



# A state-of-art-review on emerging contaminants: Environmental chemistry, health effect, and modern treatment methods

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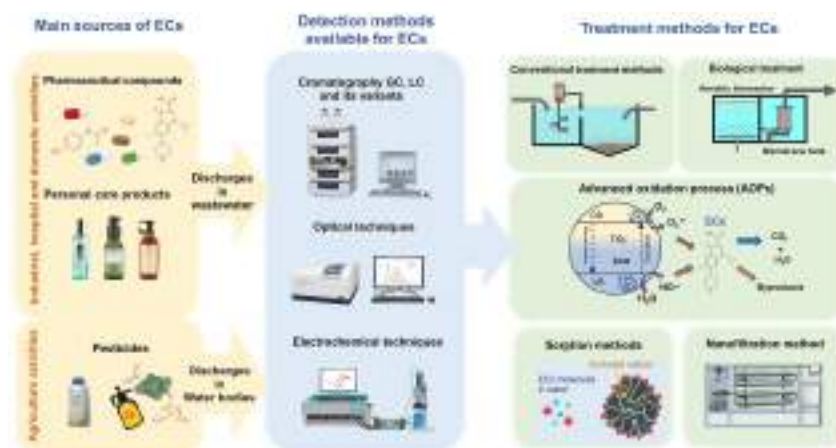
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## HIGHLIGHTS

- CECs can be toxic to all kinds of organisms if exposed for a prolonged duration
- Proper protocol needs to be followed to accurately measure low concentration of CECs
- HPLC and GC are the most commonly used instruments to detect CECs
- Biological processes are low-cost treatment processes but give low removal of CECs
- AOPs are ecofriendly technologies that can provide a high removal efficiency of CECs

## GRAPHICAL ABSTRACT



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## ABSTRACT

Pollution problems are increasingly becoming a priority issue from both scientific and technological points of view. The dispersion and frequency of pollutants in the environment are on the rise, leading to the emergence have been increasing, including of a new class of contaminants that not only impact the environment but also pose risks to people's health. Therefore, developing new methods for identifying and quantifying these pollutants classified as emerging contaminants is imperative. These methods enable regulatory actions that effectively minimize their adverse effects to take steps to regulate and reduce their impact. On the other hand, these new contaminants represent a challenge for current technologies to be adapted to control and remove emerging contaminants and involve innovative, eco-friendly, and sustainable remediation technologies. There is a vast amount of information collected in this review on emerging pollutants, comparing the identification and quantification methods, the technologies applied for their control and remediation, and the policies and regulations necessary for their operation and application. In addition, This review will deal with different aspects of emerging contaminants, their origin, nature, detection, and treatment concerning water and wastewater.

## 1. Introduction

Environmental pollution can be described as introducing hazardous substances into the environment, often termed pollutants or contaminants. Some widely known pollutants are plastics, particulate matter, oxides of Sulphur, nitrogen and carbon, volatile organic compounds, and Potentially toxic elements (PTEs). These pollutants have already exhibited disastrous effects on humankind and the environment. For instance, PTEs such as chromium, cadmium, and nickel are well-identified human carcinogens (Chen et al., 2019a). At the same time, carbon dioxide emissions lead to irreversible changes in the climate on earth (Solomon et al., 2009). A newer class of environmental pollutants has unfolded, known as the class of emerging contaminants (CECs) or contaminants of emerging concern (CECs). Briefly, CECs are anthropogenic or naturally occurring substances that are not regulated in the environment but can potentially cause adverse toxicological effects on the environment (Kumar et al., 2022). CECs can be classified into three prime categories: i) truly new contaminants such as new molecules emerging in the environment, ii) molecules that were known to exist in the environment, but their toxic effects are emerging, iii) new emerging toxicological effects are about known old contaminants (Sauvé and Desrosiers, 2014). Further, if the source or pathway to humankind of the contaminant is new, it also falls into the category of CECs (Gogoi et al., 2018). Currently, CECs consist of substances such as pharmaceutical drugs (Shah and Rather, 2021), personal care products (Anand et al., 2022), per and poly-fluoroalkyl substances (PFAS) (Chohan et al., 2021), pesticides (Morin-Crini et al., 2022a), microplastics (Dissanayake et al., 2022) and nanomaterials (Morin-Crini et al., 2022b).

CECs such as pharmaceutical drugs, PFAS, personal care products, and surfactants are highly stable organic compounds. Therefore, they persist in the environment for long periods and are difficult to remove using conventional methods (Mukhopadhyay et al., 2022; Priyadarshini, 2020). For instance, pharmaceutical drugs are not completely metabolized in our bodies, thereby entering the wastewater treatment process, wherein these molecules are not removed effectively (Most of the medicines are made of aromatic compounds, therefore, are very stable and hence challenging to degrade or remove), hence again entering the water bodies. Pharmaceutical drugs also enter lakes and rivers as industrial effluent (Patel et al., 2019). Humans get exposed to them by consuming contaminated drinking water, vegetables, and seafood. Recently, the world has witnessed a Covid-19 pandemic, which also increased the production and usage of many pharmaceutical drugs such as Remdesivir, Ivermectin, Favipiravir, and Azithromycin (Morales-Paredes et al., 2022; Deb Barma, 2021; Pandiar, 2022; Verma and Muthuswamy Pandian, 2021) Pandiar, D., et al. The increasing quantity of pharmaceutical substances and their metabolites entering the water can be dangerous. They can quickly enter human bodies through drinking water or consuming seafood and can cause health problems (Fallah et al., 2021).

Similarly, PFAS are liberated into the ecosystems via different sources like firefighting foams, packaging materials, textile industries, and the semiconductor industry (Kurwadkar et al., 2022). PFAS exhibits toxic effects on plants (inhibiting plant growth, decreasing seedlings size), animals (hormonal imbalance, altered gene expression, immune dysfunction), and humans (kidney diseases, altered metabolism, diabetes) (Dickman and Aga, 2022; Fenton et al., 2021). Therefore, a methodology must detect and remove these harmful CECs from water. Research on CECs began in the early 21st century, primarily for detecting CECs using mass spectrometry (Ferrer and Thurman, 2003). To date, thousands of research articles have been published in the literature on CECs, covering various methods for detecting and remediating CECs. Detection of CECs have been reported using techniques such as colorimetry (Lu et al., 2010), fluorimetry (Liu et al., 2015), electrochemical (Naik et al., 2020), mass spectrometry (Rodrigues et al., 2020), surface plasmon resonance (Cennamo et al., 2018), and Raman spectroscopy (Liu et al., 2016). While either removal of CECs or degrading CECs can achieve Remediation of CECs. Removal of CECs involves the use of technologies such as adsorption (dos Santos Cardoso and Vitali, 2021), membrane separation (Liu et al., 2022), and flocculation (Wang et al., 2022). In addition, the degradation techniques used are biodegradation (Bai et al., 2022), electrocatalysis (Kuang et al., 2023), and advanced oxidation process (AOP) such as photocatalysis (Muelas-Ramos et al., 2022). The remediation process's overall sustainability also involves assessing the final products formed during remediation. Often, the emphasis on the toxicity of final by-products generated or secondary pollution creation possibility is not comprehensively studied (Maryjoseph and Ketheesan, 2020; Rempel et al., 2021; Richardson and Kimura, 2017).

The growing concern towards CECs has drawn the attention of various researchers. For instance, Prajapati et al. (2023) have critically reviewed the concentrations of different CECs (such as pharmaceuticals and personal care products) in various aqueous systems. They have also reviewed the removal efficiencies of the remediation techniques used for CECs (Prajapati et al., 2023). In another review by Bolan et al. (2021), the remediation of PFAS-contaminated soil has been comprehensively analyzed, including immobilization, mobilization, and destruction remediation techniques (Bolan et al., 2021). Kumar et al. have extensively reviewed the removal of Polycyclic aromatic hydrocarbons from soil and sediments, including immobilization, mobilization, and destruction remediation techniques and various case studies. However, a comprehensive review of CECs focusing on pharmaceuticals, including the methods of detection, remediation, and economic analysis, is required (Kumar et al., 2021).

This review's objective is to critically analyze the detection methods and remediation technologies along with the pros and cons of existing methodologies, with a significant emphasis on CECs. Therefore, this review briefly describes emerging contaminants, including their sources and occurrence in the environment. Strategies adopted for the control of

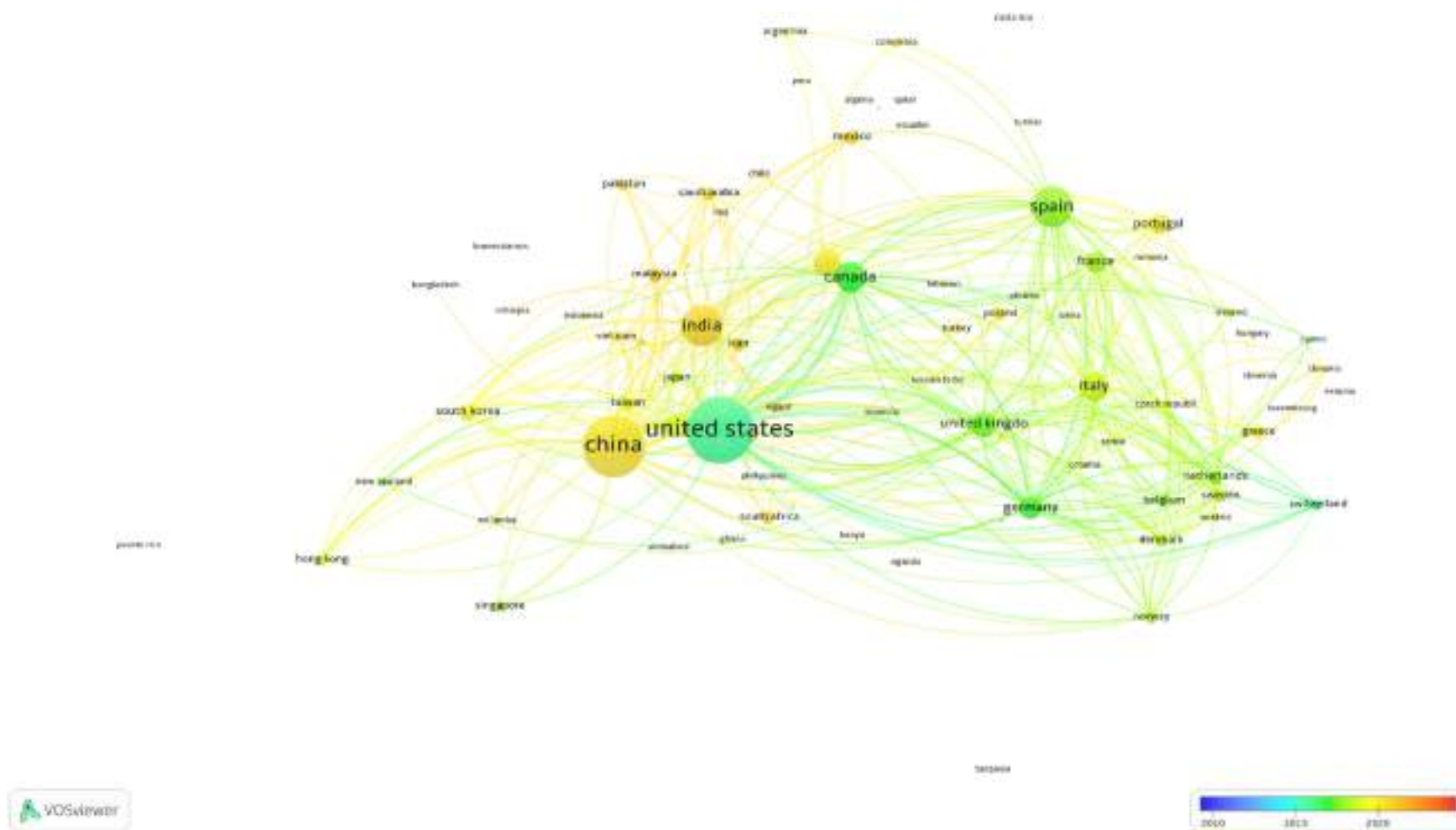


Fig. 1. Bibliometric assessment of studies related to emerging contaminants depicting the contributing countries and collaborative work.

**Table 1**

A summary of emerging contaminants with their classes found in different countries with their concentration.

Emerging contaminants	Class	Country	Concentration	Reference
Paracetamol	Analgesic	India	147.7 µg/L	Mohapatra et al. (2016)
Paracetamol	Analgesic	Portugal	683 ng/L	Paíga et al. (2019)
Paracetamol	Analgesic	Mexico	2330–14,900 ng/L	Rivera-Jaimes et al. (2018)
Ibuprofen	Analgesic	China	268 ng/L	Yan et al. (2014)
Ibuprofen	Analgesic	Spain	34,000–168,000 ng/L	Santos et al. (2009)
Ibuprofen	Analgesic	UK	7741–33,764 ng/L	Roberts and Thomas (2006)
Ciprofloxacin	Antibiotic	India	246.1 µg/L	Mohapatra et al. (2016)
Ciprofloxacin	Antibiotic	US	1100 ng/L	Yang et al. (2011)
Ciprofloxacin	Antibiotic	South Africa	501,575.5 ng/L	Faleye et al. (2019)
Erythromycin	Antibiotic	Spain	2310 ng/L	Rosal et al. (2010)
Erythromycin	Antibiotic	Canada	600 ng/L	Guerra et al. (2014)
Trimethoprim	Antibiotic	South Korea	162 µg/L	Sim et al. (2011)
Trimethoprim	Antibiotic	Switzerland	0.26 µg/L	Morasch et al. (2010)
Trimethoprim	Antibiotic	South Africa	8815.2 ng/L	Faleye et al. (2019)
Norfloxacin	Antibiotic	Spain	0.98 µg/L	Camacho-Muñoz et al. (2014)
Norfloxacin	Antibiotic	US	0.25 µg/L	Karthikeyan and Meyer (2005)
Norfloxacin	Antibiotic	India	25.3 µg/L	Mohapatra et al. (2016)
Carbamazepine	Antiepileptic	China	2499 ng/L	Zhang et al. (2018b)
Carbamazepine	Antiepileptic	Switzerland	2.5 µg/L	Morasch et al. (2010)
Carbamazepine	Antiepileptic	Greece	1.7 µg/L	Kosma et al. (2010)
Carbamazepine	Antiepileptic	Canada	1.9 µg/L	Metcalfe et al. (2003)
Atenolol	β- blocker	South Korea	11,239 ng/L	Behera et al. (2011)
Atenolol	β- blocker	Spain	2432 ng/L	Rosal et al. (2010)
Atenolol	β- blocker	US	2.642 µg/L	Mohapatra et al. (2016)
17 β -Estradiol	Hormone	Mexico	44.8 ng/L	Estrada-Arriaga et al. (2016)
Saccharin	Artificial sweeteners	Switzerland	18 µg/L	Buerge et al. (2009)
Saccharin	Artificial sweeteners	Greece	46 µg/L	Kokotou and Thomaidis (2013)
Saccharin	Artificial sweeteners	India	389 µg/L	Subedi et al. (2015)
Sucralose	Artificial sweeteners	Germany	2 µg L <sup>-1</sup>	Scheurer et al. (2009)
Acesulfame	Artificial sweeteners	Vietnam	30 µg L <sup>-1</sup>	Nguyen et al. (2018)
Acesulfame	Artificial sweeteners	Spain	25,092 ng/L	Ferreiro et al. (2020)
Acesulfame	Artificial sweeteners	US	92 ng g <sup>-1</sup>	Subedi and Kannan (2014)
Iohexol	X-Ray Contrast Media	Switzerland	35 µg/L	Morasch et al. (2010)
Iopromide	X-Ray Contrast Media	South Korea	11,133 ng/L	Ryu et al. (2014)
Iopromide	X-Ray Contrast Media	Germany	60 µg/L	Kormos et al. (2011)
Iopromide	X-Ray Contrast Media	Portugal	164 µg/L	Patel et al. (2019)
Iopamidol	X-Ray Contrast Media	Singapore	17,809–45,611 ng/L	Tran and Gin (2017)
Benzophenone-3	UV filters	China	97–722 ng/L	Li et al. (2007)
Benzophenone-3	UV filters	Germany	518 ng/L	Wick et al. (2010)
Benzophenone-3	UV filters	UK	3,975,000 ng/L	Kasprzyk-Hordern et al. (2009)
Octocrylene	UV filters	China	34–153 ng/L	Li et al. (2007)
Octocrylene	UV filters	Switzerland	12,000	Balmer et al. (2005)
Caffeine	Stimulants	China	39,665.6 ng/L	Zhang et al. (2018b)
Caffeine	Stimulants	South Korea	262 µg/L	Sim et al. (2011)
Amphetamine	Stimulants	China	603.4 ng/L	Du et al. (2015)
Amphetamine	Stimulants	US	550 ng/L	Chiaia et al. (2008)
Bisphenol-A	Plasticizer	Singapore	5325–6969 ng/L	Tran and Gin (2017)
Bisphenol-A	Plasticizer	UK	1163 ng/L	Kasprzyk-Hordern et al. (2009)
Bisphenol-A	Plasticizer	US	2469 ng/L	Mohapatra et al. (2016)
Bisphenol-A	Plasticizer	Switzerland	0.87 µg/L	Morasch et al. (2010)
Malathion	Pesticide	Spain	848 ng/L	Masiá et al. (2013)
Mecoprop	Pesticide	Germany	252 ng/L	Wick et al. (2010)
Mecoprop	Pesticide	Spain	391 ng/L	Köck-Schulmeyer et al. (2013)
Diuron	Pesticide	Germany	68 ng/L	Wick et al. (2010)
Diuron	Pesticide	Spain	2526.1 ng/L	Masiá et al. (2013)

CECs, including methodologies for detection and remediation of CECs, advantages, and disadvantages of the methods used, and parameters affecting the economics of techniques adopted, have been discussed. Further, the future scope and recommendations have also been represented in this review. To carry out the assessment, data were retrieved from the online databases of Scopus. Articles under the title, keywords, or abstract containing the words ‘emerging contaminants’, OR ‘treatment of emerging contaminants’, OR ‘detection of emerging contaminants’ were considered for this study. Subsequently, a meticulous manual screening process was conducted to discern and eliminate documents that failed to meet our study’s predetermined criteria. The search results were successfully exported in CSV format, encompassing essential components such as citation information, bibliographic details, abstract, keywords, and more. This comprehensive dataset will be utilized for meticulous bibliometric analysis. The Scopus database was

subsequently transferred to the VOS viewer software developed by Leiden University in the Netherlands to analyze and visualize the scientific landscape. The co-authorship visualization map has been provided in Fig. 1. The circles represent the publication number, and the curved lines indicate the nations’ collaborative work. It was observed that maximum research on emerging contaminants was carried out in the United States, China, India, and Canada, as depicted by their large circles. Also, significant collaborative work was observed between these countries. Also, European countries, such as Italy, the United Kingdom, Spain, Germany, Portugal, and others, have an interwoven network and a significant contribution to the publications on emerging contaminants. It was also observed that while the United States, Canada, and other European countries did a chunk of their research earlier in the 21st century, China and India have come into the picture only recently.



**Table 2**

Determination of CECs in different matrixes.

Emerging pollutant	Type of pollutant	Matrix	Extraction	Levels found	Technique	Reference
Organophosphorus esters (OPEs) and phthalic acid esters (PAEs)	Flame retardants and plasticizers	Microplastics (PP, PE, PS)	Soxhlet dichloromethane (DCM)	Σ9 PAEs: 0–80.4 ng g <sup>-1</sup> Σ4 OPEs: 0–84,595.9 ng g <sup>-1</sup>	GC–MS/MS	Zhang et al. (2018a)
Sulfonamides, β-lactams, macrolides, and aminoglycosides	Antibiotics	Raw hospital wastewater, wastewater treatment plant (WWTP), and surface water	SPE Bond Elute Plexa cartridges	Sulfamethoxazole: 20.6, 7.8, and 6.8 μg L <sup>-1</sup> sulfamethazine, sulfadiazine, and sulfanilamide: 0.4–15.7 μg L <sup>-1</sup> trimethoprim: 0.4–6.6 μg L <sup>-1</sup> up to 500–600 ng g <sup>-1</sup>	LC-MS/MS	Ngigi et al. (2019)
Estrone; ciprofloxacin and azithromycin	Antibiotics and hormone	Sludge	QuEChERS		HPLC–MS/MS	Kim et al. (2019b)
2–OH-benzothiazole, perfluorooctanoic acid,	Pharmaceuticals, industrial chemicals, and plant protection products	Leachate	SPE layered ‘mixed bed’ cartridges	Raw landfill leachates: up to 7.8 mg/L treated leachates: up to 740.2 μg L <sup>-1</sup>	UHPLC coupled with a Q-TOF mass spectrometer	Nika et al. (2020)
Citalopram, venlafaxine, fluoxetine, sertraline, amitriptyline, and caffeine	Antidepressants and caffeine	Sludge and river sediments	MAE	CIT, VEN, FLU, and AMI: 50.0–200.0 ng g <sup>-1</sup> SER: 15.0–100.0 ng g <sup>-1</sup> CAF: 40.0–150.0 ng g <sup>-1</sup>	HPLC-PDA	Junior et al. (2020)
Methylparaben and butylparaben	Personal care products	Soil	MAE	0.5–80 ng g <sup>-1</sup>	GC–MS	Llompart et al. (2019)
BPA	Phenolic derivative (plastics industry)	Sludge	MAE and SPE	100 ng g <sup>-1</sup>	GC–MS	Llompart et al. (2019)
Methylparaben, propylparaben and 4-hydroxybenzoic acid	Persistent organic pollutants (POPs), perfluoroalkyl substances (PFASs), parabens and antibiotics	Baby food	QuEChERS for POPs SPE for PFASs and antibiotics	POPs, PFASs, or antibiotics were not detected methylparaben: 4.14 ng g <sup>-1</sup> propylparaben: 1.70 ng g <sup>-1</sup> 4-hydroxybenzoic acid: 176.7 ng g <sup>-1</sup>	GC-MS/MS for POPs LC-HRMS for PFASs, antibiotics, and parabens	Nobile et al. (2020)

## 2. Occurrence of emerging contaminants in the aqueous environment and their ecological impacts

### 2.1. Occurrence of emerging contaminants

CECs are chemical compounds with no regulatory standard but can negatively impact the environment if left unmonitored. They have been present in aquatic ecosystems for a long time, and detection has only been possible due to the development of sophisticated instruments like liquid chromatography (LC), gas chromatography (GC), liquid chromatography coupled with mass spectrometry (LC-MS), and GC-MS. CECs are of various classes, including active pharmaceutical compounds (PhACs), personal care products (PCPs), disinfection by-products (DBPs), pesticides, perfluoroalkyl, and poly-fluoroalkyl Substances (PFAS). PhACs are primarily found in aqueous ecosystems due to consuming and misusing medicines that are not entirely metabolized inside the body and are eliminated as stool and urine. Malpractices, such as expelling expired medications without measures, also lead to PhACs in the aquatic environment. PPCPs, such as cosmetics, artificial sweeteners, UV filters, surfactants, detergents, and others, are primarily used in domestic households and industries producing these products, laundries, and offices. Disinfection products and pesticides, such as insecticides and herbicides, can disrupt the ecosystem when washed away and find their way into the aqueous environment. On the other hand, PFAS are complex manufactured chemicals used in everyday products and can find their way into domestic wastewater upon daily usage.

PhAC compounds have been present in the aqueous environment since the advent of drugs and medicines, with the worldwide revenue from pharmaceutical products increasing from 390 billion US\$ in 2001 to 1.25 trillion US\$ in 2019 (Majumder et al., 2019; Mikulic, 2020). The unmetabolized part of these compounds is often excreted and exists in the aqueous environment. The unregulated disposal of pharmaceuticals and effluents from industrial plants contributes to the significant occurrence of PhACs in different aqueous environments. PhACs are hydrophilic and mobile in an aqueous environment, making them difficult to remove by conventional wastewater or water treatment units

(Khan et al., 2020a; Majumder et al., 2021; Majumder and Gupta, 2020). Sucralose, acesulfame, saccharin, and other PPCPs are “low-calorie sweeteners” commonly found in aqueous environments as sugar substitutes in foodstuffs, animal products, and personal care products. They can accumulate in the aquatic ecosystem and the human or animal body because they are readily soluble in lipids or fats. Organophosphate (OP) flame retardants and plasticizers are used in consumer products such as furniture, glues, paint additives, epoxy resins, polyacrylates, lubricants, and more (García-López et al., 2010; Kim et al., 2017; Liang and Liu, 2016; Mirzaee et al., 2018). The demand for pesticides and similar compounds increased due to their low cost and broad efficacy against pests, resulting in increased production. Global pesticide consumption in 2015 totaled 2,752,758.56 t of active ingredients, ranking Asia first among consumers. Pesticide use is more prevalent in Europe, America, and Asia, with 41.6%, 28.4%, and 22.6% worldwide consumption in 2015, respectively (Debnath et al., 2019). PFASs reach the aquatic ecosystem by regularly manufacturing products and waste, such as electrical and electronic products, non-stick cookware, fire extinguishing foams, paints, and emulsions. Most PFASs are recalcitrant, with the carbon-fluoride bond in PFAS making them among the CECs in the environment with the highest resistance (Akhbarizadeh et al., 2020; Appleman et al., 2014; Lenka et al., 2021; Phong Vo et al., 2020). Research suggests that PFAS do not degrade naturally in water, and their half-lives could be anywhere from 40 to 90 years (Kucharczyk et al., 2017).

CECs are found in aquatic ecosystems, ranging from ng/L to μg/L, and are highly mobile and hydrophilic in aqueous phases. Traditional treatment technologies cannot remove these CECs due to their polar nature and toxicity. They also hinder microbial growth and can be introduced into disinfection steps. Negative removal occurs in WWTP effluent, where the compound concentration is higher than the influent. This happens when CECs remain trapped in sludge and do not undergo degradation in the treatment process. In conventional WWTPs, CECs may only undergo partial degradation, leading to an increase in the concentration of CECs. CECs are also present in surface water and groundwater, but their concentration in rivers, lakes, and groundwater

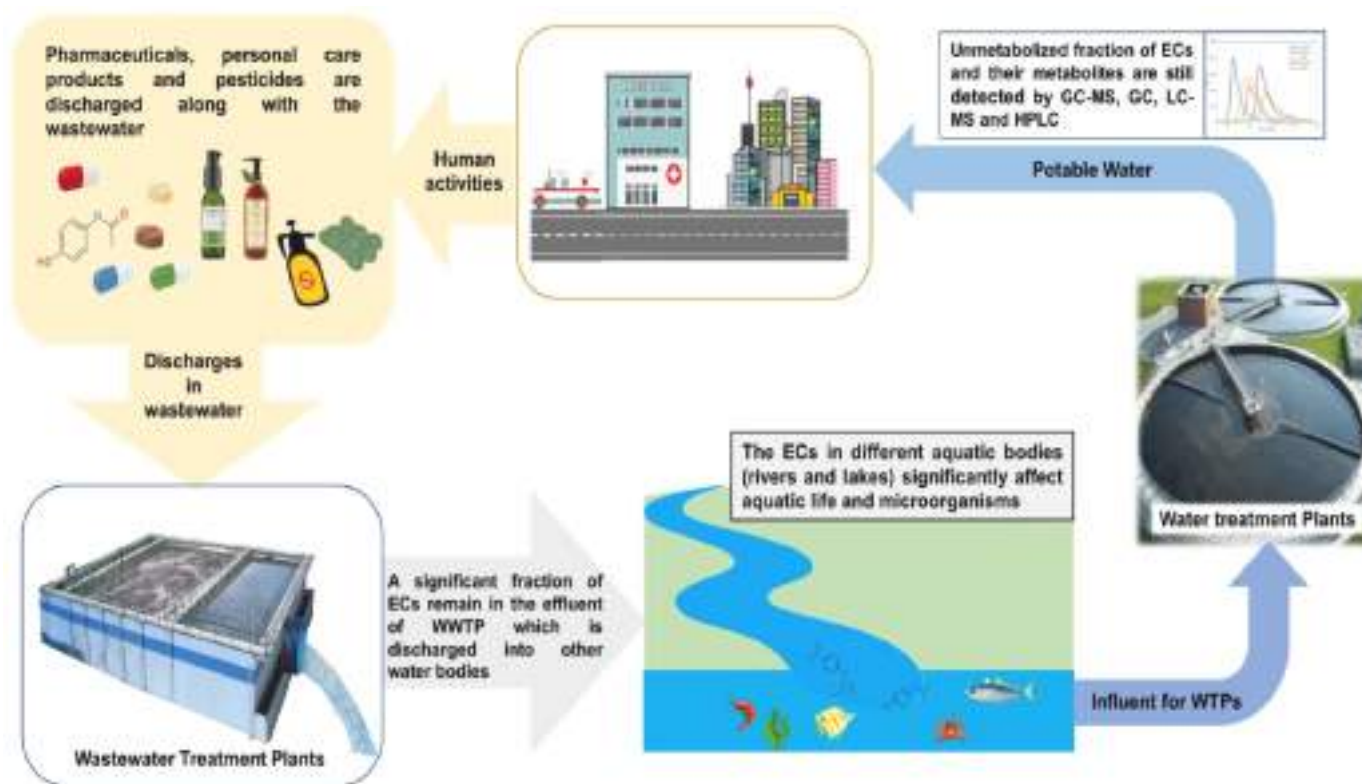


Fig. 2. CECs sources as well as pathways of existence (Khan et al., 2020a).

is below alarming levels. Negligence in removing CECs from wastewater can also raise their concentration in drinking water sources, potentially causing significant adverse impacts on life forms relying on these sources for survival. The concentration of emerging contaminants in different aqueous environments across the globe has been provided in Table 1.

## 2.2. Ecological impacts of emerging contaminants

PhACs, Surfactants, DBPs, PFAS, and pesticides are a few emerging contaminants that are of growing concern because of their potential ecological effects on aquatic ecosystems (see Table 2). These contaminants may come from different processes used in industry, agricultural operations, or consumer goods. Protecting the well-being of marine environments and living organisms requires understanding their effects. PhACs are highly toxic to aquatic life forms like fish, invertebrates, and algae, among other ecological effects. These pollutants impact populations at the population level by altering fish behavior and decreasing reproductive success. PhACs can also interfere with different species' normal reproductive and developmental processes as endocrine disruptors. Aquatic organisms are more susceptible to the effects of these substances as they consume contaminated prey, increasing the possibility of bioaccumulation and biomagnification in the food chain. PhACs can also change the microbial populations in aquatic environments, affecting crucial ecosystem functions like nutrient cycling and water quality control. PhAC exposure can cause developmental abnormalities and lower survival rates during critical developmental stages, affecting population dynamics and species abundance in affected ecosystems (Majumder et al., 2019). Surfactants entering aquatic ecosystems via wastewater discharge or other channels may have various ecological effects. One substantial effect is their toxicity to marine life, mainly fish and amphibians. Surfactants cause cell membranes to lose integrity, affecting an organism's ability to breathe and reproduce. Additionally, their presence can change species composition, abundance, and

distribution, which may lessen biodiversity overall. This is because their presence affects the behavior and physiology of aquatic organisms. Additionally, some surfactants can cause foaming in water bodies, which lowers oxygen levels and prevents light from penetrating, both detrimental to the growth of aquatic plants and other marine life (Parida et al., 2021; Rout et al., 2021). Disinfection byproducts (DBPs), were formed during the water treatment when disinfectants like chlorine react with organic matter, can also have various ecological effects. Trihalomethanes and haloacetic acids are two DBPs that are potentially toxic to aquatic life, especially delicate species like fish and amphibians. DBPs may cause changes in the distribution and abundance of species within marine ecosystems by impacting variables like turbidity and dissolved oxygen levels in the water. In aquatic ecosystems, prolonged exposure to high DBP concentrations can cause changes in community structure and overall ecosystem function (Du et al., 2017; Feng et al., 2021; Mukhopadhyay et al., 2022). Another ecological issue is PFAS (Per- and Polyfluoroalkyl Substances), which are well known for remaining in the environment. There are higher concentrations of these synthetic chemicals in higher trophic levels of the food chain due to their high propensity to accumulate in the tissues of organisms. As a result, exposure to PFAS has been linked to harmful health effects in wildlife, such as immune system suppression and developmental problems. Additionally, PFAS can contaminate soil and water, harming habitats and putting species that depend on those habitats at risk (Phong Vo et al., 2020; Sunderland et al., 2019).

Pesticides, frequently used in agriculture to control pests, can also have unintended environmental effects. These substances can harm beneficial insects, birds, mammals, and non-target species, upsetting the natural predator-prey balance and jeopardizing ecosystem stability. Some pesticides can potentially biomagnify as they move up the food chain, resulting in higher concentrations in top predators, which could affect these species' ability to reproduce and develop normally. Additionally, pesticides can contaminate water sources and leach into the soil, endangering aquatic life and possibly harming human health

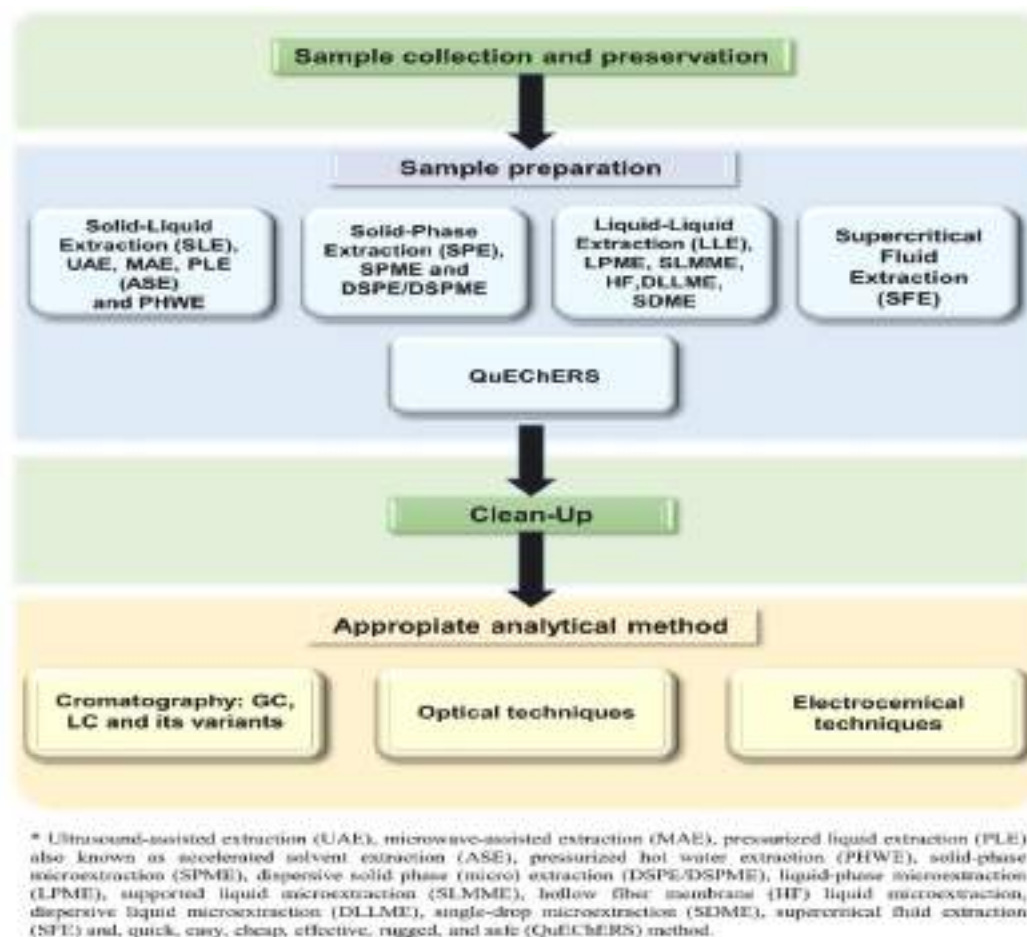


Fig. 3. Sampling strategy and analysis of emerging contaminants (Khan et al., 2020b).

through ingesting food and water. Pesticides can also affect non-aquatic and non-aquatic ecosystems by contaminating water sources (Debnath et al., 2019; Dutta Gupta et al., 2018; Sharma and Singhvi, 2017).

Emerging contaminants can infiltrate the human body via diverse routes, encompassing the ingestion of water or food that has been tainted, direct exposure to polluted aquatic environments, or the consumption of water that has been compromised. The potential health impacts are contingent upon the nature of the pollutant and the extent of one's exposure. These can encompass disturbances in the endocrine system, impairments in reproductive functions, acute and chronic toxicity manifestations, and elevated susceptibility to select cancers and diseases. The Drinking Water Equivalent Level (DWEL) is a widely recognized metric for assessing potential health risks associated with exposure to contaminants in drinking water. The term "acceptable daily intake" refers to the concentration level of a contaminant that an individual can potentially encounter throughout their lifespan without manifesting any adverse health impacts. To safeguard the well-being of the general populace, regulatory bodies employ Drinking Water Equivalent Levels (DWELs) to set thresholds for the highest permissible levels of pollutants present in potable water (Majumder et al., 2019; Parida et al., 2021).

### 2.3. Sources as well as pathways of existence

CECs are generated. The presence of microorganisms in the aqueous sample makes the PhACs or institutions, such as hospitals, offices, malls, etc. The pathway of the CECs into the aquatic ecosystem is represented in Fig. 2. As mentioned earlier, the CECs and their metabolites are discharged along with the wastewater stream of the sources. At the WWTP,

the CECs may or may not undergo various transformations and are removed along with the effluent of the WWTPs and find their way into surface water, such as rivers and lakes. Agricultural run-off directly contributes to the presence of CECs in water bodies. Even after the water treatment process persists, the drinking water continues; if there is natural organic matter in the water, DBPs are formed (see Fig. 3).

### 2.4. Conversion from one form to another during transportation in nature

One of the vital steps in detecting and quantifying organic compounds, such as PhACs, is appropriately handling the samples to be analyzed after collection. Often, this part of the research is not given sufficient priority, which leads to inaccurate measurement of the concentration of target compounds. Poor transportation and storage techniques may lead to the misinterpretation of data, thereby compromising the work's authenticity (Omar et al., 2016). Due to the physicochemical properties of PhACs, such as solubility in water, polarity, mobility, etc., they can be subjected to depletion processes in the sample containers (Mompelat et al., 2013). Although PhACs are known to be very persistent, various studies have indicated a decrease in the concentration of PhACs in the aqueous environment (Laws et al., 2011; Mompelat et al., 2013; Radke et al., 2010; Tamtam et al., 2008). As a result, this attenuation phenomenon may occur while transporting and storing PhAC-containing samples (Mompelat et al., 2013). The primary factors affecting the samples include adsorption, photo-degradation, bio-degradation, hydrolysis, chemical abiotic transformations, etc. (Mompelat et al., 2013).

The various aquatic ecosystems, such as wastewater, hospital effluent, rivers, lakes, etc., contain organic matter in suspended or



colloidal form (Białk-Bielińska et al., 2016; Majumder et al., 2019; Mompelat et al., 2013). PhACs with a high octanol/water partition coefficient (log K<sub>ow</sub>) tend to be hydrophobic and get adsorbed onto the organic matter in the aqueous environment (Majumder et al., 2019). Apart from the log K<sub>ow</sub> values of PhACs, physicochemical properties of the container material and organic matter, adsorption also depends upon the structure and concentration of PhACs, composition, temperature, pH of the water matrix, contact time, etc. (Lorphensri et al., 2007; Omar et al., 2016; Mompelat et al., 2009, 2013). They reported that 10 out of 30 PhACs in a Spanish river were found to be adsorbed onto the suspended solids (Mompelat et al., 2013). Similarly, (Aminot et al., 2018) found that 25 PhACs among 53 PhACs could be quantified in suspended solids (Aminot et al., 2018; Boulard et al., 2020) reported that positively charged PhACs were more likely to get adsorbed onto the surface of suspended particulate matter (Boulard et al., 2020). The presence of suspended solids or organic matter in the samples can interfere with the actual concentration of the PhACs in the aqueous medium because of their adsorptive properties. Alternatively, the desorption of PhACs from the organic matter in the water sample in the sampling container may lead to an excess of the original concentrations. Furthermore, these PhACs can also get adsorbed onto the surface of the sample container (Mompelat et al., 2013; Omar et al., 2016). Various PhACs form complexes with different cations present in water (Park et al., 2002). These complexes favor the adsorption of PhACs onto the surface of the glassware during sampling and storage (Mompelat et al., 2013). The phenomenon of adsorption and desorption becomes crucial during the analysis of PhAC concentration in the range of ng/L to pg/L.

## 2.5. Natural degradation of emerging contaminants in the environment

The presence of microorganisms in the aqueous sample makes the PhACs susceptible to biodegradation. Recent studies have shown that estrogenic PhACs can undergo degradation during storage and microbial activity, which is the primary reason behind the degradation of these compounds during storage (Baronti et al., 2000; Mompelat et al., 2013; Vanderford et al., 2011). Exposure to visible light irradiation may lead to the transformation of the PhACs, leading to the depletion of the parent compound before the analysis. Photo-degradation of PhACs depends on the wavelength of the light, exposure intensity, duration, and the nature and content of organic matter. The organic matter (humic acid, nitrates, etc.) present may be excited upon exposure to the ambient light, leading to the formation of reactive radicals, which could react with the PhACs to degrade them (Mompelat et al., 2009, 2013; Omar et al., 2016). Furthermore, hydrolysis leads to declining concentrations of PhACs, and this phenomenon is dependent on the stability of the PhACs in an aqueous medium (Jiang et al., 2010).

## 3. Overview of the detection methods available around the globe for CECs

### 3.1. Collection and preservation methodology adopted nowadays

Sample collection and preservation is a significant step in the identification-quantification of emerging contaminants. The most appropriate collection system is determined according to the kind of matrix to be analyzed (wastewater, surface water, stormwater, leachate, or sludge).

#### 3.1.1. Wastewater

According to scientific literature, samples are collected in both influent and effluent in triplicate under dry weather conditions, i.e., within a period without rain for 24 h and 2 mm during the 48 h prior. Samples could be placed in amber glass or high-density polyethylene bottles and kept in dark conditions at 4 °C until analyzed (Gago-Ferrero et al., 2020).

#### 3.1.2. Surface water

Sampling should be conducted throughout the water body, with sampling points from downstream to upstream defined and distributed. At each sampling point, it is recommended that samples be taken in triplicate from near the left, right, and midstream banks. Water samples can be collected between 20 and 50 cm depth (below the surface) using portable water samplers. Once the sample is taken, it can be stored in polypropylene bottles, previously cleaned with methanol and ultrapure water type Milli-Q. Once packaged, it is recommended that the samples be transported refrigerated and kept at 4 °C until they can be analyzed.

#### 3.1.3. Leachate

Samples of leachate in landfills are taken in the wells. It is important to take samples from a representative number of wells. To extract the leachate, peristaltic pumps can be used, and once the leachate is obtained, it can be stored in polyethylene (PE) or amber glass bottles; samples must be kept on ice or in a fridge before and during transport to a laboratory (Propp et al., 2021).

#### 3.1.4. Sludge

All types of sludge are susceptible to analysis (primary, secondary, digested, and compost). However, it is desirable to sample pre-stabilized sludge for final discharge. A sufficient amount of samples should be collected. It has been reported to sample up to 2 L of sludge, which can be left to air dry, then sieved and packaged, and kept refrigerated (Singh et al., 2020); another option is to take the sample and pack immediately in containers and keep refrigerated during transport to the laboratory ( $\pm 4$  °C) and freeze the samples at  $-20$  °C for seven days until the time of analysis (Pérez-Lemus et al., 2019).

## 3.2. Sample preparation for common CECs

In a large proportion of samples arriving at the laboratory that are not in a suitable form to be analyzed immediately, it is necessary to perform a preparation that may include pH adjustments, filtration, extraction processes, cleaning, and preconcentration, according to the kind and origin of the sample. Pretreatment is necessary to ensure the analyte is at the essential concentration and in a suitable matrix.

### 3.2.1. Extraction

**3.2.1.1. Solid-liquid extraction (SLE).** Extraction plays a pivotal role in chemical analyses, as it involves isolating an analyte from a solid sample matrix and transferring it into a liquid phase for quantification and identification. While the Soxhlet extraction technique stands as a widely employed method for Solid-Liquid Extraction (SLE), it does present certain drawbacks, notably the co-extraction of oils, waxes, aromatic compounds, and pigments. Ultrasound-assisted extraction (UAE) presents an alternative approach, harnessing the power of ultrasound to generate bubbles that subsequently implode during cavitation. In microwave-assisted extraction (MAE), a contemporary method, microwave energy is utilized to elevate the temperature of the matrix-solvent mixture, facilitating the extraction of target compounds. Pressurized liquid extraction (PLE), akin to accelerated solvent extraction (ASE), involves high-pressure and high-temperature solvents, resulting in shorter extraction times. Nevertheless, it necessitates a subsequent clean-up process. Pressurized hot water extraction (PHWE), characterized by its eco-friendly nature, finds frequent application in the food industry and botanical samples, although it is less commonly employed for emerging contaminants.

**3.2.1.2. Solid-phase extraction (SPE).** Solid-phase extraction is a method that allows the concentration or separation of an analyte from a complex matrix using a solid stationary phase (Ahmadi et al., 2015; Katsumata et al., 2008). This method avoids problems with liquid-liquid



extraction and enhances quantitative recovery performance. It is fast and easy to perform, with most extractions taking about 30 min. Another option is solid-phase microextraction (SPME), which separates analytes from the matrix using a fused silica fiber coated with an adsorbent. The next stage involves desorption using temperature or an organic solvent. The extraction is complete when the analyte concentration reaches an equilibrium distribution between the model and the fiber. Other techniques include dispersive solid phase (DSPE/DSPME), which combines extraction, isolation, and clean-up in the sample treatment. The process uses solid sorbents directly in the sample solution, and after dispersion, the sorbent is separated by centrifugation or filtration. Analytes or adsorbed interferences can be eluted or removed with organic solvents. Ultrasonic-assisted dispersive solid-phase microextraction (UA-DSPME) can be used for this procedure (Bahrani et al., 2017; Dimpe and Nomngongo, 2016).

**3.2.1.3. Liquid-liquid extraction (LLE).** In this extraction, liquids of different densities are separated. There is a transfer of analytes from one phase, which is generally aqueous, to another, generally organic (ethyl acetate, hexane, isooctane, toluene, chloroform, methylcyclohexane, and mixtures). The technique is simple but uses a large number of organic solvents. There are other variations, such as liquid-phase microextraction (LPME), which allows three-phase extraction (consisting of a ternary solvent system in which a second solvent disperses small volumes of extraction solvent) (Dimpe and Nomngongo, 2016). LPME techniques can be mainly classified into supported liquid microextraction (SLMME), hollow fiber membrane (HF) liquid microextraction, dispersive liquid microextraction (DLLME), and single drop microextraction (SDME).

**3.2.1.4. Supercritical fluid extraction.** Supercritical fluid extraction (SFE) separates one component from another using supercritical fluids as the extraction solvent (pressure and temperature conditions above its critical point). The extraction is usually performed from a solid matrix but can also be used in liquids. Carbon dioxide is the most commonly used supercritical fluid because of its low pressure and critical temperature ( $CT = 31\text{ }^{\circ}\text{C}$  and  $CP = 74\text{ bar}$ ). It is low-cost, non-toxic, and highly available.  $\text{CO}_2$  can also be modified with other co-solvents, such as ethanol or methanol. A remarkable advantage of this technique is that, unlike other processes, SFE leaves no solvent residues.

**3.2.1.5. QuEChERS method.** The QuEChERS method was first used for multiclass residue pesticides in agricultural products, consisting of quick, easy, cheap, effective, rugged, and safe. The technique is a simplified version of conventional extraction methods. It consists of stages that include homogenization of the sample (comminution and sample size). The target analytes are extracted from the previously homogenized sample and partitioned using a solvent (extraction and partitioning). Finally, they are purified using d-SPE to eliminate interferences (clean-up) (Kim et al., 2019a).

### 3.2.2. Clean-up

A post-extraction cleaning step is often necessary to eliminate potential interferences like surfactants and lipids that might be present in the extracted sample. In this context, ion exchange cartridges are invaluable for extraction and purification. Solid-phase cartridges, including dispersive solid-phase extraction (d-SPE), can effectively separate these interferences. For instance, the primary-secondary amine weak anion exchanger sorbent (PSA), found in SPE cartridges, is employed to eliminate polar compounds such as acids and pigments. In contrast, C18 cartridges effectively remove non-polar and moderately polar compounds. For the purification of polar or moderately polar compounds from non-aqueous samples, Supelclean<sup>TM</sup> LC-NH2 cartridges are preferred. Additionally, disposable pipette extraction tips (DPX) made from primary and secondary amine (PSA) and zirconium oxide

modified silica gel (Z-Sep) are specifically designed to eliminate co-extractives with medium or weak polarity. These versatile tools play a pivotal role in ensuring the purity of extracted compounds for subsequent analysis. (Merlo et al., 2022).

### 3.3. Analysis methods available

The main techniques used for the analysis of CECs are based on gas (GC) or liquid (LC) chromatography coupled to mass spectrometry (MS or MS/MS). The choice of the adequate method depends on multiple variables, like the properties of the analyte of interest. In this case, less volatile and polar compounds are mainly analyzed by LC and volatile and semi-volatile compounds by GC. When detection limits and good selectivity need to be determined, gas chromatography-electron capture detectors (GC-ECD), GC-HRMS, or time-of-flight gas chromatography (GC-ToF) techniques can be used. Other methods can also correspond to optical and electrochemical techniques; however, they have some limitations. The main techniques and the conditions under which they can be of greater functionality will be analyzed.

#### 3.3.1. Chromatography

Chromatography is a method for separating components in a sample by separating properties into stationary and mobile phases. Different types include planar, thin layer, column, liquid, gas, and supercritical fluid chromatography. Interactions between stationary and mobile phases include adsorption, partition, ion exchange, affinity, and molecular exclusion chromatography (SEC) (Coskun, 2016; García-Córcles et al., 2019).

Gas chromatography (GC) involves a stationary phase with a liquid-type stationary phase adsorbed on an inert solid and a carrier phase with gases like helium or nitrogen. The sample is vaporized and enters the gaseous mobile phase, dispersing components between the mobile and stationary phases. When coupled with a mass spectrometer, GC-MS combines GC's separation capacity with the mass detector's sensitivity and selective capacity, enabling the identification and quantification of trace compounds in complex mixtures. GC-MS has been used to identify and quantify various CECs, including estradiol, estriol, estrone, PCPs, alkylphenols, phenylphenols, bisphenol A, non-steroidal anti-inflammatory drugs, and pesticides. (Azzouz and Ballesteros, 2016; Ezhilarasan, 2022; Carmona and Picó, 2018; Kumirska et al., 2015). The GC-MS/MS system is similar to GC but uses two mass analyzers separated by a collision cell. It is suitable for analyzing volatile analytes, complex matrices, and low-level quantitation. It detects PCPs residues, pesticides, additives, and hormones. Gas chromatography coupled with an electron capture detector (GC/ECD) is a powerful analytical technique used to detect and quantify various atoms and molecules in gas samples. It operates based on the principle of electron capture, making it selective and responsive to molecules that contain electronegative functional groups. However, it is not sensitive to functional groups such as amines, hydrocarbons, and alcohols (Hinz et al., 2021; Yazdi et al., 2022).

When a speedy response is required, the most efficient mass analyzer is the time-of-flight (TOF). TOF mass analyzers efficiently identify molecules in samples, making them helpful in analyzing food and environmental contaminants. Gas chromatography with a high-resolution mass spectrometer (GC-HRMS) is another option. At the same time, GC-Orbitrap-MS combines mass spectrometry with high-resolution/exact mass (HR/AM) orbitrap mass spectrometry for food safety, environmental, industrial, forensic, and anti-doping purposes. (Belarbi et al., 2021; Tao et al., 2022). The most common liquid chromatography is coupled to mass (LC-MS) to analyze polar, low volatile, and thermolabile compound mixtures. The mixture can be aqueous or in a suitable polar organic solvent. The technique has been used to detect and quantify steroids and their metabolites (Llompарт et al., 2019), as well as narcotics, dyes, mycotoxins, pesticides, etc. A more significant number of papers report the use of liquid chromatography with tandem

mass spectrometry, also called (LC-MS/MS) because further improvements in sample identification and accurate quantification can be achieved by coupling two mass analyzers operating in series (Benedetti et al., 2020; Llompарт et al., 2019; Salvatierra-stamp et al., 2018).

Other detectors can also be coupled to the chromatograph, depending on the characteristics of the sample, such as liquid chromatography with fluorescence detection (LC-FLD), liquid chromatography-UV detection (LC-UVD), or liquid chromatography diode array with or without fluorescence detection (LC-DAD, LC-DAD-FLD) used to detect and quantify remnants of drugs (salicylic acid, naproxen, ibuprofen, enrofloxacin, gemfibrozil and danofloxacin, and other antibiotics), sulfonamides, and veterinary medicines (Llompарт et al., 2019). Moreover, high-performance liquid chromatography (HPLC) and ultra-high-performance liquid chromatography (UHPLC) can separate very complex samples. They can be combined with various detectors, which in turn can be mixed and matched for complementary analysis, such as the determination of CECs in water (parabens, bisphenols, hormones, and UV filters) (Morelli et al., 2020) and identification-quantification of anthelmintics in environmental water and sediment (Li et al., 2020).

### 3.3.2. Optical and electrochemical techniques

They are less common than chromatography but can be used in some cases. Optical techniques include fluorescence spectroscopy (FS), near-infrared spectroscopy (NIRS), and hyperspectral imaging (HSI). Fluorescence is an emission process in which molecules are excited by the absorption of electromagnetic radiation and release excess energy in the form of photons upon relaxation to the basal state. In NIRS, the sample to be analyzed is bombed with NIR rays with wavelengths between 780 and 2526 nm. According to the type of wavelength incident, some of the rays will be absorbed by specific chemical bonds, while other rays will be scattered and reflected by other chemical bonds. These techniques can analyze several compounds within the emerging pollutants and can be used, for example, in aflatoxin detection (Tao et al., 2018). While in electrochemical techniques, the evolution of electrochemical sensors for the detection of contaminants has become increasingly popular, specifically drug residues such as paracetamol and some antibiotics; however, it should be noted that this is a promising technology but still has several limitations (Karthik et al., 2022). Fig. S1 (supplementary information) provides an overview of the sampling strategies.

### 3.4. Quality control and data handling

The variety of matrices and CECs found in them in both type and concentration makes most samples complex. A high percentage of the reported scientific documents are centered on the analysis of target analytes; the disadvantage of selective analysis is that it ignores many contaminants that could be of interest. While non-selective analysis allows the detection and quantification of any contaminant as long as it is above the method's detection limit, although this type of analysis has the advantage of identifying many analytes in complex samples, powerful, high-resolution equipment is required. Regardless of the method (target or non-target), analyte quantification is usually performed using standards and calibration curves. Calibration curves are significant and are used to know the instrument's response to a particular analyte to calculate the concentration in an unknown sample. Typically, standard samples are run at different concentrations ranging from lowest to highest concentration, including the unknown of interest, and the instrument's response to each concentration is recorded. For greater accuracy, the procedure can be repeated at each concentration at least in triplicate so that an error bar is obtained and provides greater confidence in the measurement. When matrix effects can cause problems in the analysis of complex mixtures, these effects can be minimized or compensated for by adjusting mass spectroscopy parameters, chromatographic conditions, or improving cleanliness. When blank matrices are available, calibration can be performed using internal standards and

matrix-matched calibration standards; conversely, when empty matrices are unavailable, calibration can be performed using internal standards by subtracting the background or using surrogate matrices (Cortese et al., 2020).

The validation of an analytical procedure is an essential stage since it allows us to know the reliability characteristics of the method for its routine application. These characteristics demonstrate the analytical method's capacity to maintain the fundamental validation criteria over time under a fixed set of conditions (Gago-Ferrero et al., 2020; Gedawy et al., 2019; Peris-Vicente et al., 2015). Currently, there are a large number of institutions that have established validation methods like the Association of Official Analytical Chemists (AOAC), American Society for Testing and Material (ASTM), Codex Committee on Methods of Analysis and Sampling (CCMAS), Cooperation on International Traceability in Analytical Chemistry (CITAC), Environmental Protection Agency (EPA), European Analytical Chemistry Group (EURACHEM), Food and Agricultural Organization (FAO), Food and Drug Administration (FDA), International Laboratory Accreditation Cooperation (ILAC), International Organization for Standardization (ISO), International Union of Pure and Applied Chemistry (IUPAC) to mention a few. It is relevant to indicate that due to the diversity of validation methods, many validation guidelines consider in which cases they apply and how they should be performed. The criteria to be met for their acceptance. Generally speaking, the reliability characteristics comprise five validation criteria:

1. Selectivity: The ability of a method to determine the analyte unequivocally, even when other chemicals are present in samples.
2. Linearity and range: It should be evaluated that the method can provide results that are directly or indirectly (by mathematical calculations) proportional to the concentration of the analyte in a given range (range between the upper and lower concentration for which the correct precision, accuracy, and linearity of the method has been demonstrated).
3. Precision: the ability of a method to provide results close to each other. It can be studied at three levels (repeatability, which evaluates the method's precision; intermediate precision, which assesses the precision due to variations of the analyst, day, equipment, and reproducibility, which assesses the interlaboratory precision).
4. Accuracy: the closeness between the value conventionally accepted as the true or reference value and the value found experimentally.
5. Limit of detection and limit of quantification: The limit of detection (LOD) is the minimum quantity of analyte in a sample that can be detected, not necessarily with precision and accuracy, whereas the limit of quantification (LOQ) is defined as the minimum quantity of analyte that can be quantitatively determined with adequate accuracy and precision.

## 4. Treatment method for common emerging contaminants

### 4.1. Conventional treatment methods

Conventional WWTPs are commonly designed with three treatment stages: a first stage consisting of screening, flotation, coagulation-flocculation, and sedimentation, followed by a second treatment stage consisting of a biologically activated sludge reactor, and a final stage of disinfection using ozone or chlorine compounds. This treatment system is designed to efficiently remove components like suspended solids, organic matter, and some pollutants considered in government regulations. Still, its effectiveness may be minimal for removing specific emerging contaminants due to these compounds' low biodegradability and high persistence.

This treatment can be defined as a process that converts small, stable, non-settling, or slow-settling particles into larger particles by adding a coagulant. Subsequently, these particles coalesce to increase their volume (floc formation) and settling velocity (Amuda et al., 2006; Sun

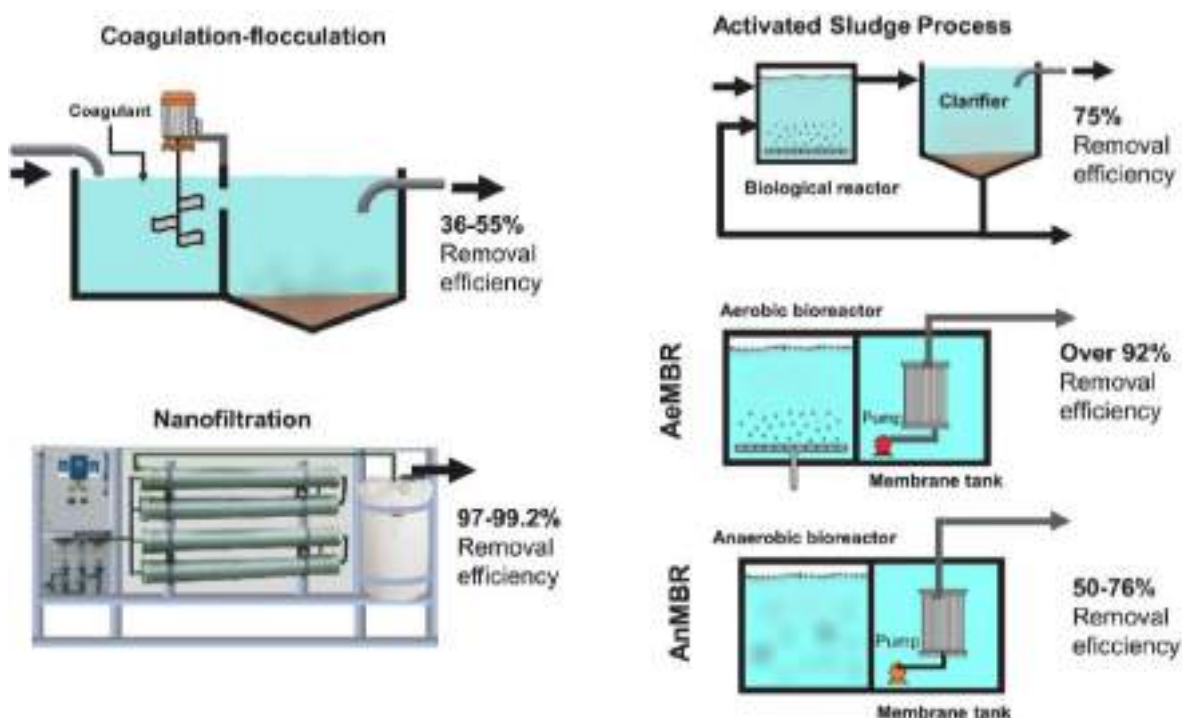


Fig. 4. Some technologies are used for the removal of CECs and their efficiency.

et al., 2020). This process is widely used for both wastewater and drinking water treatment due to its effectiveness in reducing water quality criteria which include turbidity, colour, total suspended solids (TSS), chemical oxygen demand (COD), and biochemical oxygen demand (BOD). In the literature are few studies on the efficacy of this treatment in eliminating CECs. The works reported generally refer to its evaluation of eliminating compounds for pharmaceutical use. (Suárez-Iglesias et al., 2017). In agreement with the results reported by Vieno et al., the coagulation-flocculation process did not show good results for removing drugs such as Ibuprofen, Bezafibrate, Carbamazepine, and Sulfamethoxazole. Of the compounds studied, diclofenac was the only drug removed (33%) from lake water after ferric sulfate coagulation. However, this process improves considerably with the presence of humic matter, obtaining up to 77% removal for diclofenac, 50% for ibuprofen, and 36% for bezafibrate. This indicates that treatment plants that treat highly humic water could eliminate more than 50% of certain pharmaceutical compounds contained in the water.

Recently, the use of natural coagulants for water treatment has received attention because these coagulants do not add metals to the effluent, less sludge volume is produced and, therefore, the cost for disposal is lower (Elfilali et al., 2022; Liang et al., 2014; Sivaranjani Gafoor et al., 2021; Santos et al., 2015). Santos et al., 2015 evaluated the removal of tetracycline from contaminated water using *Moringa oleifera* seed meal, obtaining up to 55% removal when particles larger than 5 mm were used and a dose of 0.5 g/L. These results indicate that using natural coagulants in the coagulation-flocculation process could be feasible for treating several pollutants like pharmaceutical waste. The use of chlorine for the disinfection process of drinking water continues to be the most widely used conventional treatment (Santos et al., 2015). Some studies also refer to its application in wastewater treatment. However, this process is not recommended for its application in the treatment of water polluted with pharmaceuticals since it has been shown that the chlorination of aromatic compounds is affected by the presence of different functional groups in the aromatic ring, so metoprolol and sulfamethoxazole generate toxic oxidation products such as chloramines (Rivera-Utrilla et al., 2013). Chlorine dioxide is an alternative to chlorine because it can degrade many organic compounds without the risk of

generating toxic organochlorine species (Rivera-Utrilla et al., 2013). Since most conventional treatments are inefficient for removing many emerging contaminants, more effective treatments like biological treatments, advanced oxidation processes, sorption methods, and nanofiltration methods are required.

#### 4.2. Biological treatment

In the secondary treatment stage of wastewater treatment, biological treatments are typically used to remove organic debris, suspended sediments, and sometimes even emerging pollutants. Commonly used technologies are conventional activated sludge process (ASP), membrane bioreactor, and biofilter. This technology is frequently employed in WWTPs because it treats high water volumes. In this technique, organic molecules are broken down in activated sludge tanks using either aerobic or anaerobic systems, with the help of constant regulation of temperature and chemical oxygen demand (COD). However, its application is excluded for treating effluents with a high concentration of toxic compounds to microorganisms. Arikian (2008) evaluated the use of this process for the degradation of chlortetracycline during anaerobic digestion; the results obtained indicate that the concentration of chlortetracycline decreased by approximately 75% (from 5.9 to 1.4 ppm) during the 33-day digestion period, resulting in a half-life value of about 18 days (Arikian, 2008). However, as previously mentioned, this technique is not always adequate for eliminating specific contaminants. For example, it has been found that it is inefficient for removing contaminants such as carbamazepine, diclofenac, sulfonamides, macrolides, and trimethoprim (Rivera-Utrilla et al., 2013).

This system integrates a biological degradation process with a membrane filtration process with a pore size ranging from 0.1 to 0.4  $\mu\text{m}$ . Membrane bioreactors are a potential invention in wastewater treatment and reuse due to their cost-effectiveness and efficiency in removing emerging pollutants (Do and Stuckey, 2019). Do and Stuckey evaluated the removal of Ciprofloxacin (CIP) using an anaerobic membrane bioreactor (AnMBR) with a mean pore size of 0.2  $\mu\text{m}$ ; the results obtained indicate that 50–76% of CIP was removed after 120 days of operation. The primary removal mechanism was the biological



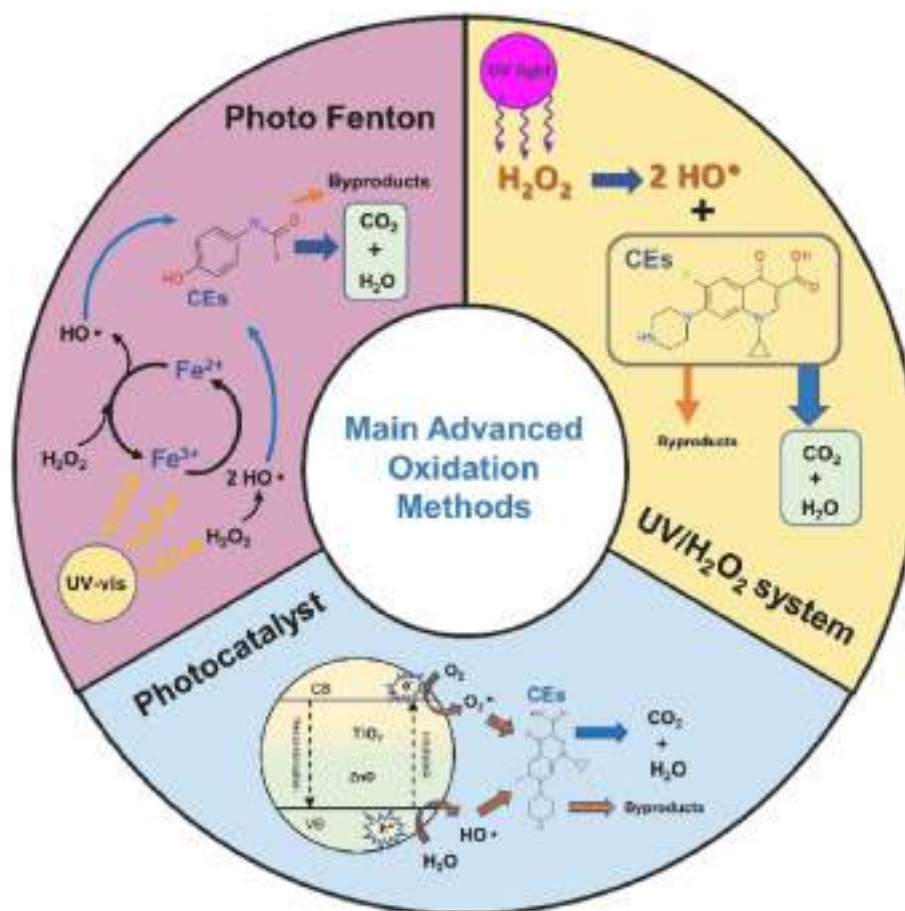
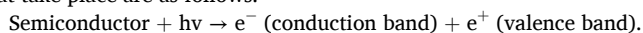


Fig. 5. Main advanced oxidation processes (AOPs) are used to remove emerging contaminants.

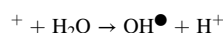
degradation of CIP, detecting few intermediate compounds; therefore, CIP adsorption on the sludge contributed only a tiny fraction of the total (Do and Stuckey, 2019). On the other hand, Wancen Liu et al. conducted a comparative study on removing 15 pharmaceutical compounds using an aerobic membrane bioreactor (AeMBR) and an anaerobic membrane bioreactor (AnMBR). The results indicate that the highest removal efficiency (greater than 92%) can be obtained using an aerobic membrane bioreactor, except for amitriptyline, carbamazepine, and atrazine. Therefore, these compounds have a higher nitrogen content in their molecular structure and are removed more efficiently using AnMBR. On the other hand, Wancen Liu carried out a comparative study on the removal of 15 pharmaceutical compounds through the use of an aerobic membrane bioreactor (AeMBR) and an anaerobic membrane bioreactor (AnMBR) (Liu et al., 2020).

#### 4.3. Advanced oxidation process (AOP)

AOPs have extraordinary potential to treat a wide variety of emerging contaminants (see Fig. 4). These processes are based on the in-situ generations of free radicals, commonly  $\text{OH}^\bullet$  hydroxyl radicals, which are highly reactive and less selective than conventional oxidants, such that they can generate a complete mineralization pathway of organic contaminants. These processes include ozonation, semiconductor photocatalysis, photolysis, Fenton, and Photo-Fenton. A few of the most commonly used AOPs used to remove emerging contaminants have been depicted in Fig. 5. The principle of this technology is to generate  $\text{OH}^\bullet$  hydroxyl radicals from water by activating a semiconductor (usually  $\text{TiO}_2$ ) with artificial light or sunlight. The reactions that take place are as follows:



During the oxidation of water or hydroxide ions in the hole of the valence band ( $h^+$ ), hydroxyl radicals ( $\text{OH}^\bullet$ ) can be generated



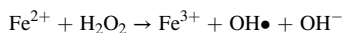
Completing compounds using this method is among the most popular modern oxidation techniques, including some pharmaceutical compounds considered emerging pollutants (Cuerda-Correa et al., 2019; Deng and Zhao, 2015). The degradation of Ciprofloxacin (CIP) has been extensively studied through the use of semiconductor materials based on  $\text{TiO}_2$  (Hassani et al., 2015; Sarafraz et al., 2020a; Xing et al., 2018),  $\text{ZnO}$  (Wolski et al., 2021),  $\text{FeWO}_4$  (Ahmad et al., 2021b) and graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) (Jiménez-Salcedo et al., 2020). The highlighted results were obtained by Sarafraz et al., who received a 100% degradation of CIP (with mineralization of 82%) after 70 min of irradiation with a visible LED light. This behavior is attributed to the extraordinary energy absorption in the visible light region by the semiconductor ( $\text{Ti}^{3+}/\text{N-TiO}_2$ ) generated by the band gap decrease to a value close to 2.0 eV (Sarafraz et al., 2020b).

Ozone alone cannot wholly oxidize organic compounds since it is weak and requires much. Thus, ozone oxidation is typically combined with other techniques (Singh et al., 2021b). The application of ozone and its combination with hydrogen peroxide or UV are interesting processes for treating CECs (Dhondu Borikar and Sc, 2014; Pelalak et al., 2020). The  $\text{O}_3/\text{H}_2\text{O}_2$  system has received more attention than the conventional ozone process because it has the advantage of higher efficiency and faster reaction rate compared to the results obtained when using both techniques separately, in addition to minimizing the generation of bromates. Pelalak et al. evaluated the degradation of four

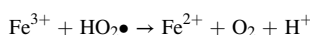
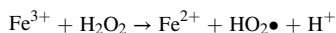


antibiotics using the combined  $O_3/H_2O_2$  system. They obtained degradation values in the 38.01%–79.60% range, which were higher than those obtained with the simple ozone system (26.90%–61.44%). As expected,  $H_2O_2$  catalyzes the decomposition of  $O_3$ , leading to the formation of more  $OH^\bullet$  radicals and, ultimately, more significant degradation of the contaminants (Pelalak et al., 2020).

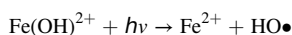
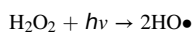
The conventional Fenton process uses  $Fe^{2+}$  salts as catalysts and  $H_2O_2$  as oxidants to generate hydroxyl radicals  $OH^\bullet$  under acidic conditions. The reaction mechanism for the generation of radicals is described in the following reactions (Babuponnusami and Muthukumar, 2012):



The Fenton reaction is complemented by the Fenton-like reaction where the regeneration of ferrous iron occurs in reactions of iron (III) with the radical intermediates of the hydroxyl radical degradation process, which are by:



A critical advantage of this process is that it can degrade CECs under atmospheric temperature and pressure conditions. For example, this process was applied for the degradation of doxycycline, obtaining removal percentages of 100%. (Borghi et al., 2015). However, some of the problems with this process are that the Fenton-like reaction is much slower than the Fenton reaction and the risks generated by the handling and storage of the  $H_2O_2$  required to be added during the reaction. Therefore, modifications have been made to the conventional process to catalyze the reaction of  $Fe^{3+}$  and  $Fe^{2+}$  or for the in-situ generation of  $H_2O_2$  (Khan et al., 2021). An interesting variant of the conventional Fenton process is the photo-Fenton system, which consists of applying a UV–vis light source to increase the concentration of  $OH^\bullet$  radicals generated, either by the direct decomposition of  $H_2O_2$  or by the photo-reduction of  $Fe^{3+}$  to  $Fe^{2+}$ , as indicated in the following reactions:



Recently, the application of this technology in the degradation of many emerging pollutants has been reported (Bautitz and Nogueira, 2010; Carra et al., 2015; Soriano-Molina et al., 2019). One of these studies demonstrated the implementation of this process for treating municipal wastewater with different compositions, removing more than 80% of the total CECs in about 15 min of treatment (Soriano-Molina et al., 2019; Soriano-Molina et al., 2019). According to the results obtained, it can be concluded that this technology is one of the advanced oxidation processes with the most significant prospects for development and utilization for the degradation of emerging pollutants.

AOPs have gained popularity due to their remarkable efficacy in removing many contaminants from water. These processes use highly reactive and potent oxidizing agents to decompose and degrade emerging contaminants. AOPs are environmentally friendly because they eliminate pollutants without producing harmful byproducts (Ameta and Ameta, 2018; Majumder et al., 2019; Oturan and Aaron, 2014). Unlike conventional treatment methods, AOPs degrade pollutants into harmless carbon dioxide ( $CO_2$ ), water ( $H_2O$ ), and inorganic salts. This ensures ecologically sound and secondary pollution-free effluents. AOPs often require significantly less chemical utilization for them to function. Photocatalysis or sonolysis can produce highly reactive species without using harmful chemicals. To reduce environmental impacts by reducing risks and improving treatment process eco-friendliness. AOPs' versatility boosts their environmental appeal. These treatments are effective against pharmaceuticals, pesticides, industrial chemicals, and emerging contaminants. AOPs are effective at removing organic and inorganic pollutants from water. This includes

treating recalcitrant compounds using conventional methods, which is problematic. AOPs also reduce sludge generation during treatment. Pollutant degradation in certain AOPs produces minute amounts of inorganic byproducts or gaseous end products. This method reduces sludge production, a problem with some conventional treatment methods, and its environmental impacts. AOPs have significant environmental benefits but must be carefully evaluated for each pollutant and treatment scenario before use. To implement AOPs optimally and effectively, various factors must be assessed. These include pollutant types, water quality, energy availability, and treatment scale (Ameta and Ameta, 2018; Majumder et al., 2019; Oturan and Aaron, 2014).

#### 4.4. Sorption methods

Sorption can be defined as a physicochemical phenomenon where a gas or liquid (sorbate) is fixed or captured by a substance in a condensed state (solid or liquid), called a sorbent (Ho and McKay, 1999; Wan et al., 2021). When a gas or liquid phase component binds to the internal surface of a porous solid, this phenomenon is called “adsorption.” In contrast, when this component binds to a liquid sorbent, it is designated as “absorption.” The sorption process is another promising method for removing CECs from drinking water and wastewater; for example, in the adsorption technique, a drug molecule or its metabolites can be retained on the surface of solid adsorbent material simply and effectively. However, it requires high operational costs for generating commercial adsorbents such as activated carbon, minerals, and clays. To reduce costs and environmental effects, many researchers are working to prepare adsorbent materials from agricultural and industrial waste as an alternative to commercial adsorbents (Kumar and Singh, 2018; Singh et al., 2018, 2021a; Vyas et al., 2021).

Biochar is one of the most studied alternative adsorbents because of its high surface area, its content of non-carbonized components, its porous structure, and its significant variability of surface functional groups (Kim and Kan, 2016; Lu et al., 2022; Singh et al., 2020, 2022; Zhou et al., 2014). This material can be obtained by a thermal or hydrothermal process when the biomass is heated to a high temperature with low or no oxygen, and the primary raw materials for its production are animal manure, agricultural and forestry residues, industrial bio-waste, and aquatic organisms (Singh et al., 2023a,b,c). Mandal et al. evaluated the physicochemical properties of biochar prepared from the pyrolysis of five different materials: bamboo chips, corn cob, eucalyptus bark, rice husk, and rice straw. The results indicate that biochar's physicochemical properties and capacity to adsorb atrazine and imidacloprid from water vary considerably depending on the raw material used. The biochar obtained from rice straw showed the highest adsorption of atrazine (70.7%) and imidacloprid (77.8%) (Mandal et al., 2017). Biochar adsorbent, prepared by pyrolysis of the avocado seed, was used to remove five pharmaceutical compounds from synthetic wastewater. The results obtained indicate that it was possible to remove altogether (100%) paracetamol, propranolol, and tetracycline contained in the synthetic wastewater, while amoxicillin and diclofenac sodium were at least 92.7% and 91.8%, respectively. This indicates that the material obtained from the avocado seed is an adsorbent with a high sorption capacity that can remove these five pharmaceuticals from hospital effluents (Leite et al., 2018; Lima et al., 2019b).

#### 4.5. Use of nano-composite treatment

A nanocomposite combines two or more materials at the nanometer scale. Nanocomposite materials are designed to have properties that exceed the individual capabilities of the components. Nanocomposites are classified into polymer-based (polymer/ceramic, inorganic/organic polymer, inorganic/organic hybrid, and polymer/layered silicate) and non-polymer-based (metal, ceramic, and ceramic/ceramic) (Guo et al., 2016; Pandey et al., 2017). These materials can be used in different applications such as energy storage, sensors and actuators, medicine,

catalysis, and environmental remediation, to mention a few, the last two being of most significant interest for treating emerging pollutants. These materials are used in different technologies to treat emerging pollutants, such as adsorption, catalysis and its variants (photocatalysis and sonocatalytic), Fenton-like processes, filtration (membranes), and electrochemistry.

Among the best-known materials to obtain nanocomposites with polymers are polysaccharides (cellulose, chitosan, and alginate) due to these materials being environmentally friendly. Alginate is an anionic polysaccharide that is non-toxic, biodegradable, and biocompatible, usually extracted from brown algae or microbial culture. The FDA recognizes it for use in both food and drugs in humans and animals. Another essential feature is that alginate has surface functional groups among the most common carboxyl and hydroxyl groups that can capture metals (Rigoletto et al., 2022). Of these alginate-based materials (alginate/graphene oxide, alginate/magnetic compound, and alginate/metallic organic frameworks, MOF), research has been conducted to treat some emerging contaminants, mainly antibiotic residues (ciprofloxacin, tetracycline, and norfloxacin). In this sense, Fei et al. reported maximum adsorption capacities of tetracycline and ciprofloxacin on GAD (alginate/reduced graphene oxide double-network hydrogel) of 290.70 mg/g and 344.83 mg/g, respectively (Fei et al., 2016). At the same time, Zhuang et al. used 3D alginate-based MOF hydrogel for tetracycline adsorption, achieving maximum adsorption of 364.89 mg/g MA-M (Zhuang et al., 2017).

On the other hand, chitosan is a natural polymer product of the deacetylation of chitin, with properties such as biocompatibility, biodegradability, and biofilm formation, which are of great environmental application. Chitosan presents amino and hydroxyl functional groups capable of interacting with different molecules, which have been exploited for the adsorption of pharmaceutical compounds. Sun et al. (2022) employed an integrated photo-Fenton system to degrade diclofenac sodium in an aquatic medium, achieving a removal efficiency of 96.4% in 40 min using an adsorbent prepared by coating polydopamine-chitosan onto Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Sun et al., 2022). Finally, cellulose, a homopolysaccharide (composed of a single type of monosaccharide), contains several hundred to several thousand  $\beta$ -glucose units linked together by the 1 $\beta$ -4 glycosidic bond. Cellulose is one of the most critical polysaccharides present in nature, found in the stems of leaves and tree trunks. It has been employed to treat carbamazepine, achieving a total photochemical abatement in 120 min with g-C<sub>3</sub>N<sub>4</sub>@cellulose aerogel (Chen et al., 2019b). In membrane technology, using cellulose nanocrystals in graphene oxide allowed an effective rejection of three antibiotics, 74.8%, 90.9%, and 97.2% for sulfamethoxazole, levofloxacin, and norfloxacin, respectively (Gao et al., 2021).

Regarding the use of the nanocomposites in advanced oxidation processes (photocatalysis and Fenton processes), some papers report the use of ZnO-based materials and enzymes hybrid systems, for example, SMA-Ce-ZnO-SBP (SMA nanofibres + ZnO (Ce) nanoparticles (10% weight/weight) + soybean peroxidase added to the solution), leading a complete abatement of diclofenac and 2,4-DCP, 90% of naproxen, 85% of imidacloprid and 70% of iopamidol and bisphenol A all within 24 h (Sarro et al., 2018). Pylypchuk et al. evaluated the *Trametes versicolor* Laccase immobilized system on Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTPA hybrid nanocomposites. The results indicate that the system could remove 99% of paracetamol and 95% of diclofenac in 18 h via oxidation/polymerization (Pylypchuk et al., 2018). The use of Fe (4.3) CNS nanocomposites in conjunction with O<sub>3</sub> and visible light (LED) for the degradation and mineralization of bisphenol A (97.8%) has also been reported (Jorshabani et al., 2019). While in sonocatalytic technology, Gholami et al. showed the performance of nanocomposite materials type Fe-Cu layered double hydroxide/biochar for the treatment of cefazolin sodium, the best efficiency (97.6%) was achieved by using 1.0 g/L of catalyst, 0.1 mM of contaminant, and an ultrasonic power of 300 W (Gholami et al., 2020). The versatility of using these materials allows the combination of technologies, such as ultrasound and UV, with a heterogeneous Fenton

process (Dihingia and Tiwari, 2022). It has been shown that such a system (ZnS QDs/SnO<sub>2</sub> nanocomposites) is capable of degrading pharmaceutical compounds, such as roxithromycin (86.65%) and clarithromycin (90.25%) (Hosseini et al., 2018).

Scientific work in electrochemistry is more focused on modifying electrodes with doped materials for use as sensors of pollutants. However, it is also possible to find some work where nanocomposite materials are used for the electrochemical oxidation of contaminants. In this sense, Xu et al. used Fe-Ce co-doped Ti/TiO<sub>2</sub> NTs/PbO<sub>2</sub> nanocomposite in electrodes to oxidize methylene blue, achieving a COD removal of 81% (Xu et al., 2018). For their part, Seid et al. degraded phenol using Ni-PPy and Cu-PPy composite materials with an efficiency of 38% and 56%, respectively (Seid et al., 2022).

#### 4.6. Using the nanofiltration method

Nanofiltration (NF) is a membrane separation process frequently used in water treatment to separate monovalent and divalent cations. The membranes used for nanofiltration have a pore size in the range of 1 and 10 nm, a value slightly more extensive than that of membranes used for reverse osmosis (Laeq Khan et al., 2021). In addition to its application in water softening, this technology is also helpful for the withdrawal of DBPs as well as natural organic matter (NOM), which can react with some sanitizers used in the water treatment process to form potential carcinogens (Isik et al., 2022). Extensive studies demonstrated that nanofiltration had been efficiently implemented to remove PhACs and other micropollutants (Hoseinzadeh et al., 2022; Owusu-Agyeman et al., 2019; Siddique et al., 2020; Silva, 2018; Worou et al., 2021; Zhou et al., 2023). It is essential to mention that solubility, diffusion, steric effect, hydrophilic and hydrophobic forces, and electrostatic repulsions can remove CECs from polluted water. Thus, membranes remove polar pollutants through electrostatic interactions and uncharged organic contaminants via steric effect (Kamrani et al., 2018).

From the reported results, it can be confirmed that nanofiltration (NF) membranes are feasible and efficient for eliminating CECs that, under normal circumstances, can't be eliminated using traditional procedures. The primary obstacles to their widespread use are their high energy demand and soiling due to the deposition of organic and inorganic waste (biofouling). To address this problem, the modification of conventional membranes incorporating nanocomposites has been investigated (Kamrani et al., 2018; Mastropietro et al., 2021; Mokhena and Luyt, 2017). Kamrani et al. evaluated the incorporation of chitosan into nanofiltration membranes to decrease the biofouling problem. As a result, the roughness and contact angle of the membrane decreased considerably. Obtaining its highest efficiency for diphenhydramine (97%) and mebeverine (~98%) removal and with the lowest fouling (22.6 L/m<sup>2</sup>h, FRR = 94.21%) at a pH of 3 (Kamrani et al., 2018). Another proposal studied is the incorporation of carbon nanotubes and graphene oxide. The nanofiltration membrane was prepared with several layers of carbon nanotubes, interposed between graphene oxide (GO) nanosheets to form a three-dimensional (3D) structure with a total thickness of 4.26  $\mu$ m. As a result, this membrane showed a 99.23% adsorption of tetracycline hydrochloride (Yang et al., 2018).

### 5. Pros and cons of detection and remediation methods

In this section, the advantages and disadvantages of methods for detection and remediation have been discussed. Table S1. Summarizes the advantages and disadvantages of various detection methods, as mentioned in section 3. For instance, the colorimetric sensor requires a small sample amount and detects rapidly along with high sensitivity; however, it only works for colored samples and compromises selectivity and reproducibility. Similarly, a fluorometric sensor requires a small sample volume and gives high sensitivity and specificity with fast detection; however, fluorescence is needed either in the analyte or the sensing material. On the other hand, electrochemical sensors exhibit

**Table 3**

Different treatments remove (CECs) and their main characteristics from water.

Treatment type	Technology	Parameters	Contaminants	Remotion rate (%)	Reference
Conventional	Coagulation-flocculation	Synthetic wastewater Coagulant: ferric sulphate Dosage: 350 $\mu\text{mol}$ (Fe)/L	Diclofenac Ibuprofen Bezafibrate	77% 50% 36%	Vieno et al. (2010)
	Coagulation-flocculation	Synthetic wastewater Coagulant: poly-aluminium chloride Dosage: 5 mg/L	Tetracycline (TC), Oxytetracycline-HCl (OTC) Minocycline-HCl (MNC) Meclocycline-sulfosalicylic (MCC) Demeclocycline-HCl (DMC)	~50%	Choi et al. (2008)
	Coagulation-flocculation	Synthetic water Natural coagulant: Moringa oleifera seed meal Dosage: 0.5 g/L	Tetracycline	55%	Santos et al. (2015)
	Ozone	Synthetic water Initial antibiotic concentration: 10 mg/L $\text{O}_3 = 5 \text{ mg/L}$ Ozone gas flow rate = 1 L/h Reaction time: 40 min	Sulfasalazine Sulfamethoxazole Sulfamethazine Metronidazole	26.9% a 61.4%	Pelalak et al. (2020)
	Ozone	Ozone gas flow rate = 8 L/min	Diclofenac Atrazine Carbamazepine Naproxen Gemfibrozil Bisphenol A Fluoxetine Triclosan Ibuprofen Atorvastatin	10% 25–36% 47% 51%	Dhondu Borikar and Sc (2014)
	Ozone	Ozone gas flow rate = 8 L/min	Chlortetracycline (CTC)	~75%	Arikan (2008)
Biological	Activated sludge process (ASP)	Synthetic water 33 days of anaerobic digestion	Ciprofloxacin	50 a 76%	Do and Stuckey (2019)
	Anaerobic membrane bioreactor (AnMBR)	Membrane with an average pore size of 0.2 $\mu\text{m}$ . 20 days of operation			
	Aerobic membrane bioreactor (AnMBR)	Synthetic water Membrane with a nominal pore size of 0.4 $\mu\text{m}$ Temperature: 22 °C	Ketoprofen Naproxen Ibuprofen Gemfibrozil Diethyltoluamide Benzophenone Bisphenol A Oxybenzone Triclosan 4-tert-Octylphenol	Over 92%	Liu et al. (2020)
AOPs	Photocatalytic degradation	Synthetic wastewater Semiconductor: $\text{FeWO}_4/\text{NC}$ Irradiation with visible light Time: 100 min	Ciprofloxacin	92.2%	Ahamad et al. (2021a)
	Photocatalytic degradation	Synthetic water Semiconductor: N-TiO <sub>2</sub> Irradiation with visible light Time: 90 min	Ciprofloxacin	90%	Xing et al. (2018)
	Photocatalytic degradation	Synthetic water Semiconductor: Ti <sup>3+</sup> /N-TiO <sub>2</sub> Visible LED light irradiation Time: 70 min	Ciprofloxacin	100%	Sarafraz et al. (2020b)
	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	Initial antibiotic concentration: 10 mg/L $\text{O}_3 = 5 \text{ mg/L}$ $\text{H}_2\text{O}_2 = 0.1 \text{ mM}$ Ozone gas flow rate = 1 L/h Reaction time: 40 min	Sulfasalazine Sulfamethoxazole Sulfamethazine Metronidazole	38%, 79.6%,	Pelalak et al. (2020)
	UV/H <sub>2</sub> O <sub>2</sub>	UV dose in $\text{mJ}/\text{cm}^2$ (approx.) = 250 a 1000 $\text{H}_2\text{O}_2 = 5 \text{ mg/L}$	Triclosan Diclofenac Fluoxetine Atorvastatin Atrazine Carbamazepine Naproxen Gemfibrozil Bisphenol A Ibuprofen	100% 81–97% 64–78%	Dhondu Borikar and Sc (2014)
	Fenton	Initial antibiotic concentration: 100 mg/L $\text{Fe}^{2+} = 25 \text{ mg/L}$ $\text{H}_2\text{O}_2 = 611 \text{ mg/L}$ T = 35 °C	Doxycycline	100%	Borghi et al. (2015)

(continued on next page)

Table 3 (continued)

Treatment type	Technology	Parameters	Contaminants	Remotion rate (%)	Reference
Sorption methods	Photo-Fenton	Initial antibiotic concentration: 100 mg/L 3 mg Fe/L high-intensity UVC-LED (20 W/m <sup>2</sup> ) 20 min A sewage treatment plant effluent. Pharmaceuticals compounds concentration: 25 mg/L. 0.20 mM (ferrioxalate, FeSO <sub>4</sub> or Fe (NO <sub>3</sub> ) <sub>3</sub> ). solar radiation 60 min Secondary effluents from municipal WWTPs 0.88 mM H <sub>2</sub> O <sub>2</sub> 0.1 mM Fe <sup>3+</sup> Fe <sup>3+</sup> -EDDS molar ratio of 1:1 Radiation solar 15 min	Acetamiprid	100%	Carra et al. (2015)
			Lincomycin Diazepam	65% 80%	Bautitz and Nogueira (2010)
		Materials: a mixture of Natural iron oxide (N.I.O.) and oxalic acid (OAA) 10 min irradiation: visible (UVA-Vis) light source	18 to 45 compounds. These compounds were mainly pharmaceuticals, some pesticides, antibiotics and opioids.	80%	Soriano-Molina et al. (2019)
	Adsorption	Adsorbent: Activated carbon prepared from avocado seed	Propranolol	Superior a 95%	Remache et al. (2022)
			Paracetamol Propranolol Tetracycline Amoxicillin Sodium diclofenac	100% 92.7% 91.8%	Lima et al. (2019a)
		Adsorbent: Biochar obtained from rice straw Chitosan-modified acrylic nanofiltration membrane with an effective filtration area of 32 cm <sup>2</sup> PDDA-functionalized multi-walled carbon nanotubes (MWCNTs)	Atrazine Imidacloprid Diphenhydramine Mebeverine Tetracycline hydrochloride	70.7% 77.8% 97% ~98% 99.2%	Mandal et al. (2017) Kamrani et al. (2018) Yang et al. (2018)
Membrane technologies	Nanofiltration				

high sensitivity and selectivity along with rapid detection and give excellent reproducibility of results. However, the working electrode durability is challenging (Manivannan et al., 2022; Ryu et al., 2021). Most of the techniques administered for detecting CECs nowadays have pros and cons. False results due to interfering molecules are one of the significant challenges in most of the methods. Therefore, more selectivity toward the target analyte is needed (Manivannan et al., 2022; Rodriguez-Mozaz et al., 2007; Ryu et al., 2021). Hence, more research is required to overcome the existing challenges in detecting CECs (see Table 3).

Table 4 summarizes the advantages and disadvantages of remediation methods, as discussed in Section 4. For instance, advanced oxidation process such as photocatalysis that uses sunlight as a source of energy offers the advantages of a renewable energy source and removes organic substances effectively by converting or degrading them to their metabolites (Neelgund and Oki, 2020). However, this technique faces scalability issues and catalysts reusability and regeneration (Younis and Kim, 2020). On the other hand, nanofiltration provides high efficiencies and rejects all salts and organic pollutants. At the same time, it requires high pressures to operate and suffers from membrane fouling (Ismail et al., 2020). It also leaves us with further treatment of the retentate generated during filtration. Regeneration and reusability issues with the remediating material, such as adsorbents, membranes, and catalysts, along with the analysis of the formation of by-products during remediation, are critical and must be addressed for maintaining the sustainability of the entire remediation process.

## 6. Economics of adopting the particular type of methods

Many parameters affect the cost of adopting a particular type of method. Fig. S1 summarizes the parameters often considered to determine the economics of adopting a specific detection method. For instance, considering the detection method as mass spectrometry generally includes parameters (but are not limited to): i)

instrumentation and maintenance costs, ii) cost of solvents as well as equipment required for sample pre-treatment, and iii) trained personnel salary (Bell et al., 2018).

On the other hand, considering adsorption for remediation, the parameters to be considered broadly involve the cost of i) chemicals, ii) energy consumption, and iii) capital investments (Kumar et al., 2019). Adsorbent synthesis requires chemicals and instrumentation; the adsorption process includes the experimentation setup and instrumentation, and desorption experiments include the use of temperature or solvents required for desorption. Fig. S2 summarizes the parameters often considered to determine the economics of adopting a particular remediation method.

## 7. Detailed summary and future prospects

As the name implies, emerging contaminants (CECs) suffer from inadequate regulatory oversight, resulting in their rapid dissemination into soil, water bodies, and the atmosphere. CECs encompass a broad range of substances, including pharmaceutical drugs, personal care products, per- and poly-fluoroalkyl substances (PFAS), pesticides, and nanomaterials. This review offers a concise overview of emerging contaminants, with a particular emphasis on pharmaceutical drugs. We discuss various methodologies for detecting and remediating CECs, considering their advantages and disadvantages. Additionally, we delve into the economic factors that influence the viability and feasibility of the adopted techniques. Various methods have been explored for the detection (colorimetry, fluorimetry, electrochemical, high-performance liquid chromatography (HPLC), and mass spectroscopy (MS)) and remediation (conventional methods, adsorption, nanofiltration, biological treatment, AOPs) of CECs. These techniques offer various advantages but have certain limitations. Therefore, it opens up opportunities for researchers to overcome these limitations by combining two or more processes or developing new methodologies.

Furthermore, it's noteworthy that sustainability considerations are



**Table 4**  
Advantages and disadvantages of CEC remediation methods.

Remediation method	Advantages	Disadvantages	References
<b>Conventional treatment methods</b>	<ul style="list-style-type: none"> <li>Scalable</li> <li>Removes most types of pollutants</li> <li>Well established</li> </ul>	<ul style="list-style-type: none"> <li>Removal efficiency is not good</li> <li>High maintenance and operational costs</li> <li>Generates enormous amounts of sludge</li> </ul>	Ismail et al. (2020)
<b>Biological treatment</b>	<ul style="list-style-type: none"> <li>Environment friendly</li> <li>Low cost of operation</li> <li>Effective for organic pollutants</li> </ul>	<ul style="list-style-type: none"> <li>Slow rate</li> <li>Optimum conditions</li> <li>Production of by-products, such as harmful gases</li> </ul>	(Ahmed et al., 2021; Hussain et al., 2021)
<b>Advanced oxidation process</b>	<ul style="list-style-type: none"> <li>High conversion efficiencies</li> <li>Rapid response time</li> <li>Renewable energy source</li> </ul>	<ul style="list-style-type: none"> <li>Operational costs</li> <li>Catalysts' reusability and regeneration</li> <li>Scalability</li> <li>Toxic intermediates production</li> </ul>	(Ismail et al., 2020; Neelgund and Oki, 2020; Younis and Kim, 2020)
<b>Sorption methods</b>	<ul style="list-style-type: none"> <li>Simple design</li> <li>Low cost</li> <li>High efficiencies</li> </ul>	<ul style="list-style-type: none"> <li>Adsorbent regeneration and reuse</li> <li>Adsorbent cost</li> </ul>	(Gkika et al., 2022; Ismail et al., 2020; Rashed and Rashed, 2013)
<b>Nanofiltration</b>	<ul style="list-style-type: none"> <li>Higher efficiencies</li> <li>Rejection of all salts and organic pollutants</li> </ul>	<ul style="list-style-type: none"> <li>High-pressure requirements, therefore, high energy consumption</li> <li>Membrane fouling</li> <li>High installation cost</li> <li>Retentate further treatment</li> </ul>	Ismail et al. (2020)

frequently overlooked in these studies. This oversight pertains to the regeneration and reusability of the materials used for CEC remediation. The materials employed in the remediation of current CECs mustn't themselves become CECs in the future. The field of CECs holds immense promise and an enduring scope for development. As time progresses, the molecules falling under the category of CECs will evolve, presenting an ongoing challenge and opportunity. Even now, numerous CECs remain primarily unexplored in detection and remediation. For instance, there are thousands of PFAS available. However, most studies only revolve around a few popular PFAS (Ryu et al., 2021). Further, here are our few recommendations that can be considered by research groups while working on CECs:

- Careful handling of the samples collected for detection, as often poor transportation and storage of samples leads to misinterpreted data
- More focus on fundamental sample analysis involving the lake and river waters instead of standard spiking methods in simulated samples
- Study of more chemical compounds to give clarity on interference during detection and avoid false positive results
- Development of better detection processes by combining two or more techniques, which can overcome the existing drawbacks and avoid false results
- Use of biomaterials for detection as well as remediation, which will avoid the usage of toxic metallic compounds that are hazardous to the environment

- Development of better remediation processes by combining two or more techniques, such as adsorption for separation followed by advanced oxidation processes for degradation
- More focus on desorption studies or material regeneration to maintain the overall sustainability of the remediation process
- Suggestions on proper discarding of the material used for remediation in case its regeneration is not possible
- And conversion studies of CECs into valuable materials such as fuels or value-added chemicals

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NA.

#### Ethical approval

Informed consent was obtained from all participants during the epidemiological investigation at every healthcare center, but we only used data without identifiers in the analysis.

#### Credit author statement

The corresponding author hereby confirm that the given information is correct as per his knowledge. Even though at various stages of work contribution roles were often interchanged however the table below presents the primary contribution of individual author.

Nadeem A Khan, Simranjeet Singh, Eduardo Alberto López-Maldonado, Abhradeep Majumder: Writing-original draft, Methodology, Visualization, Writing-review; editing.; Afzal Husain Khan, Radhika Varshney, J R López, P F Méndez: Methodology, Visualization.; Mohammad Amir Khan: Methodology, Supervision, Visualization, Methodology, Writing-review; editing.; Issam H Aljundi, Praveen C Ramamurthy, Mohammad Amir Khan: Reviewing and editing. Nabisab Mujawar Mubarak Waqas Amhad and SZM Shamshuddin: Writing-review; editing.

#### Declaration of competing interest

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

#### Data availability

No data was used for the research described in the article.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2023.140264>.

#### List of abbreviations

CECs	Emerging Contaminants
PFAS	Per and poly-fluoroalkyl substances
AOP	Advanced oxidation process

PhACs	Pharmaceutically active compounds
PCPs	Personal care products
PFAS	Polyfluoroalkyl Substances
WWTP's	Wastewater treatment plants
OP	Organophosphate
WHO	World Health Organization
PE	Polyethylene
SLE	Solid-liquid extraction
UAE	Ultrasound-assisted extraction
MAE	Microwave-assisted extraction
PLE	Pressurized liquid extraction
ASE	Accelerated solvent extraction
PHWE	Pressurized hot water extraction
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
PDMS	Polydimethylsiloxane
PA	Polyacrylate
DSPE/DSPME	Dispersive solid phase (micro) extraction
UA-DSPME	Ultrasonic-assisted dispersive solid-phase microextraction
LPME	Liquid-phase microextraction
SLMME	Supported liquid microextraction
HF	Hollow fibre membrane
DLLME	Liquid microextraction, dispersive liquid microextraction
SDME	Single drop microextraction
SFE	Supercritical fluid extraction
PSA	Primary, secondary amine
GC	Gas chromatography
LC	Liquid chromatography
MS or MS/MS	Mass spectrometry
ECD	Electron capture detector
GC-ECD	Gas chromatography-electron capture detector
GC-ToF	Time-of-flight gas chromatography
GC-MS	Gas chromatography coupled with mass spectrometry
GC/ECD	Gas chromatography coupled to an electron capture detector
TOF	Time-of-flight
GC-HRMS	gas chromatography with a high-resolution mass spectrometer
GC-Orbitrap-MS	Gas chromatography-orbitrap mass spectrometry
HR/AM	High resolution/exact mass
LC-MS	Liquid chromatography coupled with mass
LC-MS/MS	Liquid chromatography with tandem mass spectrometry
LC-FLD	Liquid chromatography with fluorescence detection
LC-UVd	Liquid chromatography-UV detection
LC-DAD, LC-DAD-FLD	Liquid chromatography diode array with or without fluorescence detection
HPLC	High-performance liquid chromatography
UHPLC	Ultra-high-performance liquid chromatography
FS	Fluorescence spectroscopy
NIRS	Near-infrared spectroscopy
HSI	Hyperspectral imaging
OPEs	Organophosphorus esters
PAEs	Phthalic acid esters
DCM	Dichloromethane
POPs	Persistent organic pollutants
PFASs	Perfluoroalkyl substances
AOAC	Association of Official Analytical Chemists
ASTM	American Society for Testing and Material
CCMAS	Codex Committee on Methods of Analysis and Sampling
CITAC	Cooperation on International Traceability in Analytical Chemistry
EPA	Environmental Protection Agency
EURACHEM	European Analytical Chemistry Group
FAO	Food and Agricultural Organization
FDA	Food and Drug Administration
ILAC	International Laboratory Accreditation Cooperation
ISO	International Organization for Standardization

IUPAC	International Union of Pure and Applied Chemistry
LOD	Limit of detection
LOQ	Limit of quantification
TSS	Total suspended solids
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
TC	Tetracycline
OTC	Oxytetracycline-HCl
MNC	Minocycline- HCl
MCC	Meclocycline-sulfosalicylate
DMC	Demeclocycline-HCl
ASP	Activated sludge process
AnMBR	Anaerobic membrane bioreactor
CTC	Chlortetracycline
AeMBR	Aerobic membrane bioreactor
N.I.O	Natural iron oxide
OAA	Oxalic acid
MWCNTs	Multi-walled carbon nanotubes
MBR	Membrane bioreactor
CIP	Ciprofloxacin
MOF	Metallic organic frameworks
NF	Nanofiltration
NOM	Natural organic matter
GO	Graphene oxide

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