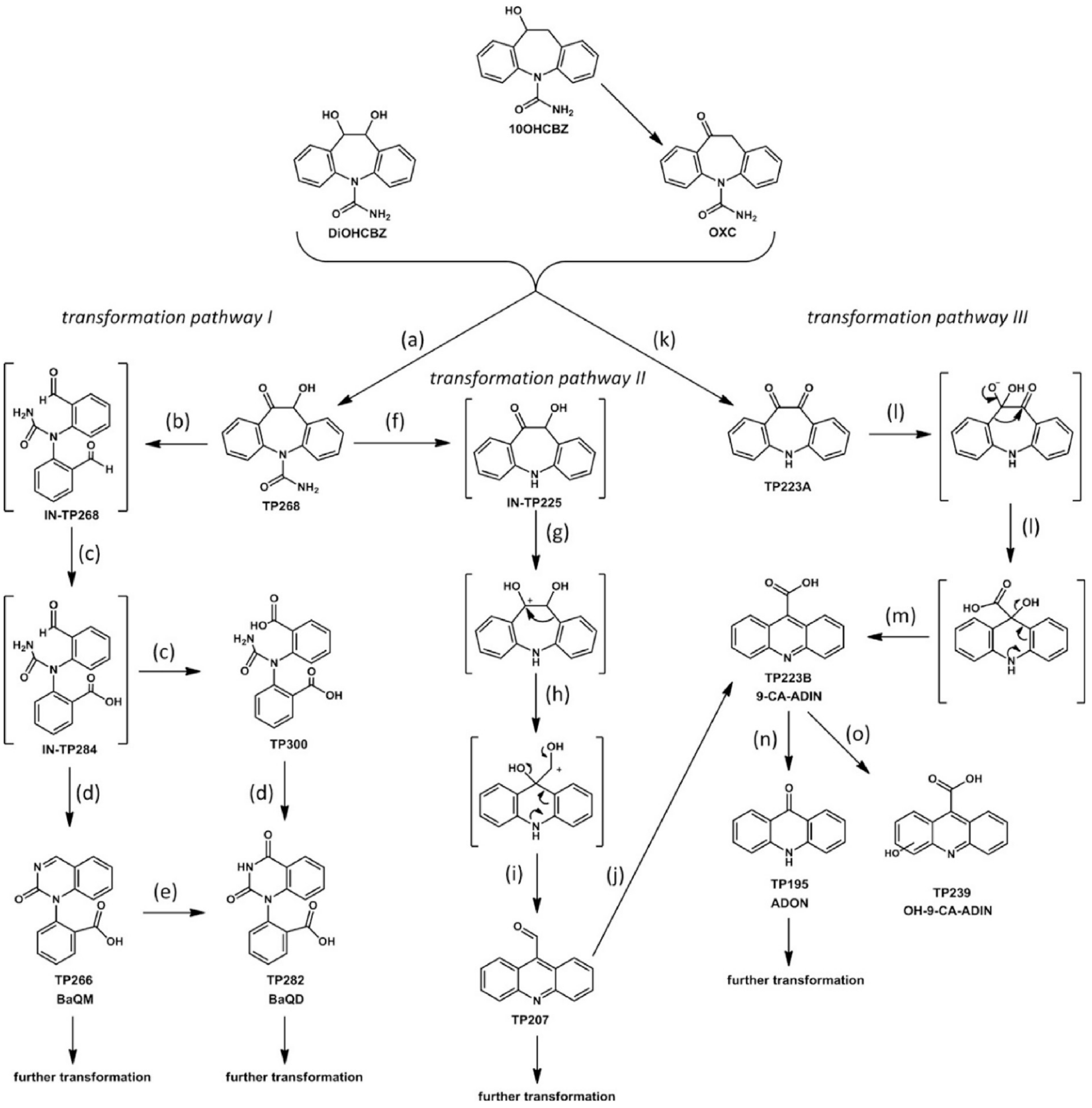

Fig. 2. Proposed transformation pathway of DiOHCBZ, 10OHCBZ, and OXC. Compounds in brackets are proposed intermediates. Reactions are (a) dehydrogenation for DiOHCBZ, hydroxylation for 10OHCBZ with subsequent dehydrogenation, and hydroxylation for OXC, (b) C10–C11 bond cleavage, (c) oxidation, (d) intramolecular ring closure and loss of water, (e) oxidation, (f) loss of the carbamoyl group, (g) α-ketol rearrangement, (h) ring contraction, (i) elimination of the hydroxyl group, (j) oxidation, (k) loss of the carbamoyl group followed by oxidation (DiOHCBZ) and hydroxylation followed by oxidation (OXC and 10OHCBZ), (l) benzylic acid rearrangement, (m) loss of water, (n) decarboxylation, hydroxylation, and oxidation, and (o) hydroxylation. The Figure is reproduced with permission from Kaiser et al. [26].

Abbreviations: 10OHCBZ: 10-hydroxy-carbamazepine; DiOHCBZ-10,11-dihydro-10,11-dihydroxy-carbamazepine; OXC: oxcarbazepine; BaQD: 1-(2-benzoic acid)-(1H,3H)-quinazoline-2,4-dione; BaQM: 1-(2-benzoic acid)-(1H,3H)-quinazoline-2-one; 9-CA-ADIN: 9-aldehyde-acridine, 9-carboxylic acid-acridine; ADON: hydroxyl 9-CA-ADIN, acridone.

understood and mainly involves a series of defluorination reaction. Fig. 3 presents the generation of various transformation products during PFAS degradation and defluorination.

The fate of TPs of a particular EC can vary depending on the type of technique used for the wastewater treatment, obviously due to different degradation mechanisms followed in the wastewater treatment. For instance, in a study done by Elisa De et al., it was identified that the TPs of acetaminophen formed during the photodegradation process were completely different from the microbial degradation products or human metabolites, which indicates the complexity of the transformation process [165]. In addition, the TPs can remain stable or may further degrade during wastewater treatment. For instance, in two different studies done on PPCPs, the authors reported different behavior of TPs. A study reported by Larsson et al. [165], the TPs, which include Carboxyibuprofen, *O*-Desmethylnaproxen and 2-Hydroxyibuprofen at average concentrations of 63000 ng/L, 45000 ng/L and 35000 ng/L, respectively, were noticed to be higher in the influents when compared to their concentrations in the effluents. The effluent concentrations of all TPs together were reported to be below 1000 ng/L. In contrast, the TPs of diclofenac were noticed to be higher in the effluent, indicating the stable nature of some TPs formed during the treatment process [166].

Apart from influent and effluent, the formation of TPs from the parent EC compounds is greatly influenced by the type of the treatment process [167]. Photolytic reactions are often considered

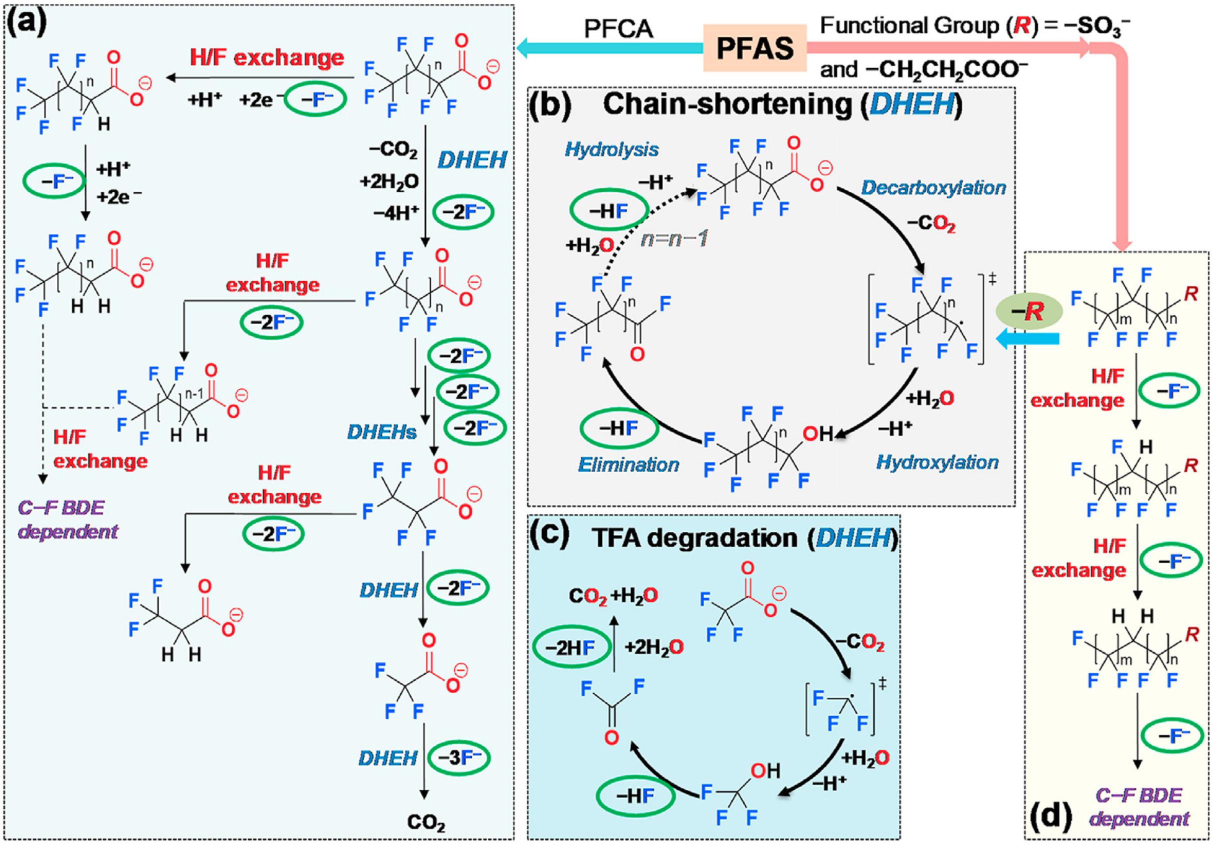

Fig. 3. Reaction Mechanisms for PFAS Degradation and Defluorination. Reproduced with permission from Bentel et al. [155].

complex reactions and result in several reaction products [168]. Biodegradation, often seen in WWTPs, is another important technique for eliminating ECs either partially or completely. In a study done by Lee et al. [166], 2-hydroxyibuprofen was the dominant species in the influent; however, 1-hydroxyibuprofen was found at high concentrations in the effluent following the activated sludge processes. Disinfection processes in WWTPs, such as ozonation and chlorination, generally remove trace organic compounds from secondary wastewater effluents. Disinfection by-products (DBPs) and some of their TPs have been shown to be toxic or estrogenic [169]. It is not surprising that most of the ECs produce DBPs as they have aromatic rings that can react with oxidants like ozone, chlorine, or chloramines [170].

Laboratory studies and environmental screening are the two different approaches that have been considered to identify TPs in wastewater. While a laboratory study facilitates the simulation of transformation processes under controlled conditions, environmental monitoring allows identification of at least a few of these compounds [171]. Environmental monitoring is important as TPs formed and released via WWTP may be subjected to biotic and abiotic processes and further degradation [172]. To date, laboratory studies have been conducted in different scales, bench- (1–20 L capacity), pilot- (20–100 L capacity) and demonstration-scale (operating the equipment at full commercial feed rates). Laboratory scale experiments can be carried out employing different operational conditions: anaerobic, aerobic and anoxic and the physicochemical characteristics of the solid fraction can be monitored and adjusted to facilitate the direct comparison with environmental conditions.

Along with the PPCPs, other ECs such as flame retardants, micro and nano-plastics, EDCs, and surfactants have been extensively studied to understand the transformation processes in the WWTP and their impact on the receiving habitats. There are several compounds under each category of above-mentioned ECs. For instance, polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyl (PCB) congeners have been found to be linked to wastewater sludge and compounds such as triphenyl phosphate (TPP) have been noticed to be associated with aqueous fraction [173]. In a recent study reported by La Guardia et al. [174], the authors reported the possibility of biotransformation of decabromodiphenyl ether (BDE-209) in the fish population of the receiving aquatic habitat. The authors mentioned that BDE-209, which is initially found in the sludge samples, was not seen in the tested fish population. However, congeners such as BDE-179, -184, −188, −201, and −202 were detected, indicating the metabolic debromination of BDE-209. Recently, debromination metabolites of bis(dibromopropyl ether), such as nona-, octa-, hepta-, hexa- and pentabromodiphenyl were detected in snails [175].

The treatment of surfactants in WWTPs leads to the release of complex mixture of transformation products into receiving bodies. In a study analyzing 33 conventional WWTPs in Germany, the authors reported that despite a very high treatment efficiency, alkyl ethoxysulfates (AES) and linear alkylbenzene sulfonates (LAS) were still available in the effluents. In addition, concentrations of byproducts and TPs, which include di-alkyl tetralin sulfonates (DATSs) and sulfophenyl alkyl carboxylic acids (SPACs) and sulfotetralin alkyl carboxylic acids (STACs), in the effluents surpassed the concentrations of the precursors [176]. Ashfaq et al. [177] investigated the occurrence of EDCs and their transformation products during wastewater treatment process under varying operational conditions. The authors considered eight EDCs for the study and noticed that a majority of EDCs were removed during the treatment process, however, two EDCs, namely triclosan and triclocarbon, and their transformation products which include methyl triclosan (MeTCS), carbanilide (NCC) and dichlorocarbanilide (DCC), were noticed in the effluents [177]. The possibility of the TPs exhibiting the endocrine disrupting activity cannot be overlooked and the information on fate of EDCs and its TPs in the solid fraction of the WWTPs is sparsely available [177], however, many studies affirmed the persistent nature of EDCs and their accumulation in the effluent of WWTP could be a potential environmental hazard [178]. Another study was conducted by a group of Turkish researchers on the five EDC model compounds in a membrane bioreactor. The results of the study suggested that anaerobic digestion was not effective in removing the selected EDCs that are sorbed onto the sludge [179]. The elevated concentrations of EDCs in the sludge can be considered as an indication for the need of effective sludge treatment to control EDCs in the environment.

3.2. Transformation of microplastics

Microplastic particles (MPs) undergo significant physicochemical changes during the sewage treatment, especially the surfaces of the MPs become quite rough, fragile and contain an enhanced number of pores [103]. In addition, transformation in physicochemical characteristics such as surface charge and dissociation of certain chemicals has been demonstrated due to weathering, photo-oxidation, mechanical and biological activities during the sewage treatment [180]. Consequently, MPs accommodate or adsorb more toxic pollutants like heavy metals, polyaromatic hydrocarbons (like naphthalenes, phenanthrene), polychlorinated biphenyls, antibiotics (tetracycline, ciprofloxacin, trimethoprim) on its surface from the surrounding environment. The adsorption of all the pollutants on MPs follows similar mechanisms with some variations. Generally, the factors that contribute to the adsorption of the pollutants involve the presence of oxygen-containing chemical groups, hydrophobicity, hydrogen bonding, electrostatic forces, and van der Waals forces [112,180]. However, the type of polymer, due to the unique chemical composition, may exhibit different adsorption activities for the pollutants. For instance, a study by Li et al. [181] demonstrated the adsorption of heavy metals like Cd, Pb, Co and Ni. The results of the study are shown in Fig. 4. It can be clearly seen from the results that MPs extracted from the sludge showed considerable adsorption for Cd, Pb and Co, while the adsorption for Ni was lower for MPs compared to the sludge samples. The enhanced adsorption of the heavy metals was attributed to the accumulation of oxygen-containing groups like $C-O$ and $O-H$ on the surface of MPs post sewage treatment. On the other hand, virgin MPs like polyamide, polyethylene, and polypropylene showed higher adsorption for heavy metals compared to other counterparts like polyvinyl chloride and polystyrene [181]. It has been noticed that different functional groups modify the hydrophobicity of the microplastic surface, which ultimately affects the adsorption of heavy metals. Also, the enhanced affinity of pollutants has been observed for aged MPs (aging MPs change their surface properties afterexposure to environmental conditions and other forces), probably due to the breaking of chemical bonds and formation of free radicals [95]. Since MPs adsorb antibiotics, they are also known to enrich antibiotic-resistant genes, subsequently leading to the generation of an increasing number of antibiotic-resistant microorganisms [182].

4. Strategies for EC detection and quantification

To examine the physicochemical properties and composition of ECs completely involves three major steps, such as sample

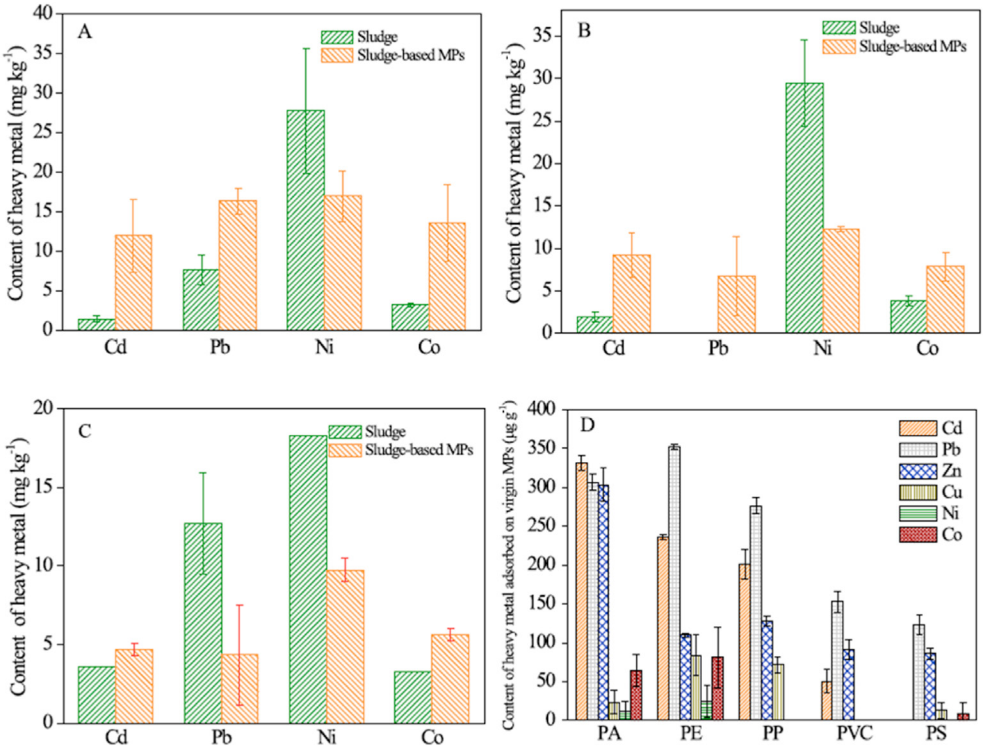

Fig. 4. The content of metals in sewage sludge and adsorbed on the sludge-based MPs (A–C) and virgin MPs (D). The figure is reproduced with permission from Li et al. [181] Note: PA-polyamide; PE-polyethylene; PP-polypropylene; PVC-polyvinyl chloride; PS-polystyrene.

collection, pre-treatment and extraction techniques, and analytical techniques for identification. All these steps and their types are discussed in the following sections.

4.1. Sample collection

In wastewater treatment plants, the selection of sampling location largely depends on the type of sludge sample required for analysis. While most of the studies reported in the literature used samples that are collected after the final dewatering step to make sure the sample collected is a representative sample, few studies considered the samples after the anaerobic digestion unit [183–185]. However, there are studies that considered sludge samples from primary and secondary flow for analysis [185,186]. Composite sampling on a long-term could be a better representative sample as it can accurately show the fluctuations and better indicate the performance of the production batch over a protracted period of time. This sampling process is often tedious and not generally accepted [8,187,188]. Grab sampling is less labour intensive and, at the same time, is considered comparable to 20–30 days composite sampling. Hence, grab on sampling is often preferred as an alternative for sample collection of sludge/biosolids [8,189–192]. In general, amber bottles and jars [184–186,188,191,193] or stainless-steel buckets [194,195] are used for sample collection. The use of these containers for sample collection protects them from the effect of photodegradation, humidity and other external environmental factors. Other popular storage containers include aluminium foils [187,188,196] and/or polyethylene bags or containers [8,187,189]. The samples are usually transported to the laboratory and preserved at −20 °C until used further for the extraction and analysis.

4.2. Sample preparation, extraction and clean-up

For efficient extraction of ECs, the samples are to be either in the form of liquid or in finely divided solid. For a few categories of ECs, for instance, pharmaceutical samples, having acidic groups and those present in ionized form with neutral pH, may need acidification for efficient extraction [197]. Thus, sample pre-treatment is essential to concentrate the analyte and minimize the effect of matrix interference with instrumental determination [28]. Sample preparation often involves the process of extraction followed by a clean-up step. A wide range of extraction techniques has been reported in the literature, of which traditional techniques such as the Soxhlet method and ultrasound, along with the latest approaches such as microwave and pressurized liquid extraction, have gained popularity. Solid-liquid extraction (SLE), in which a solvent is used for the extraction of ECs from solid samples, serves as a technique to remove and separate the compounds of interest from high-molecular-weight fractions and other compounds that may affect the downstream steps [198]. Soxhlet process can be considered as an example for the SLE group processes. Soxhlet technique is a traditional method used to extract the compounds from solid samples that have limited solubility with solvents and are insoluble to the impurities. The equipment used for Soxhlet extraction involves a porous thimble that contains the sample placed in the main chamber of the Soxhlet extractor. A condenser and a siphon side arm is used to reflux the solvent through the thimble. The extraction cycle is repeated many times. Some advantages of this process include; (i) repeated contact of samples with fresh portion of the extractant which facilitates the displacement of transfer equilibrium; (ii) elimination of the filtration step increases the sample yield; (iii) low cost of the equipment facilitates simultaneous parallel runs [199]. However, there are a few shortcomings associated with the Soxhlet method; it is labour intensive, time-consuming and requires a large sample size (10–30 g) and a large volume of solvents (300–500 mL).

Ultrasound-assisted extraction (UAE) is often considered an alternative to the Soxhlet process. The acoustic cavitation generates ultrasound energy which significantly impacts the liquid media and generates bubbles that have the potential to mechanically erode and rupture the solid samples. Reduced extraction time and requirement of less volume of solvent are the advantages of UAE over the Soxhlet method [200]. It can be applied to solid and liquid

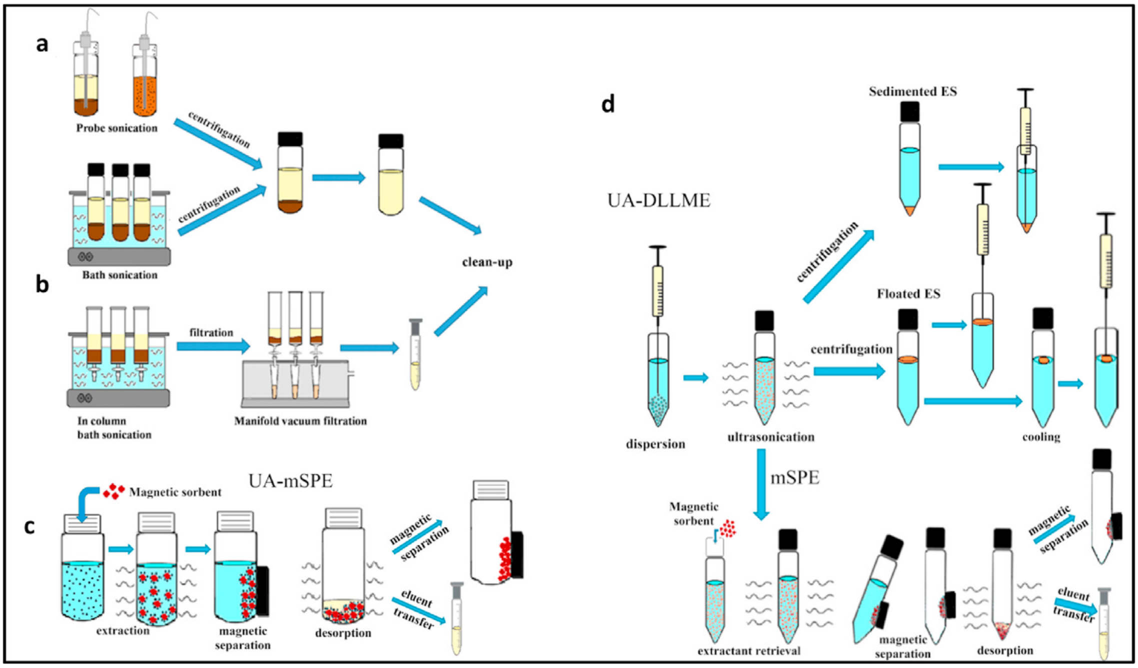

Fig. 5. Diagram of UAE for solid samples using (a) an ultrasonic probe (b) an ultrasonic bath, (c) UAE for liquid samples using magnetic solid-phase extraction and (d) dispersive liquid-liquid microextraction procedures. The figure is reproduced with permission from Alberto et al. [207].

samples using an ultrasonic probe or ultrasonic bath, steps involved in UAE for both types of samples are given in Fig. 5. A wide range of analytes has been tested using UAE. For instance, pharmaceuticals [189,196,201], personal care products [202–204], endocrine-disrupting chemicals [205–207], flame retardants [208,209], xenobiotic compounds [210,211], PAHs [212], and PCBs [213]. The selection of a solvent in the UAE process depends on the physical properties, such as vapour pressure, viscosity and surface tension of the solvent as cavitation phenomena is significantly affected by these properties [214]. A variety of solvents has been used to extract ECs; for instance, a mixture of H_2O and methanol at 1:1 v/v was used to extract pharmaceutical compounds [201,202,215], acetonitrile and methanol were used to extract organophosphorus flame retardants [216], perfluoroalkyl substances [217] and octylphenol ethoxylates [193]. UAE has significant advantages over the Soxhlet method since it is very quick and requires less amount of solvents. For instance, where the Soxhlet method requires 300–500 ml of the solvent, UAE requires 10–50 ml of the solvent and takes approximately 30–40 min compared to 12–48 h of the Soxhlet method [37]. Some advantages and disadvantages of UAE has been listed in Table 4.

Pressurized liquid extraction (PLE) has gained immense attention as a novel extraction technique, given the advantages like shorter extraction times, the requirement of low quantities of solvents and the possibility to fully automate the extraction process. The instrumentation of a PLE system could be either static or dynamic or both. Fig. 6 shows a schematic diagram of a static and dynamic PLE system. Both types of PLE systems contain a solvent reservoir, which is connected to a high-pressure pump. The pump helps to introduce the solvent into the system and later helps the extract push out after the process. It contains an oven with an extraction cell where the extraction process is carried out. Different valves and restrictors are used in the system to maintain the pressure. In the last phase, a collecting vial is used to collect the extract. An inert gas cylinder is often used in the process to flush out the solvent. In contrast to the static system, the dynamic PLE system additionally contains a sophisticated pressure restrictor, solvent preheating coils and a micro metering valve. PLE employs solvent extraction at elevated pressures usually up to 200 bar) and temperatures (usually up to 200 °C), always below their respective critical points, so that the solvent remains in a liquid state throughout the extraction process [218]. In addition, the possibility to choose particular conditions results in a change in the physicochemical properties of solvents, which in turn decreases the surface tension and viscosity, and increases the mass transfer rates and solubility of analytes [35]. However, it is worth pointing out that the temperature may play a negative role in the extraction process. Though, in theory, the higher the temperature, the greater the yields, the higher temperature might have a negative effect on thermolabile compounds, particularly the bioactive compounds. Also, the influence of pressure beyond a certain point where the solvent is not in a liquid state is insignificant [219]. A wide variety of ECs has been determined from sludge samples using PLE as the extraction technique. For instance, bisphenols congeners and BPA [220], flame retardants such as BFRs and chlorinated flame retardants, alkylephenols [220], pharmaceuticals [221], and hormonal steroids [220] were extracted using the PLE technique. The sensitivity achieved with the PLE method results in the efficient extraction of the target analyte, and post-extraction clean-up method and instrumental techniques for identification allow detection of target analytes below ng g^{-1} of the sample. For instance, as noticed in the study by Garcia-Galan et al. [222], sulphonamides and their metabolites below 0.03 ng/g were detected in sewage sludge samples. Along with the temperature and pressure, other important parameters that are to be taken into consideration in PLE include extraction time and a number of cycles. While the temperature range in the PLE process varied from 40 to 200 $^\circ C$, the extraction pressure varies between 6.9 and 13.8 MPa [28]. However, few studies employed extraction pressures of 1000 psi [223], 1250 psi [224] and 2001 psi [183]. The extraction time varied from 2 to 16 min [183,225], and the number of cycles employed varied from 1 to 4 [187,226]. In general, clean-up is necessary to improve the pre-concentration of the sample and minimize the matrix effect [223]. Though PLE offers several advantages like high extraction efficiency, low extraction time, less amount of solvents, there are certain disadvantages associated with the technique, are reported in Table 4. For instance, it might require higher temperature ($40-200^\circ C$) and pressure conditions (6.9–13.8 MPa) to migrate the contaminants from the matrix material into the extraction solvent phase. In addition, it needs multiple extraction cycles to obtain the compound which is generally followed by a post extraction clean up method to purify the compound. The overall process, especially dynamic could be expensive compared to Soxhlet and LLE considering the operational parameters (including the cost of solvents and inert gas) and capital cost of the instruments.

The microwave-assisted extraction (MAE) technique has been used for more than three decades for the extraction of various organic compounds and other pollutants [227]. MAE depends on the application of microwave energy. Microwave energy is non-ionizing radiation in the range of frequency between 300 and 300000 MHz. Microwaves are electromagnetic waves made up of electrical fields and magnetic fields. Microwaves penetrate the sample materials and interact with polar constituents of the compound and transform them into heat. The transformation of electromagnetic energy into heat occurs mainly via two mechanisms that are dipole rotation and ionic conduction [227]. Generally, the MAE system is operated in two modes which can be further modified. One is called pressurized MAE,which comprises a closed extraction vessel in controlled temperature and pressure. It contains a magnetron tube, an oven with extraction vessels and monitoring devices for controlling temperature and pressure. The increase in temperature and pressure generally enhances the absorption of microwave energy by the solvents, consequently, increases the extraction rate of the compounds. However, such extreme operating conditions may also lead to the losses of volatile samples. Second is called focused MAE, comprised of a focused microwave oven at atmospheric pressure. Fig. 7 shows different types of MAE systems employed for the extraction of various contaminants.

MAE uses microwave energy to heat the solvent-sample mixture. It is to be noted that the extraction solvents suitable for MAE are limited to those that can absorb the microwave energy, solvents with permanent dipole leading. Simultaneous extraction from a large number of samples, shorter extraction time, lower requirements of solvents and small sample quantity are a few important advantages of the MAE process [228]. Also, this green technology offers better protection for thermolabile components [214]. With MAE, sample digestion is required before determining the metal contents in complex matrices. Thus, to determine ECs such as nanoparticles, acid digestion is often suggested for sludge samples [7,229]. MAE has been successfully deployed to extract a wide variety of ECs from sludge matrix, for instance, hormonal steroids [228], pharmaceuticals and personal care products [230], chloro- and bromo-derivatives [231], PBDEs [232], few EDCs such as bisphenol A [4], nanoparticles and parabens [233] were extracted using MAE process. MAE method has proved to be highly efficient compared to the Soxhlet method and UAE method. A study carried out a comparative analysis to demonstrate the recovery efficiency of three extraction techniques, such as MAE, UAE and

Table 4
Methods for sample preparation, extraction, and clean-up of emerging contaminants.

No	Method	Contaminants detected	Extractants	Advantages	Disadvantages	References
1.	Mechanical shaking	PBDE congeners, antibiotics, benzothiazoles and benzophenones, bisphenols, parabens	Methanol, methanol with water (5:3, v/v), cyclohexane, acetone (1%) acetone-hexane (1:1, v/v), and acetonitrile	- simple and quick - low cost	- not very efficient - requires additional extraction methods like solid phase extraction	[37]
2.	Solid-phase extraction	Steroid hormones, alkylphenol ethoxylates, bisphenol A and phthalates, pharmaceuticals, antibiotics, personal care products, endocrine disrupting chemicals, flame retardants	- Hexane, hexane: dichloromethane (3:1, v/v), dichloromethane, methanol with water	- low volume of solvents - high extraction efficiency - effective cleanup technique - easier to automate and less manual effort	- time consuming - expensive cartridges - difficult precision - coextraction of non-target compounds can cause significant signal suppression	[236-241]
3.	Soxhlet extraction	Flame retardants, organophosphorus compounds, PBDEs congeners, PBs, phenyl phenols, triclosan	Dichloromethane, Acetone: hexane (1:1,v/v), Dichloromethane-ethyl acetate (1:1,v/v), Methanol	- repeated contact of samples with fresh portion of the extractant which facilitates the displacement of transfer equilibrium - elimination of filtration step increases the sample yield - low cost	- time consuming (12-48 h) - requires large sample size (10-30 g) - requires large volume of solvents (up to 500 mL)	[200]
4.	Ultrasound assisted extraction	Pharmaceuticals, personal care products, endocrine disrupting chemicals, flame retardants, xenobiotic compounds, PAHs, and PCBs	Methanol: water (1:1, v/v) + 0.5% FA, Acetone: acetonitrile (70:30, v/v), Methanol, Hexane: acetone (30:70, v/v), Acetonitrile: water (9:1 v/v), Acetonitrile, Hexane: dichloromethane (1:1, v/v), Water/methanol/acetone (1:2:1, v/v)	- very quick (takes 30-40 min) - consumes less amount of solvent (10-50 ml) - low-cost equipment - low temperature requirement - high extraction efficiency	- may change the sample properties - lack of uniformity in the distribution of ultrasound energy - filtration required	[189, 196, 201] [202-204], [205-207] [208, 209]
5.	Pressurized liquid extraction	Bisphenols congeners and BPA flame retardants (BFRs and chlorinated flame retardants), alkylephenols, pharmaceuticals and hormonal steroids	Methanol: acetone (1:1, v/v), water: methanol, water: isopropyl alcohol (1:4, v/v), and acetonitrile: water (1:3, v/v), Hexane: dichloromethane	- high extraction efficiency (in the range of 56–119%) - short extraction time (<30 min) - requires low amount of solvent - high level of automation can be achieved - ability to perform multiple extractions simultaneously - highly reliable and accurate	- high temperatures and pressures are required for the method to keep the solvents at liquid state - post extraction clean up method is required - could be expensive - requires multiplication of extraction steps - emulsion's difficulties that restricts complete recovery of the target compound	[218], [219], [220], [221], [222]
6.	Microwave assisted extraction	Pharmaceuticals, personal care products, endocrine disrupting chemicals, flame retardants, metal nanoparticles, quinolone antibiotics	Dichloromethane, methanol, hexane, ethanol, cyclohexane, acetonitrile, acetone: hexane (1/1), v/v), acetone: cyclohexane (70:30, v/v), acetone/petrol ether (1:1, v/v)	- high recovery rate (90-99%) - short extraction time - requires low amount of solvent - multiple samples can be extracted at the same time	- high capital cost - limited solvents - post extraction clean up method is required - limited extraction volumes	[228], [214], 302, [231], [232], [4], [233]
7.	Liquid-liquid extraction	Pharmaceuticals, personal care products, endocrine disrupting chemicals, flame retardants	Water, methanol, ethanol, water: methanol (1:1, v/v), hexane: methanol, water: hexane (1:1, v/v)	- simple and easy to use - cost effective - low operational cost	- time consuming - requires large amount of solvents - low extraction efficiency - formation of complex emulsion which are hard disintegrate - problems with handling large volume of samples - difficult to automate	[244], [200], [245, 246]
8.	Pressurized hot water extraction	Nitrogen-based pollutants, dioxins, brominated based compounds, chlorinated organic pollutants and surfactants	Water	- environmentally friendly - cost effective - low extraction time	- post extraction clean up method is required - can be applied to extract limited number of samples	[219, 247-249]
9.	Solid-phase microextraction	Pharmaceuticals, personal care products, endocrine disrupting chemicals, flame retardants	Polydimethylsiloxane-divinylbenzene and Divinylbenzene-carboxen-polydimethysiloxane	- environmentally friendly - cost effective - low extraction time - high recovery rate (up to 99%)	- limited number of commercially available stationary phases - problems during the extraction of polar analytes using a polar matrix	[250, 251, 253, 260]
10.	Liquid-phase microextraction	Pharmaceuticals, personal care products, endocrine disrupting chemicals, flame retardants, surfactants, parabens, linear alkyl sulfonates	Methanol, water, acetone, water: methanol (5:5, v/v), water: acetone (5:5, v/v)	- environmentally friendly - cost effective - low extraction time high recovery rate (up to 96%)	- low sensitivity and precision - limited number of solvents - unsuitable for samples with a complex matrix composition	[254], [255], [257], [258]

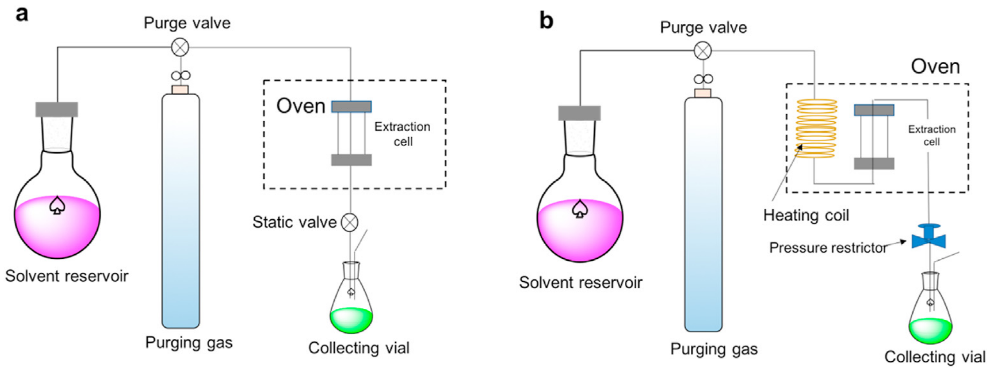

Fig. 6. Schematic diagram of (a) a static and (b) dynamic PLE system.

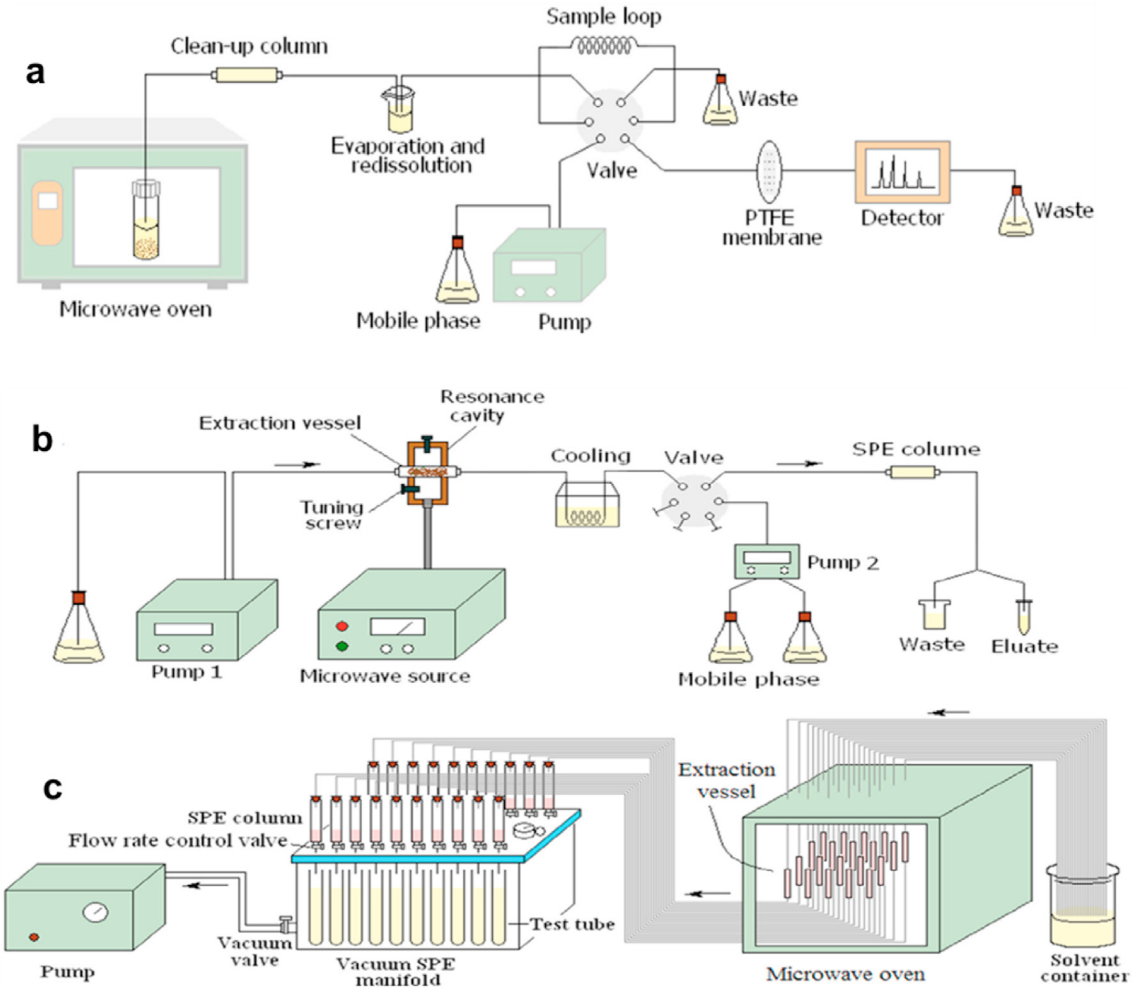

Fig. 7. Types of MAE systems. (a) On-line microwave-assisted extraction system, (b) Mono-sample dynamic microwave-assisted extraction-solid-phase extraction (DMAE-SPE) system, (c) Multi-sample DMAE. The figure is reproduced with permission from Wang et al. [227].

Soxhlet, for various EDCs, including parabens, alkylphenols, phenylphenols, bisphenol A, and triclosan [234]. Authors reported that MAE (with operating parameters-of 350 W microwave power, 3 min extraction time, and 10 ml solvent) resulted in the highest recoveries, in the range of 90–99% for the majority of the EDCs. In rival to MAE, UAE and Soxhlet required a longer extraction time, >30 min and 18 h, respectively, and achieved the recovery rates of 81–95% and 70–89% [234].

Though MAE has significant positives, such as high extraction efficiency less time consuming, it also has a few challenges, which include the requirement of a filtration step after extraction and expensive equipment [214].

Most of the solid-liquid techniques used for the extraction of ECs in sludge are not selective, and thus, a clean-up step is often needed after extraction. A clean-up step minimizes the possible interference matrix effects and also results in the pre-concentration of

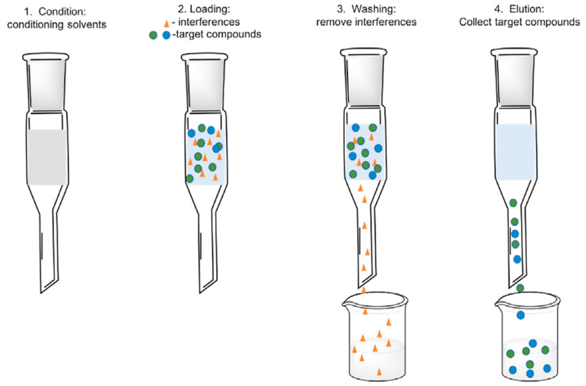

Fig. 8. Steps involved in Solid-phase extraction of emerging contaminants.

target compounds [210]. Compounds such as lipids, surfactants and polymer colloids are the most common interfering constituents in sludge. Solid-phase extraction (SPE) is one of the common methods for the pre-concentration of contaminants in the sample and has been tested to analyze parabens in different matrices. In a simple SPE method, four steps are followed that are shown in Fig. 8, which consists of conditioning of solvents, loading of samples, washing with solvents to remove the interferences and elution of target compounds with different solvents. The most commonly used sorbent for the extraction of a wide range of ECs are polymer-based sorbents like Oasis HLB (copolymer of lipophilic divinylbenzene and hydrophilic *N*-vinylpyrrolidone) silica, and bonded silica sorbents. Oasis HLB is the most versatile sorbent with a unique hydrophilic-lipophilic balance value and thus is ideal for the purification and extraction of acidic, basic and neutral ECs [235]. Oasis HLB is synthesized by manufacturer Waters [235]. The selection of a sorbent generally depends on the interaction mechanism of sorbent and target compounds, which could be hydrogen bonding, van der Waals forces, dipole-dipole interactions, and cation-anion interactions. Thus, based on the interaction mechanism between sorbents and analytes, SPE is of three classes. Reverse-phase SPE, normal-phase SPE and mixed-mode SPE have been reported for the clean-up of sludge extracts. In reverse-phase SPE, the retention mechanism involves the van der Waals forces between the non-polar functional groups on the sorbent and the non-polar groups on the target compounds. This interaction is facilitated by polar solvents; therefore, most of the studies reported in the literature that used SPE considered polar solvents for extraction purposes [236–241]. The mixed-mode SPE approach deals with sorbents that exhibit multiple interactions with the target analyte to retain them. Sorbents used in mixed-mode SPE possess ion-exchange functional groups in combination with hydrophobic functional groups. For instance, sorbents with hydrophobic alkyl chains and cation or anion-exchange sites on the same sorbent material (Mixed-mode Cation exchange, MCX or Mixed mode Anion exchange MAX, respectively). Mixed-mode sorbents have the advantage of interacting with different functional groups either on a single target or on multiple targets [242]. SPE can be performed in both online and offline modes and can avoid many problems connected to other modes of extraction, which include less-than-quantitative recoveries, disposal of large quantities of solvents and partial phase separation [243].

Liquid-liquid extraction (LLE) is another effective strategy for separating compounds with different solubility in two immiscible liquids, generally with polar solvents like water, methanol, acetic acid, and non-polar solvents like hexane and benzene. The technique is also known as solvent extraction. The extraction mechanism of a pollutant generally driven by the chemical potential in this method, relies on the net transfer of one or more target compounds from one liquid phase to another, for instance, from aqueous layer to organic layer or vice-versa. Fig. 9 shows the illustration of the LLE method. As shown in the figure, the target pollutant moves from the aqueous layer to the organic layer after the extraction. Usually, nonpolar compounds prefer the organic layer, while polar compounds are extracted into an aqueous layer. In salting-out systems where conventional LLE methods were not found to be effective, water-miscible solvents were explored to extract or concentrate the target compounds [244]. LLE is often referred to as a time-consuming technique, difficult to automate and often require a huge volume of organic solvents [200]. With an advantage for processing heat-sensitive products, LLE has gained considerable attention in the pharmaceutical industry [245].

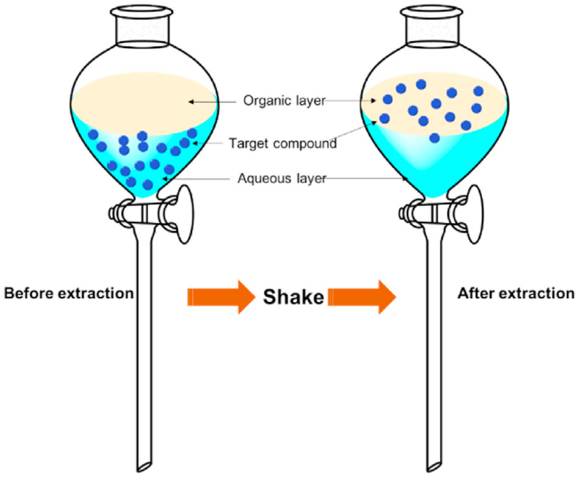

Fig. 9. LLE of an organic compound with polar and nonpolar solvents.

Recently, a study by Murrell and Dorman [246] demonstrated the application of LLE for different types ECs, including pharmaceuticals (Dimenhydrinate, Doxepin, Crotamiton, Methadone, and Ibuprofen etc.) and personal care compounds (Oxybenzone, Maltol, 2-Butanol, Homosalate, and Caffeine etc.) and compared the extraction activity with another method called stir bar sorptive extraction (SBSE). The results revealed that for 14 ECs, the LLE method was able to extract them with a higher recovery rate, of a range 19%–159% with a median value of 74%, while for SBSE, the recovery rate for the studied ECs was between 19% and 117%, with a median value of 66% [246]. However, the SBSE method was found more effective to discover new ECs. Evidently, with SBSE, 13 ECs were identified, while LLE could identify only 6 ECs. This suggests that the LLE method could be preferred to achieve a higher recovery rate for known ECs, but SBSE can potentially be applied to identify unknown ECs in sludge/biosolids samples.

Pressurized hot water extraction (PHWE) is an environmentally friendly extraction strategy that avoids the usage of expensive and harmful organic solvents and utilizes water as the extraction solvent under high temperature and pressure conditions. It follows similar principles of the PLE method [247]. The other parameters involved in the process are similar to the PLE, such as the number of cycles, pressure, temperature, and extraction time. The instrumentation set-up of a PHWE system is given in Fig. 10. Typically, it contains a solvent system (water), a pump to push the solvent, a preheating coil to heat the solvent, an extraction cell where the extraction process takes place, a collecting flask to collect the extract, and a back-pressure regulator to generate the backpressure. The polarity of water can be modified to dissolve a wide range of solutes. The temperature range for the process varies between 25 and 250 °*C* and the pressure of 10–220 bar [247]. In PHWE, the

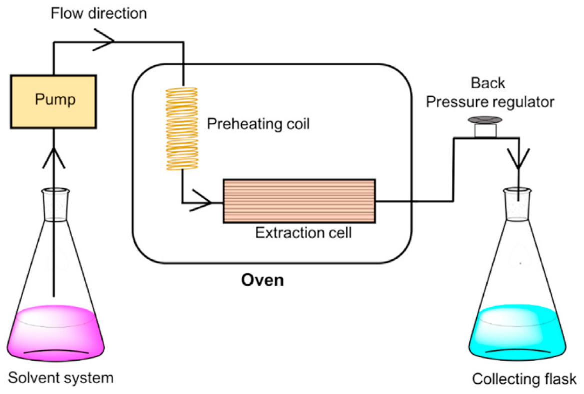

Fig. 10. A schematic diagram of the PHWE system.

density of the water remains constant to minimize the effect of pressure on water characteristics [219]. PHWE has been reported for several ECs like nitrogen-based pollutants, dioxins, brominated based compounds, chlorinated organic pollutants and surfactants extracted from sludge samples [219,247–249]. The significant advantages of PHWE are that it is environmentally friendly as it does not use toxic and hazardous organic solvents, cost-effective, low extraction time. Since this method only applies water as the solvent, certain ECs with low solubility with water cannot be extracted using this method. In other words, it could be applied to extract limited number of ECs. More pros and cons of the techniques are listed in Table 4.

Solid-phase microextraction (SPME) is a renowned, environmentally friendly and solvent-free efficient technique for extracting various types of ECs from wastewater and sludge samples [250,251]. It is also known as the single-step extraction method since it combines steps like sampling, isolation, and analysis. This method requires a thin rod made up of fused silica containing a small extracting phase. Extracting phases generally used in SPME are polydimethylsiloxane-divinylbenzene and divinylbenzene-carboxen-polydimethylsiloxane. The device utilized for SPME is tiny, which allows rapid mass transfer during the extraction process and produces relatively accurate results. SPME is generally operated in three primary modes, which are direct immersion SPME (DI-SPME), headspace SPME (HS-SPME), and membrane SPME (M-SPME). However, other modifications have also been demonstrated to improve the performance of SPME, which are thoroughly discussed somewhere else [252,253]. Fig. 11 shows the schematic diagram of SPME techniques for the extraction of ECs from wastewater samples. In DI-SPME, the silica fibre coated with an extracting phase (adsorbent) is directly immersed in the sample matrix, and the analytes are translocated directly from the sample to the extracting phase. HS-SPME is generally applied to extract high-molecular-weight molecules, volatiles and semi volatiles and complex samples. In this method, the fibre with an adsorbent is exposed in the headspace above the sample, and the analytes, mostly volatiles and semi volatiles that equilibrates between the sample and headspace, is captured by the coated silica fibre. This is the main reason that favours HS-SPME to extract pure form of analytes and also results in higher selectivity. In M-SPME, a membrane is usually applied to carry out the extraction of small-sized analytes into the extraction phase while restricting the entry of large-sized molecules. The SPME process is generally coupled with analytical techniques like GC or HPLC to identify ECs [250].

Liquid-phase microextraction (LPME) is a miniature form of LLE and follows a similar mechanism for extracting contaminants [254]. LPME process is carried out in a very small device, thus requiring a small amount of the solvent, which poses a negligible environmental risk [255]. Thus, LPME can be regarded as an eco-friendly extraction process. Similar to SPME, LPME also combines all the steps like sampling, isolation, and analysis into one extraction step. As shown in Fig. 12, LPME can be of different types like single-drop LPME (SD-LPME), drop to-drop LPME (DD-LPME), and hollow-fiber LPME (HF-LPME). In LPME, the extraction of contaminants takes place by translocation of analytes present in the aqueous layer to a drop (microliter) water-immiscible solvent. Several variables affect the extraction process, including the type of solvent, extraction time, agitation, and drop volume [254]. In SD-LPME, a micro drop of water-immiscible solvent is used so that there is a constant equilibrium of the analyte's concentration between the aqueous and the organic layer.

Further, the analyte present in an aqueous sample is extracted into the microdrop of the solvent. This microdrop can be directly analyzed for the identification of ECs in GC or MS techniques. In DD-LPME, the sample, as well as the extractant, are in microliters. Thus, this approach can be adopted where the sample size is very small. DD-LPME leads to high selectivity. In HF-LPME, the sample and the extractant solvent are not in direct contact. However, a hollow fibre is installed in the sample and vigorously shaken or vibrated. The analytes transfer passively through the organic layer (supported liquid membrane) and then into acceptor solvent present in the lumen [256]. Considering the significant advantages of LPME, it has been widely used to extract various contaminants from wastewaters and sludge samples [257]. For instance, Amin et al. [258] demonstrated the extraction of multiple parabens from municipal wastewater and sludge samples using LPME coupled with GC-MS, and varying types of solvents such as methanol (10 ml), acetone (10 ml), water: methanol (5:5, v/v), and water: acetone (5:5, v/v). The results revealed that a recovery rate of up to 95% could be achieved using this extraction method and methanol showed the best recovery results compared to the counterparts [258].

Table 4 summarizes all the extraction methods and outlines their advantages and disadvantages. Alternative techniques such as stir bar sorptive extraction (SBSE) and Matrix solid-phase dispersion have been applied more recently owing to their advantages over SPE and LLE, particularly in minimizing the use of solvents operational time and ease in handling [259].

4.3. Analytical methods for determining ECs in biosolids

Gas chromatography (GC) is a relatively inexpensive technology applied to determine a wide variety of ECs in sludge. For instance, GC has been used to determine PAHs [261,262], aliphatic hydrocarbons [263], PBDEs [264], BPA [265], flame retardants [266,267], pharmaceuticals and personal care products [268], PFAs [269], and plastics [270] in sludge samples. Flame ionization (FID), mass spectrometry (MS), electron capture (ECD), and tandem MS (MS/MS) are detectors that are commonly coupled to GC. Although thermolabile compounds and polar compounds such as alkylphenols, alkylphenol ethoxylates, hormones and bisphenol A can be separated by GC to improve the sensitivity, selectivity and peak separation and thus to improve the overall chromatographic behavior, a derivatization step is often needed [187]. The derivatization step minimizes the adsorption of the target compound onto the column and prevents thermal decomposition at the injector port [4]. However, derivatization presents many disadvantages, such as an increase in the complexity of the treatment process, total analysis time and high chances of errors. Most methods reported for flame retardants with PBDE congeners do not necessitate the derivatization step. At the same time, few compounds such as natural and synthetic hormones, pharmaceuticals and phenolic compounds require silylation before being processed in GC [271].

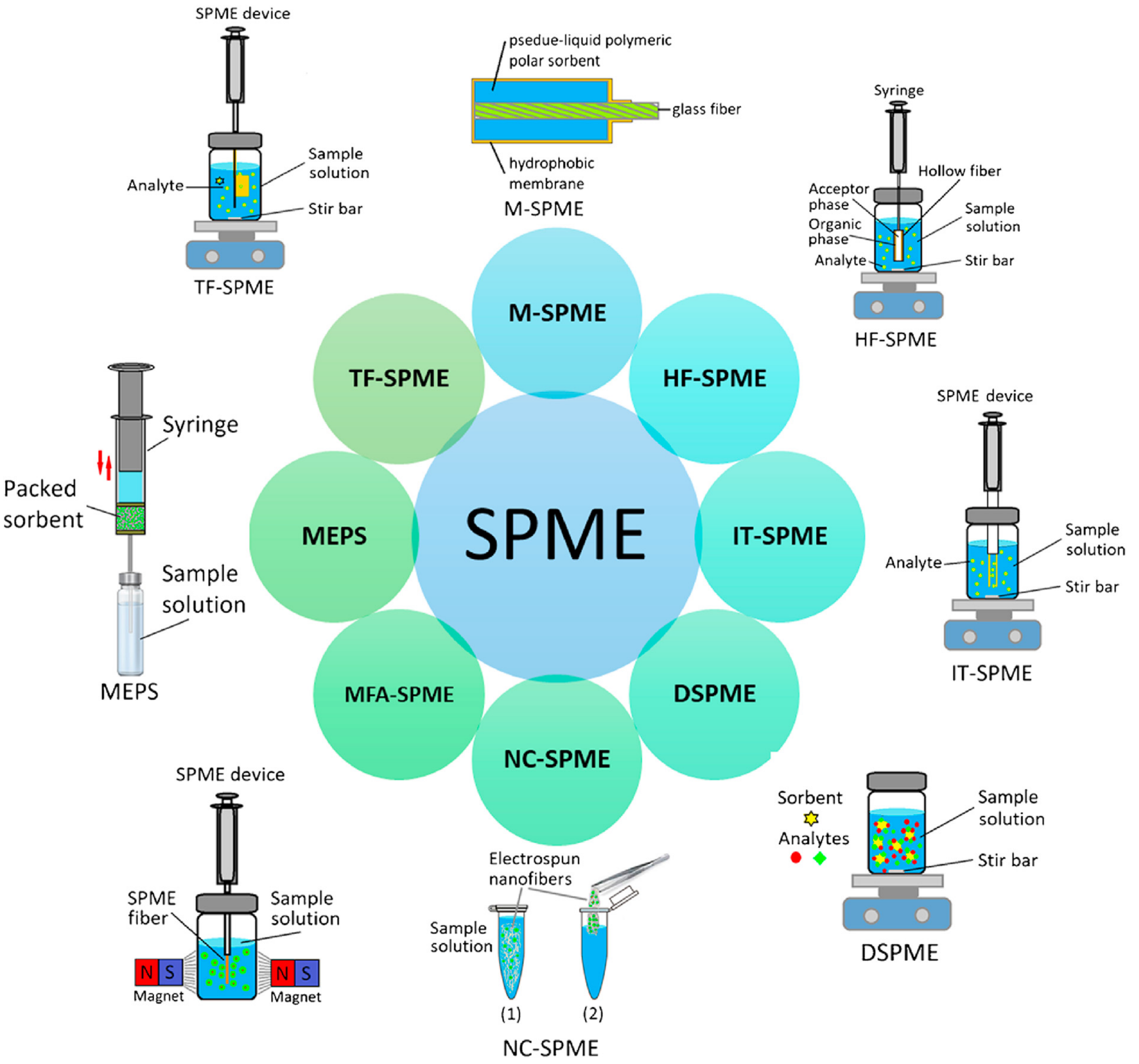

Fig. 11. Different types of SPME techniques and their schematic representation for the extraction of ECs from wastewater samples. The figure is reproduced from Seresthi et al. [253] Note: DI-SPME: direct immersion SPME; HS-SPME: headspace SPME; IT-SPME: in-tube SPME; M-SPME: membrane SPME; TF-SPME: thin film-SPME; DSPME: dispersive SPME; MA-SPME: magnetic field-assisted SPME; MEPS: microextraction by packed sorbent; HF-SPME: hollow fiber-SPME, and *N*C-SPME: nanofiber cloud SPME.

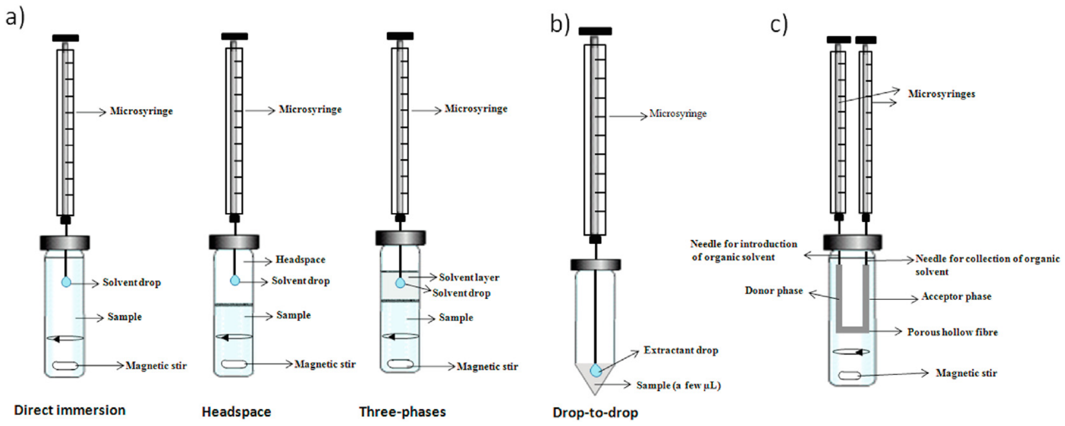

Fig. 12. Types liquid-phase microextraction (LPME) procedures. (A) Single-drop microextraction; (B) drop-to-drop microextraction; (C) hollow-fiber liquid-phase microextraction. The figure is reproduced with permission from Barroso et al. [254].

The common technique used for sludge samples is GC coupled to MS and MS/MS since the analysis of ECs require low limits of detection and high selectivity. Also, depending on the type of ionizer selected, MS detector offer great sensitivity and selectivity [272]. GC in combination with MS and having ionization modes as electron ionization (for detecting EDCs) [177,273], negative chemical ionization (for detecting PBDEs) [191,231], electron capture negative ion (for detecting flame retardants) [188] and collision induced dissociation (for detecting nitrosamines) [274] have been reported as successful techniques to determine ECs in sludge samples. Fig. 13 shows identification of 2-hydroxyatrazine, 10, 11-dihydro-10,11-dihydroxycarbamazpine, triisopropanolamine, and phenmetrazine [61].

Liquid chromatography (LC) based analysis has become a popular technique in the determination of ECs in sludge samples. LC coupled to MS, or MS/MS, is often considered an effective choice to analyze a wide range of ECs such as PPCPs, EDCs, and flame retardants in sludge samples. The LC-based analysis is highly versatile as a wide range of compounds can be analyzed with no prior derivatization step [275]. Though MS is a widely accepted option, few studies reported the use of fluorescence for the detection of ECs [276,277]. The most used ionization approach reported in the literature is electrospray ionization. Electrospray ionization allows partial ionization of the target analyte and unfragmented molecular ions [278]. However, electrospray ionization might not be appropriate for polar compounds, and atmospheric pressure chemical ionization is recommended for such compounds [279]. LC has been employed successfully to detect a wide range of ECs in sludge samples, and the categories of ECs include EDCs [280], pesticides [281], pharmaceutical residues [282], parabens [283], flame retardants [284], and microplastics [285]. High-performance liquid chromatography (HPLC), and up-gradation of classical LC, cite the theory of GC and characteristics of LC [286]. Therefore, HPLC is a high-speed, high-pressure, high-sensitive and wide-ranging sample analysis tool and is widely used to analyze ECs in various environmental matrices [287–289]. Another emerging chromatographic technology is ultra-high performance liquid chromatography (UHPLC), which works on the same principles of HPLC, which has the advantage to increase the throughput of the analysis and the capacity of chromatographic peaks. In addition, the speed, sensitivity, resolution and efficiency are several folds higher than HPLC [290].

Capillary electrophoresis (CE) is an electrophoretic analysis and separation technique with high electrostatic voltage and capillary as driving force and separation channel, respectively. CE is comparable to HPLC in the capacity to separate target compounds of different physicochemical properties, flexibility in experimental conditions and versatility. In addition, the advantages such as faster separation, lower requirements of reagents and consumables, small sample size, use of single capillary to separate multiple samples,

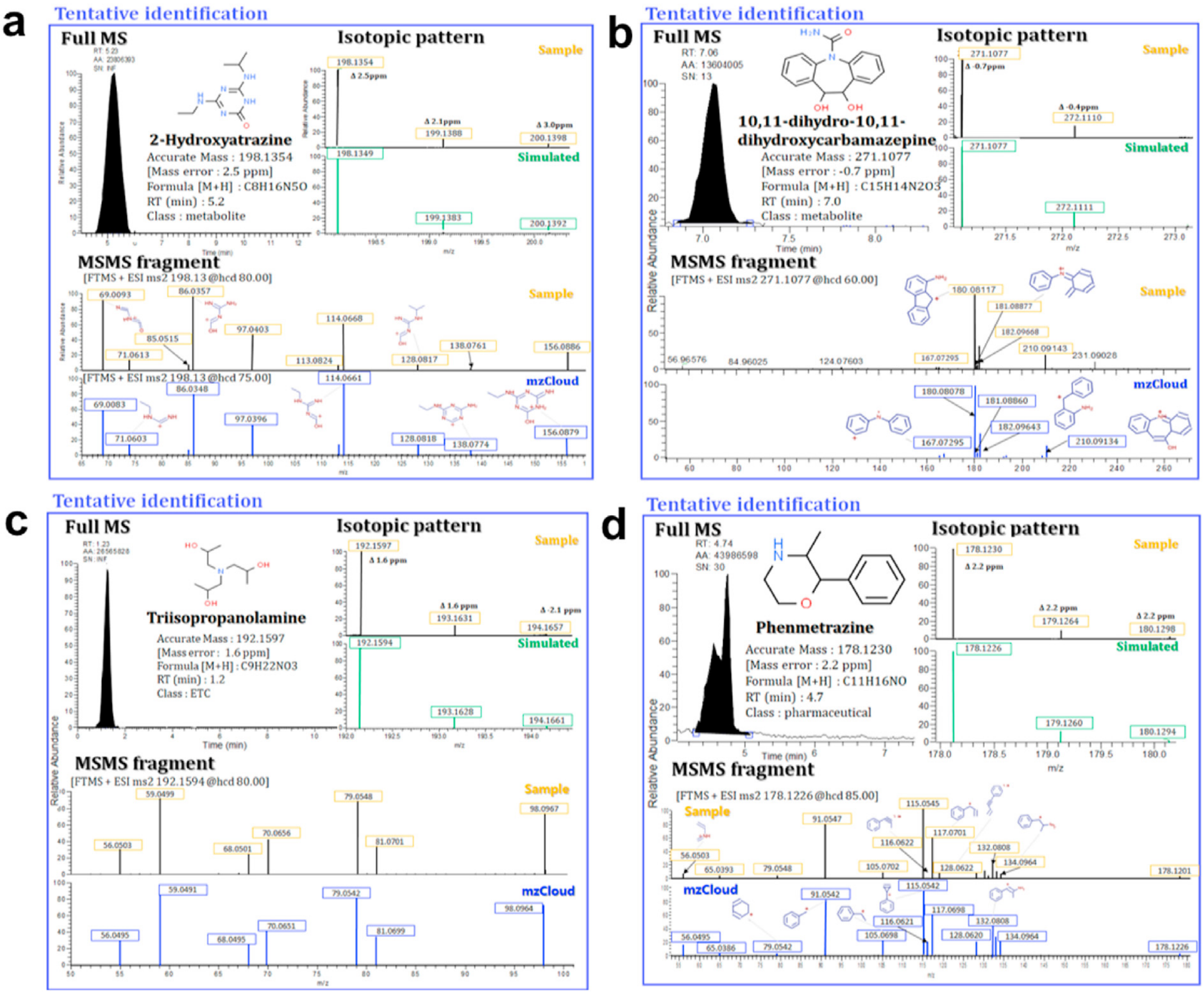

Fig. 13. Tentative identification of (a) 2-hydroxyatrazine, (b) 10, 11-dihydro-10,11-dihydroxycarbamazpine, (c) Triisopropanolamine, and (d) Phenmetrazine with high resolved accurate mass, isotopic pattern, and MS/MS fragment evaluation. The Figure is reproduced with permission from Choi et al. [61].

high separation efficiency and simple design make the CE approach better than other chromatographic techniques [291]. Capillary zone electrophoresis (CZE), a free solution, is an essential form of conventional CE methods employed to detect charged solutes. The analyte separation is decided by the background electrolyte, experimental conditions that control the electroosmotic flow and the electrophoretic mobility of the analyte. Voltage is an important parameter in the CZE method as high voltage can alter the electrolyte viscosity and cause deterioration in the sample [292]. Another commonly used technique based on CZE is micellar electrokinetic chromatography (MEKC). With the addition of one or more micelles into the CZE buffer, the compound to be measured is dispersed between the micelle phase and water phase and then migrates in the capillary tube for separation [286].

Prior to the identification and analysis of MPs, the samples are generally purified to remove the inorganic and organic matter since the impurities attached to the surface of MPs may cause significant complications during the identification. Therefore, precise methods are employed to purify MPs, such as flotation, centrifugation, ultrasonic separation, enzymatic or chemical digestion, and filtration. Usually, the separation method is selected depending on the types of contaminants present in the samples. Once the microplastic samples are contaminant-free, they can be identified and analyzed using different techniques. The most common analytical techniques employed to identify and characterize MPs include microscopic and spectroscopic analyses [103,113]. Table 2 summarizes a few studies that employed microscopic and spectroscopic analyses for the identification and quantification of MPs in sludge or biosolids samples.

Microscopic techniques offer very simple, direct and cost-effective methods to identify MPs. Therefore, microscopes such as digital and optical microscopes, scanning electron microscope (SEM) and transmission electron microscopes (TEM) have been frequently applied for the identification and quantification of microplastics obtained from sludge or biosolid samples. The stereomicroscope is often considered superior to optical microscopes since the latter shows poor resolution, while the former provides a high-resolution image with a three-dimensional view. A stereomicroscope utilizes the reflected light from the sample, whereas an optical microscope uses the transmitted light. Thus, a stereomicroscope is more beneficial to study the surface and structural characteristics of microplastics in a three-dimensional view. There are two attractive characteristics of a stereomicroscope. The first is it exhibits a more significant working distance and larger depth of field [293]. However, there are also particular challenges. For example, it is considered a qualitative approach since it cannot differentiate types of microplastics like synthetic or natural microplastics. Besides, it can also be proved a time-consuming approach. To examine the MPs more clearly from various matrices, dye compounds can be used along with microscopes. MPs are usually stained with an organic or fluorescent dye like Nile red, which interacts with the polymers through hydrophobic interactions [294].

On the other hand, SEM can be coupled with energy dispersive X-ray (EDX) spectroscopy to examine the chemical and surface properties of MPs with a nanosized range of 100–250 nm. Since SEM utilizes scattered electrons for image formation, only surface properties of MPs can be observed. To examine the internal structure of MPs, TEM can be employed since it uses transmitted electrons for image formation. TEM could be more beneficial for MP analysis compared to SEM as it exhibits higher resolution and can detect MPs of a size up to 0.5 Å [293]. Other microscopic techniques such as hyperspectral imaging and confocal laser scanning microscopy have also been reported for microplastic analysis [293].

Though microscopic techniques are useful to examine the surface properties of MPs and count the number of particles in the samples, they could not provide insightful information on the composition of MPs. In this regard, vibrational spectroscopic techniques such as FTIR and Raman spectroscopy, along with microscopic techniques (called micro-FTIR and micro-Raman spectroscopy), can be employed to examine the chemical properties of MPs. In both techniques, molecular vibrations of an MP are excited and detected, leading to unique spectral fingerprints of a chemical structure. The obtained results are confirmed by comparing with known reference spectra [295]. FTIR has been widely used to analyze MPs with a size range of 10–100 μm, while Raman spectroscopy is employed to analyze smaller MPs of up to 1 μm [103, 107. FTIR can be useful for MP analysis to differentiate polymers such as polyethylene, polypropylene, polystyrene, polyamide, polyester, polyvinyl chloride, polyurethane, polyethylene terephthalate, ethylene vinyl acetate, acrylonitrile butadiene styrene, and polylactide. Micro-FTIR shows enhanced spatial resolution and can identify infrared bands of smaller MPs. The technique is very simple and time-saving as it does not require complex sample preparation. FTIR can be operated in two modes, either reflected (ATR micro-FTIR) or transmission mode (FPA micro-FTIR) [293,296]. ATR-FTIR can be used to identify thick and non-infrared-transparent samples but cannot be used for MPs with irregular shapes and MPs of varying sizes that are proximate with each other due to refractive errors [296]. On the other hand, transmission mode could provide better quality results quickly since it can record several spectra within a single measurement. However, certain challenges related to the thickness of the sample could be raised. For instance, very thin microplastic samples may not absorb the detectable amount of infrared radiations, while thick microplastic samples could lead to total absorbance [295]. Overall, FTIR has proved to be the most valuable technique to analyze MPs from different sources [297]. However, it could not be used to examine very small particles with a size of <1 μm. In this regard, Raman spectroscopy could be highly useful to identify smaller MPs and be more accurate compared to FTIR [298,299]. A number of studies have demonstrated the application of micro-Raman spectroscopy for microplastic analysis [103,299,300]. Raman spectroscopy analyzes MPs with respect to the size, shape, and chemical properties simultaneously. Compared to FTIR where IR is used as the light source, in Raman spectroscopy, monochromatic light (laser) is used. In addition, FTIR is more useful to detect the functional groups like carbonyl groups as the IR absorption depends on the change of the permanent dipole moment of a chemical bond, while Raman spectroscopy is more helpful to detect the chemical bonds such as $C = C$ and $C - H$ as it depends on the change in the polarisability of a chemical bond. Generally, these techniques are jointly applied for microplastic analysis and usually complement each other, indicating that bands that show weaker Raman intensities could show higher IR intensities and vice-versa. In this study, MPs with a size of >500 μm were characterized using FTIR and Raman spectroscopy techniques, suggesting that the combination of both techniques is imperative to understand the thorough and reliable chemical composition of microplastics samples [295].

Spectroscopic techniques, as mentioned before, are valuable tools for the complete analysis of MPs; however, there are certain challenges associated with them. For instance, polymers like polyvinyl chloride and polyesters are difficult to identify correctly using FTIR and Raman spectroscopy, respectively. In FTIR, thick MPs may lead to total absorption, while Raman may take a longer measurement due to weak scattering intensity.

Thermal analysis methods such as thermogravimetric analysis (TGA) and pyrolysis coupled with gas chromatography (GC) and mass spectroscopy (MS) have been widely accepted to examine MPs [293]. These techniques are temperature-dependent and study the effect of temperature on mass loss, heat flow, gases evolved during the analysis. TGA and pyrolysis can be coupled with FTIR or GC-MS to detect and identify pyrolytic products or gases released during the thermal analysis. The released analytes can provide helpful information about the chemical composition of MPs. Pyrolysis-GCMS is considered an advanced technique for quantifying individual polymer in a mixture of microplastics [118]. In micro-spectroscopic techniques, mass quantification of MPs is performed by estimating the volume of each particle and its density by assuming the shape and thickness of the target MP particle; pyrolysis-GCMS requires one-step flash pyrolysis, analyzing the pyrolyzed products with coupled GCMS. Generally, the technique is ideal for the quantification of the individual particle but can also be applied to composite MP particles with varying polymers after the filtration process [119]. Identification of each polymer in mixed MP particles is easily done by chromatographic separation in combination with mass spectral analysis of the separated pyrolyzates characteristic, based on a database of Py-GC/MS. The main advantages of the technique are, it is less time consuming and requires a small amount of sample, around 1 mg or even less [301]. However, weighing precision is critical when creating calibration curves of solid standard polymers [119]. In addition, analysing a mixed MP sample is challenging since there is the possibility of reaction between pyrolyzates from different polymers [298]. This could affect the pyrolytic yields of the polymer composition and might result in systematic errors in the quantification of MPs [300].

5. Challenges and future perspectives

In future, substantial research activities should be dedicated to developing suitable analytical techniques followed by appropriate treatment technologies. There is still substantial risk associated with the reuse of wastewater treatment effluents and the use of sludge for agricultural applications. It is quite evident that several ECs that reach wastewater treatment plants cannot be removed entirely and are ultimately concentrated in the sludge or biosolids. Noticeable concentrations of various contaminants have been reported, as discussed previously in the article. Even though identifying many contaminants and transformation products formed during the wastewater treatment is one of the significant challenges. Especially to confirm the chemical composition of fragment molecules, there are no advanced techniques to identify them and the absence of extensive standard libraries makes the identification process more complex. To a greater extent, high resolution-mass spectroscopy (HRMS) has successfully identified several unknown chemicals based on accurate mass measurements [302,303]. Prior to HRMS analysis of an EC, key steps such as sample pre-treatment and purification are important to prepare a sample free of matrix interferences, which might increase the overall cost of analysis. Hence, more efficient and cost-effective methods could be developed. On the other hand, it is important to note that HRMS generates the potential molecular structures of unknown TPs, which are considered tentative until confirmed with additional identification techniques like nuclear magnetic resonance (NMR) spectroscopy. HRMS-NMR approach has been found advantageous to detect TPs at lab-scale studies as the concentration of TPs is generally high; however, it is challenging to identify TPs using HRMS-NMR in the natural environment (in wastewater of biosolids) since the concentration of TPs is deficient. Therefore, identification techniques should be combined with advanced chemical and biological assays to identify the TPs and ECs more accurately at very low concentrations in the natural environment. Moreover, very less is known about the toxic and hazardous effects of intermediate compounds or TPs or even novel ECs identified recently. Since different ECs may show a variety of modes of action in humans, animals or microorganisms, it is important to know their toxicity on animals or microorganisms and potential human health risks. Therefore, laboratory-based studies can examine their ecological toxicity and persistency or stability.

Few studies have been carried out to demonstrate the effectiveness of treatment techniques on the accumulation of contaminants and TPs in biosolids [304,305]. Hence, more studies can be conducted to investigate the effect of various treatments on the removal of pollutants and the formation of different metabolites or TPs. Besides, the effects of operational parameters of the specified technique can be further studied.

There are no uniform standardization methods for sample collection, efficient pre-treatment and characterization techniques for microplastics. For instance, MPs are generally treated with acidic and alkaline solvents such as NaOH and HNO_3 or H_2O_2 to extract from sludge or biosolid samples, which may damage MPs. Hence, more advanced, efficient and safe methods should be investigated and developed for the extraction of MPs. As discussed previously, MPs have the substantial ability to adsorb different organic pollutants and heavy metals during sewage treatment. However, very less information is available on the adsorption mechanisms of pollutants. Therefore, studies should be conducted to identify the adsorption mechanisms of different pollutants. Since various techniques can be employed for sewage treatment, their impact and other parameters should be thoroughly examined to understand their effect on the adsorption of pollutants. In addition, MPs carrying heavy loads of pollutants could be translocated to the soil since sludge/biosolids are frequently used for soil amendment. However, MPs' translocation mechanisms and the exact capacity to carry the pollutants into the soil are unclear. Thus, more studies are proposed to examine the translocation of pollutants from MPs surface to the soil, including adsorption and releasing mechanisms. For this purpose, experiments can be conducted in laboratories using a standard amount of MPs, individual pollutants (e.g., heavy metals or antibiotics) or a complex mixture of different pollutants (e.g., heavy metals + antibiotics + surfactants) and their application for soil amendment. These studies can help to understand the fate of MPs to adsorb pollutants and their import mechanism into the soil and potential transfer to the food chain. Moreover, the interaction mechanism of MPs (containing pollutants) with microorganisms in the soil needs further investigation.

6. Conclusions

This review article presents a recent update on different types of ECs in sludge or biosolid samples from WWTPs. The presence of a vast group of ECs, even at trace levels, is of continuous apprehension for the health and safety of humans as well as the environment. Anthropogenic activities are primarily responsible for the accumulation of these compounds in significant quantities. Physicochemical properties of ECs like hydrophobicity play a vital role in the adsorption of ECs on the sludge. Moreover, ECs can be converted into multiple intermediates and TPs during wastewater treatment, which could be more hazardous than the parent compounds. A number of extraction techniques have been applied to extract EC samples from sludge/biosolids. Solid-phase extraction combined with ultrasound and microwave-assisted extraction techniques have been found more advantageous than other techniques. Once extracted and cleaned up, the samples are subjected to identification and quantification analyses. Mainly chromatographic techniques, such as GC, LC and HPLC coupled with MS are commonly used for the identification of ECs, while FTIR and Raman spectroscopy coupled with microscopy provide complete physical and chemical analysis of microplastics.

Declaration of interests

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

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