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Review

Current research trends on emerging contaminants pharmaceutical and personal care products (PPCPs): A comprehensive review

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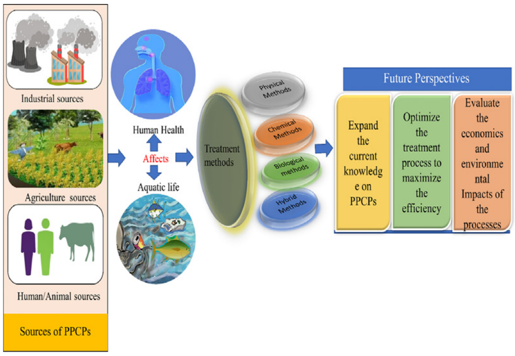
HIGHLIGHTS

- Pharmaceutical and personnel care products (PPCPs) are a potential hazard.
- PPCPs are resistant to biodegradation due to their stable chemical structures.
- Integrated/hybrid technologies are effective in removal of PPCPs from wastewater.
- Combining ozonation with activated carbon (AC), significantly remove PPCPs.
- Spain, Canada, and the USA have guidelines for PPCPs disposal and management.

GRAPHICAL ABSTRACT



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ABSTRACT

Pharmaceutical and personnel care products (PPCPs) from wastewater are a potential hazard to the human health and wildlife, and their occurrence in wastewater has caught the concern of researchers recently. To deal with PPCPs, various treatment technologies have been evolved such as physical, biological, and chemical methods. Nevertheless, modern and efficient techniques such as advance oxidation processes (AOPs) demand expensive chemicals and energy, which ultimately leads to a high treatment cost. Therefore, integration of chemical techniques with biological

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Abbreviations: AC, activated carbon; AOP, advance oxidation process; ASP, activated sludge process; BOD, biological oxygen demand; BPA, bisphenol A; COD, chemical oxygen demand; CWs, constructed wetlands; DNA, deoxyribonucleic acid; E1, estrone; E2, β-estradiol; E3, estriol; ECD, electrochemical degradation; ECs, emerging contaminants; EDCs, endocrine disruption chemicals; EE2, 17α-ethynylestradiol; EU, European Union; EV, β-estradiol 17-valerate; Fe, Iron; $Fe(OH)_3$, iron (III) hydroxide; FeO_4^{2-}, ferrate(VI); FTIR, Fourier transform infrared; FWS, free water surface; GAC, granular activated carbon; GC, gas chromatography; GC–MS, gas chromatography-mass spectrometry; HSSF-CWs, horizontal subsurface flow constructed wetlands; K_{ow}, octanol-water partition coefficient; LC, liquid chromatography; LC-MS, liquid chromatography-mass spectrometry; MBR, membrane bioreactor; μg, microgram; MOF, metal-organic frameworks; MS, mass spectrometry; NF, nanofiltration; ng, nanogram; NSAIDs, non-steroidal anti-inflammatory drugs; PBT, persistence bioaccumulation toxicity; PFCs, perfluorochemicals; pH, potential of hydrogen; PPCPs, pharmaceutical and personal care products; PZC, point of zero charge; RO, reverse osmosis; SEM, scanning electron microscopy; SF-CWs, surface-flow constructed wetlands; TiO_2, titanium dioxide; UF/PAC, ultrafiltration with powdered activated carbon; UK, United Kingdom; USA, United States of America; USD, United States dollar; US-ECD, ultrasound electrochemical degradation; USFDA, United States Food and Drug Administration; UV, ultraviolet; VSSF-CWs, vertical subsurface flow constructed wetlands; WWTPs, wastewater treatment plants; WWTW, wastewater treatment works; XRD, X-ray diffraction.

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Emerging contaminants (ECs)
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Chemical treatment
Biological treatment
Hybrid technologies

processes has been recently suggested to decrease the expenses. Furthermore, combining ozonation with activated carbon (AC) can significantly enhance the removal efficiency. There are some other emerging technologies of lower operational cost like photo-Fenton method and solar radiation-based methods as well as constructed wetland, which are promising. However, feasibility and practicality in pilot-scale have not been estimated for most of these advanced treatment technologies. In this context, the present review work explores the treatment of emerging PPCPs in wastewater, via available conventional, non-conventional, and integrated technologies. Furthermore, this work focused on the state-of-art technologies via an extensive literature search, highlights the limitations and challenges of the prevailing commercial technologies. Finally, this work provides a brief discussion and offers future research directions on technologies needed for treatment of wastewater containing PPCPs, accompanied by techno-economic feasibility assessment.

Contents

1. Introduction

Many studies in the recent years have documented the occurrence of emerging chemical pollutants at varying trace concentrations (ng/L – μg/L) from various environmental compartments (Surana et al., 2022; O'Connor et al., 2022), popularly known as "emerging micro-pollutants" which do not have legislative regulations yet (Büning et al., 2021; Sarkar et al., 2022). As of 2000, 33 chemical compounds identified in surface water (of both freshwater and marine water bodies) have been emphasized by the European Union (EU) as priority pollutants to be removed within two decades to protect the ecological status of the aquatic environment (Hena et al., 2021). In 2007, a few more chemical compounds known as pharmaceutical and personal care products (PPCPs) including phthalates, iopamidol, diclofenac, carbamazepine, triclosan, clofibric acid, musks, and ibuprofen, etc., were added to the list of priority pollutants. Most of these toxic compounds are well-established to be endocrine disruptive chemicals (EDCs) or even carcinogens (Priya et al., 2022). These anthropogenic micropollutants comprise mainly industrial chemicals (Surana et al., 2022), pesticides (Nie et al., 2020) and PPCPs (Rogowska et al., 2020). Among these, the major group of chemical pollutants are PPCPs, which find various day-to-day applications. These are vast group of compounds mainly utilized for beautification, personal hygiene and therapeutic (Büning et al., 2021). The EU market has registered around 3000 commonly used pharmaceuticals, with their applications still increasing globally (Patel et al., 2019). Therefore, legislating and maintaining the regulatory guidelines for PPCPs, and understanding their distribution in the environment are tedious and challenging (Reyes et al., 2021). Moreover, there are additional pharmaceutical compounds which are listed, but not commonly used. Lately, PPCPs have attracted the attention of researchers due to various reasons: (i) PPCPs have become abundant in the environment (Oluwole et al., 2020); (ii) PPCPs possess significant ecological risks (endocrine disruption, bioaccumulation, inducing bacterial antibiotic resistance, clinical toxicity, etc.) (Liu et al., 2020), and (iii) recent advancements in the sampling and instrumental methods have increased the sensitivity of analytical tools, enabling the detection of PPCPs even at trace levels (Priya et al., 2022).

The conventional wastewater treatment plants (WWTPs) have not been designed to remove PPCPs. Therefore, most of the available wastewater treatment technologies result in incomplete removal of PPCPs (Porter et al., 2020). Discharge from pharmaceutical plants (Scott et al., 2018), inappropriate domestic disposal through drain (Pereira et al., 2020b), or ingestion and the following excretion of these pharmaceutical compounds lead them to WWTPs (Pereira et al., 2020a). Unwarranted use of PPCPs and their inefficient removal from WWTPs have made them a ubiquitous group of contaminants in the environment. PPCPs are resistant to biodegradation due to their stable chemical structures, which makes them bioavailable in the aquatic ecosystems (Hena et al., 2021). As the wastewater sludge and the treated effluent from WWTPs may contain traces of PPCPs, soil irrigation, sludge fertilizer and biosolid applications are potential routes that transfer PPCPs to the terrestrial ecosystem, which have raised a major concern in the recent years (Reyes et al., 2021; Porter et al., 2020).

Though traces of PPCPs have been prevalent in the environment since a long time, their concentrations have been increasing recently, as their recently reported levels in surface water have surpassed the instrumental detection limits, raising concerns on environmental risks (Ślósarczyk et al., 2021). The detection of trace concentrations of PPCPs from complex environmental matrices have been realized through advancement in integrated analytical techniques: gas chromatography (GC) and liquid chromatography (LC) combined with mass spectrometry (MS) (Pérez-Lemus et al., 2019; Prasad et al., 2019), enabling their documentation from wastewater (Rogowska et al., 2020) and surface water (de Santiago-Martín et al., 2020). Interestingly, even trace amounts of PPCPs in water can significantly impact human health, biota, and the drinking water quality (Chaturvedi et al., 2021). However, it is unclear if the long-term exposure of PPCPs along with their conjugates and metabolites at combined low concentrations can potentially cause chronic health impacts (Hena et al., 2021).

Subsequently, PPCPs get discharged to the environment from WWTPs and it is important to develop, modify or improve their removal technologies in WWTPs (Masud et al., 2020; Cheng et al., 2019). Many reviews have focused on the presence of PPCPs in various environmental compartments, particularly, freshwater (Ebele et al., 2017) and wastewater (Oluwole et al., 2020; Patel et al., 2019). Some reviews have also discussed the available instrumentation and analytical methods for PPCPs (Pérez-Lemus et al., 2019), and their treatment and remediation methods (Priya et al., 2022). A few recent reviews have focused on the available modern treatment techniques like exploiting advanced oxidation process (AOP) for photocatalytic degradation (Oluwole et al., 2020). Some broadly discussed the treatment processes such as flocculation, coagulation, adsorption, membrane-based, and advanced oxidation, etc. for removal of PPCPs (Luo et al., 2014; Patel et al., 2019). Some have focused on the microbial bioremediation or biotransformation of PPCPs into less or non-toxic forms (Porter et al., 2020; Prabha et al., 2021), or microalgal remediation of PPCPs in wastewater (Hena et al., 2021). Several review studies also focused on the increasing environmental risks and concerns, ecotoxicity, and the physicochemical (mainly adsorption) remediation methods for PPCP removal (Patel et al., 2019). Recent studies have explored the use of AC and biochar as adsorbents to remove PPCPs (Zhu et al., 2022). Nevertheless, understanding and discussing the recent progress, feasibility, advantages and limitations of various novel technologies proposed to treat PPCPs are crucial to develop, integrate and implement a robust low-cost approach or combined techniques. Hence, as per the author's best knowledge, a comprehensive summary of PPCPs health and environmental impacts along with their remediation technologies from wastewater have not been systematically documented at one place in the previous literatures. Table 1 summarize the recent progress and existing knowledge about PPCPs and emerging contaminants (ECs) and their remediation approaches.

Therefore, the present review critically investigates the recent research and technological advancements in remediation of PPCPs from the environment (particularly water), with comprehensive discussion on their health implications, types, sources and environmental distribution. Additionally, the economic feasibility along with the pros and cons linked with various remediation technologies has also been discussed. The review also provides insights on the future prospects for research and the global legislative policies and strategies to minimize the use and hazards of PPCPs.

2. Review methodology

Related literature was collected from established databases like Google Scholar, Web of Science, ScienceDirect, Scopus, and other reliable web sources. The following were the key words used: Personnel care products; Pharmaceutical products; Pharmaceutical and personal care products; Toxicity of pharmaceutical and personal care products; Physical remediation of pharmaceutical and personal care products; Chemical remediation of

Table 1
Comparison of current review article with recently published review articles.

Articles	PPCPs and emerging pollutants discussed	Biological techniques	Physical techniques	Chemical techniques	Hybrid techniques	Nanotechnology	Problems	Perspectives
Current review	General	Conventional + non-conventional	Membrane adsorption technology	Available	Available	Available	Available	Available
Cheng et al. (2021)	General	Not available	Biochar adsorption technology	Not available	Not available	Not available	Not available	Available
Rout et al. (2021)	General	Membrane bioreactors + activated sludge + biodegradation	Volatilization + activated carbon adsorption	Ozonation + photodegradation + advanced oxidation	Not available	Not available	Available	Available
Rathi et al. (2021)	General	Membrane anaerobic bioreactors + constructed wetlands	Membrane adsorption technology	Ozonation + photocatalysis	Not available	Not available	Not available	Available
Ji et al. (2020)	General	Anaerobic membrane bioreactor	Not available	Not available	Various	Not available	Not available	Available
Maryjoseph and Ketheesan (2020)	General	Treatment based on microalgae	Not available	Not available	Not available	Not available	Available	Available
Bilal et al. (2019)	General	Enzyme catalysed biodegradation	Not available	Not available	Available	Not available	Not available	Available
Yap et al. (2019)	General	Not available	Not available	Sono + photocatalysis	Chemical hybrid techniques	Not available	Not available	Not available
Bedia et al. (2018)	General	Biochar + activated carbon adsorption	Not available	Not available	Not available	Not available	Not available	Available
Lima (2018)	General	Not available	Adsorption	Not available	Available	Not available	Not available	Not available
Rodriguez-Narvaez et al. (2017)	General	Not available	Membrane adsorption technique	Advanced oxidation technique	conventional + non-conventional process	Not available	Not available	Available
Wang and Wang (2016)	Special (PPCPs)	Activated sludge treatment + biodegradation	Adsorption	Fenton oxidation + UV treatment + Ionizing irradiation	Sono-photocatylsis + sono-photolysis	Not available	Not available	Available

pharmaceutical and personal care products; Bioremediation of pharmaceutical and personal care products; Phytoremediation of pharmaceutical and personal care products; Emerging/hybrid remediation technologies of pharmaceutical and personal care products. The present review aims to provide insight on the existing remediation technologies of PPCPs from diverse environmental matrices and emphasized the knowledge on the microbial assisted bio-and-phytoremediation approaches along with the emerging hybrid technologies for environmental remediation of PPCPs. The review also overviews the existing data to highlight the key areas for future research in order to address the existing knowledge gaps, especially in regard to the commercial feasibility of current technologies and recommends a few promising futuristic policy-based approaches.

3. Types and sources of PPCPs in the environment and their impacts

3.1. Types of PPCPs

Pharmaceuticals can be categorized into various groups of active organic compounds Table 2: Antibiotics [sulfonamides, β-lactams (penicillin), fluoroquinolones, macrolides, protein synthesis inhibitors (tetracycline), etc.] (Patel et al., 2019); Endocrine disruptors (steroid hormones like estrogens, estrone, estriol, 17-β-estradiol, 17-α-ethinylestradiol, testosterone, etc.) (Oluwole et al., 2020); Analgesic and non-steroidal anti-inflammatory drugs (NSAIDS) (most prescribed groups are ibuprofen, naproxen, acetaminophen, and diclofenac) (Veras et al., 2019); Antiepileptic drugs (carbamazepine for epileptic seizures) and blood lipid regulators (gemfibrozil, bezafibrate, clofibric acid, fenofibric acid) (Keerthanan et al., 2021); β-blockers (for hypertension and cardiac dysfunctions: theophylline, sotalol, atenolol, metoprolol, salbutamol); Antineoplastics (cancer therapeutics like cytostatic drugs) (Reyes et al., 2021). Based on the nature of application, certain products can also be classified as pharmaceuticals: disinfectants, preservatives, synthetic musk (used in disinfectants, antiseptics and surface sterilant), sunscreen lotions (UV filters), antimicrobial agents (fungicides), etc. (Keerthanan et al., 2021).

Personal care products broadly comprise the following groups: Pesticides and insect repellants; Synthetic fragrance (synthetic musk: used in perfume, essence, body lotion, skin or hair care products, shower and bath products) (Oluwole et al., 2020); Soaps and detergents; Sunscreen UV filters (UV absorbers for dermal protection) (Chaturvedi et al., 2021); Triclosan (present in detergents, hand soap, deodorants, toothpaste, shampoos, sunscreen, etc.); Antiseptics and preservatives (used in functional clothing, packaging textiles, medical devices, and household items) (Tseng and Tsai, 2019; Juliano and Magrini, 2017). The details about the sources and environmental persistence of PPCPs are discussed below.

Table 2
Types and physicochemical characteristics of common PPCPs.

PPCP	Chemical formulae	Mol. weight (g/mol)	Solubility (mg/L)	pKa	Reference
Antibiotics					
Clarithromycin	$C_{38}H_{69}NO_{13}$	747.95	0.33	8.99	Xie et al. (2019)
Chlortetracycline	$C_{22}H_{23}ClN_2O_8$	478.88	288	–	Madikizela et al. (2018)
Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	331.34	<1 mg/mL	6.09	Lee et al. (2019)
Clindamycin	$C_{18}H_{33}ClN_2O_5S$	424.98	30.6	7.60	Subedi et al. (2015)
Difloxacin	$C_{21}H_{19}F_2N_3O_3$	399.40	–	0.89	Lee et al. (2019)
Enrofloxacin	$C_{19}H_{22}FN_3O_3$	359.4	53.9	–	Lee et al. (2019)
Flumequine	$C_{14}H_{12}FNO_3$	261.25	–	1.60	Lee et al. (2019)
Lincomycin	$C_{18}H_{33}ClN_2O_5S$	424.98	30.6	7.60	Subedi et al. (2015)
Norfloxacin	$C_{16}H_{18}FN_3O_3$	319.33	1.78	6.34	Lee et al. (2019)
Ofloxacin	$C_{18}H_{20}FN_3O_4$	361.37	28.3	5.97	Lee et al. (2019)
Oxytetracycline	$C_{22}H_{24}N_2O_9$	460.43	313	3.27	Madikizela et al. (2018)
Pefloxacin	$C_{17}HFN_3O_3$	333.36	11.4	–	Lee et al. (2019)
Roxithromycin	$C_{41}H_{76}N_2O_{15}$	837.05	0.0189	–	Jiang et al. (2014)
Sulfamethazine	$C_{12}H_{14}N_4O_2S$	278.33	1500	7.59	Prosser and Sibley (2015)
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	253.28	610	5.70	Lee et al. (2019)
Sulfadiazine	$C_{10}H_{10}N_4O_2S$	250.28	77	6.36	Lee et al. (2019)
Tetracycline	$C_{22}H_{24}N_2O_8$	444.43	231	3.30	Madikizela et al. (2018)
Thiamphenicol	$C_{12}H_{15}Cl_2NO_5S$	356.22	–	–	Xie et al. (2019)
Trimethoprim	$C_{14}H_{18}N_4O_3$	290.32	400	7.12	Kumar et al. (2019)
Tylosin	$C_{46}H_{77}NO_{17}$	916.10	–	7.73	Jiang et al. (2014)
Anti-inflammatory drugs					
Acetaminophen	$C_8H_9NO_2$	151.16	1.4	9.38	Wang and Wang (2016)
Aspirin	$C_9H_8O_4$	180.16	4600	3.50	Wang and Wang (2016)
Diclofenac	$C1_4H_{11}Cl_2NO_2$	296.15	2.37	4.15	Wang and Wang (2016)
Ibuprofen	$C_{13}H_{18}O_2$	206.28	21	5.30	Wang and Wang (2016)
Indomethacin	$C_{19}H_{16}ClNO_4$	357.79	0.937	4.50	Wang and Wang (2016)
Ketoprofen	$C_{16}H_{14}O_3$	254.28	51	4.45	Wang and Wang (2016)
Naproxen	$C_{14}H_{14}O_3$	230.26	15.9	4.15	Wang and Wang (2016)
Nimesulide	$C_{13}H_{12}N_2O_5S$	308.31	–	–	Wang and Wang (2016)
Phenazone	$C_{11}H_{12}N_2O$	188.23	5.19	1.40	Wang and Wang (2016)
Stimulant drug					
Caffeine	$C_8H_{10}N_4O_2$	194.19	2.17	14.00	Nonthakaew et al. (2015)
Cytostatic drugs					
Cyclophosphamide	$C_7H_{15}Cl_2N_2O_2P$	261.09	1–5	–	Liu and Wong (2013)
Ifosfamide	$C_7H_{15}Cl_2N_2O_2P$	261.09	3780	–	Liu and Wong (2013)
Synthetic hormone					
Ethinylestradiol	$C_{20}H_{24}O_2$	296.40	11.3	1.70	Gogoi et al. (2018)
Antiepileptic drugs					
Carbamazepine	$C_{15}H_{12}N_2O$	236.27	17.7	13.90	Madikizela et al. (2018)
Dilantin	$C_{15}H_{12}N_2O_2$	252.27	32	8.33	Madikizela et al. (2018)
Primidone	$C_{12}H_{14}N_2O_2$	218.25	500	12.30	Madikizela et al. (2018)

3.2. Sources and concentration of PPCPs in the environment

Terrestrial and aquatic systems are the major sinks of PPCPs in the environment. Both industrial (commercial WWTPs, sewage, pharmaceutical and drug manufacturing companies) (Tasho and Cho, 2016) and domestic (human and animal excreta, manure and biosolids for agricultural applications, domestic waste and urban landfill) (Madikizela et al., 2018; Yang et al., 2017) sources contribute to the environmental accumulation of PPCPs (Fig. 1). Another major source of PPCPs are the effluents and solid waste from hospitals and clinical laboratories (Evgenidou et al., 2015). Besides this, the principal pathway through which PPCPs enter the environment is known to be sewage and WWTPs. The effluents of sewage and water treatment systems contain various classes of PPCPs: hormones (endocrine mimicking substances), anti-inflammatory drugs, lipid regulators, β-blockers, antibiotics, etc. (Hong et al., 2019; Tarpani and Azapagic, 2018; Yang et al., 2017). Furthermore, PPCPs undergo frequent metabolic transformations upon interactions with biological systems. Usually, they undergo incomplete metabolic transformations, which lead to these PPCPs being excreted in the feces or urine as such (unaltered form) or metabolites (often more bioavailable forms of PPCPs) (Tasho and Cho, 2016).

Moreover, increased production and use of personal care products like toothpaste, sun-creams, synthetic perfumes, soap, detergents, cosmetic products, cosmetic supplements, have been persistently accumulating PPCPs in the environment (Yang et al., 2017). Additionally, the reckless use and inappropriate disposal of expired PPCPs or the dumping of unused cosmetic or medicinal products in landfills have significantly increased the global concentrations of PPCPs in the terrestrial and aquatic ecosystems (Al-Farsi et al., 2017). Table 3 outlines the Global occurrence of detected PPCPs in various environmental matrices. Peng et al. (2014) reported the highest PPCP concentration in China, when 4500 g/L of BPA was found in landfill leachates. BPA is used in a variety of industrial and manufacturing processes. It frequently serves as a plasticizer, food container protective layer, and an ingredient in the production of thermal paper (Kumar et al., 2021a). BPA functions as an antioxidant and a product stabilizer in cosmetics (Deng et al., 2018). Most of the high PPCP concentrations were found in raw wastewaters (1353 ng/L-3854 g/L) and surface water bodies (35 ng/L-42 g/L) in Asian nations (Reyes et al., 2021). The substance that has been discovered to have the most reports of having higher concentrations in various water matrices is caffeine. In Tran et al. (2014) investigation, caffeine concentrations of up to 3594 g/L were found in a raw wastewater sample from Singapore. Additionally, Archana et al. reported finding a significant amount of caffeine (499 g/L) in a raw wastewater sample from India (2017). Both investigations pointed to a person's lifestyle or eating habits as the main reason for the high levels of caffeine found in wastewater. Compared to the levels found in wastewater, caffeine concentrations in surface water bodies were relatively lower.

Picó et al. (2020) identified about 21 g/L of caffeine from an irrigation water source in Saudi Arabia, whereas Tamura et al. (2017) reported a measured caffeine concentration of 5330 ng/L in Japanese streams. In general, rivers and flowing streams' natural purifying processes might also result in a decrease in the amount of PPCP chemicals present in natural water bodies. Acetaminophen was the PPCP component with the highest concentration in the Australian region. A wastewater sample from New Zealand contained 118 g/L of acetaminophen, according to Kumar (2020). Additionally, it was shown that acetaminophen was among the list of frequently prescribed medications in New Zealand, contributing to the substance's high quantity

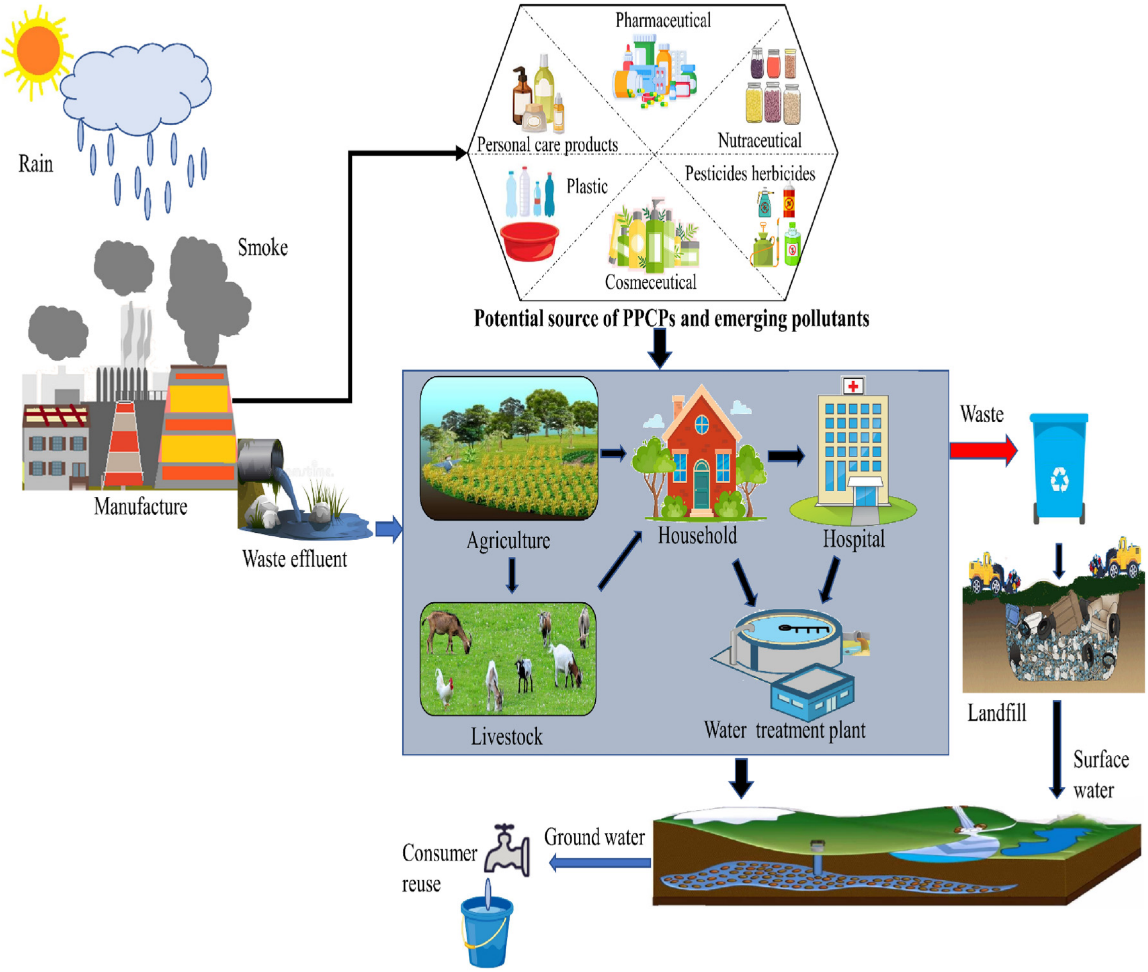

Fig. 1. Potential sources and pathways of PPCPs and emerging pollutants in the environments.

Table 3
Global occurrence of detected PPCPs in various environmental matrices.

Country	PPCPs	Concentration (ng/L)	Source	Reference
Australia	Sulfamethoxazole	3.00	Wastewater effluent	Watkinson et al. (2009)
Canada	Ibuprofen	5–8	Wastewater effluent	Brun et al. (2006)
China	Clofibric acid, ibuprofen, carbamazepine, naproxen	30, 420, 170, 30	Wastewater effluent	Lin et al. (2005)
France	Acetaminophen	11.3	WWTP effluent	Chiffre et al. (2016)
Germany	Arbamazaepine, clofibric acid, diclofenac, propranolol and sulfamethoxazole	6.3, 1.6, 2.1, 0.29, 2	Effluent	Ferrari et al. (2004)
India	Ciprofloxacin	31	Effluent	Larsson et al. (2007)
	Benzophenone	1.5–8.58	Sewage treatment plant	Archana et al. (2016)
Japan	sulfamethoxazole, sulfapyridine, trimethoprim, erythromycin-H_2O, azithromycin, clarithromycin, and roxithromycin	4–448	River water	Managaki et al. (2007)
Korea	Ibuuprofen, carbamazepine, atenolo, clarithromycin, mefenamic, erythromycin, propranolol, indomethacin, fluconazole, levofloxacin. Ifenprodil	414, 595, 690, 443, 326, 137 40.1, 33.5, 87.4 35.4	River water	Kim et al. (2009)
South Africa	Sulfamethoxazole Aspirin Ibufrpfen Acetaminophen Diclofenac Triclosan	29.9, 44.20. 62.82, 5.76, 22.3, 78.40–127.70	Wastewater influent and effluent	Amdany et al. (2014) Matongo et al. (2015) Agunbiade and Moodley (2016)
Spain	Aspirin	2.56, 0.034, 0.012	Wastewater effluent and surface water	Gros et al. (2009)
USA	17-β-Estradiol	0.0041	Municipal wastewater effluent	Huang and Sedlak (2001)
UK	Propranolol, diclofenac, ibuprofen, mefenamic acid, dextropropoxyphene, trimethoprim, erythromycin, cetylsulfamethoxazole, sulfamethoxazole, tamoxifen	76, 10, 424, 3086 133, 195, 70, <10, <50, <50	Sewage treatment plant	Ashton et al. (2004)
Vietnam	sulfamethoxazole, sulfamethazine, trimethoprim and erythromycin-	7–360	River water	Managaki et al. (2007)

in wastewater. The majority of the highest PPCP compound concentrations (5 ng/L-221 g/L) in European countries were found in raw wastewater. Acetaminophen (158 g/L), dipyridamole (166 g/L), and caffeine (221 g/L) were the three substances with the greatest concentrations (Reyes et al., 2021). Chemical personal care product additives have also been found in significant concentrations in European surface waterways, in addition to pharmaceuticals. In the Italian Alpine rivers, Mandaric et al. (2017) determined the seasonal trends of a few PPCPs. River water samples had up to 748 ng/L and 5720 ng/L of the UV filters octyl-dimethyl-p-aminobenzoic acid (OD-PABA) and benzophenone, respectively. Additionally, it was noted that anthropogenic activities and seasonal variations impacting the dilution of pollutants had a significant impact on PPCP detection frequencies and concentrations.

In general, it can be inferred that non-point sources of pollution and land use can have a big impact on the amount of PPCP compounds that are deposited in the environment. The Americas had the highest concentration of prescription medicine metformin (211 g/L) and over-the-counter drugs including acetaminophen (218 g/L) and naproxen (210 g/L) identified in raw wastewaters. The most often used NSAIDs in the United States were acetaminophen and naproxen, while metformin use as an anti-diabetic medication was also widespread there (Raval and Vyas, 2020). In the South American region, evidence of elevated PPCP concentrations in surface water bodies has also received substantial media coverage. According to Chaves et al. (2020), the amounts of caffeine, acetaminophen, and methylparaben in a Brazilian river system were 13 g/L, 1716 ng/L, and 660 ng/L, respectively. Additionally, persistent PPCP chemicals were found, according to Aristizabal-Ciro et al. (2017), in Colombian tributary rivers that flow into drinking water reservoirs. The main sources of PPCP chemicals in the drinking water were discovered to be benzophenone (502 ng/L), methylparaben (425 ng/L), and ibuprofen (62 ng/L) in the tributaries. Additionally, trace levels of PPCP compounds (7 ng/L-80 ng/L) were found in finished drinking water, demonstrating that the treatment system was ineffective at removing polar pollutants.

Consequently, the environmental occurrence and functional states of PPCPs are governed by their chemical stability and ecological or biological metabolisms (Al-Farsi et al., 2017). The key to comprehend the fate of PPCPs in the environment is to estimate their occurrence and abundance in various environmental compartments. Environmental reactions like hydrolysis, photolysis, redox, and biodegradation (Keerthanan et al., 2021), and environmental conditions like medium (soil, water, air, sediment), microbial activity, sunlight exposure, and temperature (Bu et al., 2016) influence the abundance and occurrence of PPCPs in the environment. Generally, the half-life of individual chemical compounds in a given medium decides the abundance of PPCPs in the environment. For instance, tetracycline has been reported to have half-lives of >30 days in soil (chlortetracycline), and 150 days in marine sediments (oxytetracycline) respectively; sulfonamides and fluoroquinolones in sediments have half-lives of >40 days and >30 days respectively; ciprofloxacin begins to degrade within 40 days of environmental exposure (Keerthanan et al., 2021). In four different types of agricultural soil, a study found different ranges of half-lives for different compounds: triclosan (12.65–15.68 days), naproxen (5.68–16.82 days), diclofenac (3.07–20.44 days), ibuprofen (4.52–18.48 days), bisphenol A (0.81–5.5 days), clofibric acid (0.91–6.09) (Xu et al., 2009). Likewise, Biel-Maeso et al. (2019) studied the biodegradation of 13 different pharmaceutical compounds (like sulfamethizole, sulfamethoxazole, carbamazepine, gemfibrozil) under aerobic condition for 30 days, and reported degradation (36 %–100 %) of 12 tested compounds excluding carbamazepine (recalcitrant, no decay). Nevertheless, to date, the environmental occurrence and persistence of all different groups of PPCPs are poorly understood, however, their health impacts and environmental impacts has been studied thoroughly.

3.3. Health impacts

3.3.1. Impact on human health

Phthalate substitutes, brominated flame retardants, bisphenol-A, polycyclic siloxanes, triclosan, synthetic muscles are a few ECs of concern that have significant health implications to humans upon long-term exposure (Priya et al., 2022) (Fig. 2). For instance, bisphenol A, a universal plasticizer, is a well-established endocrine disruptor, contributing to several hormonal abnormalities in humans including breast cancer, thyroid disorders, male genetic disorders (anti-androgen, male feminization) (Jafari et al., 2021; Kumar et al., 2021b). Pesticide exposure also impairs the endocrine cycle leading to microbial induction, cancer, genotoxicity, cytogenetic

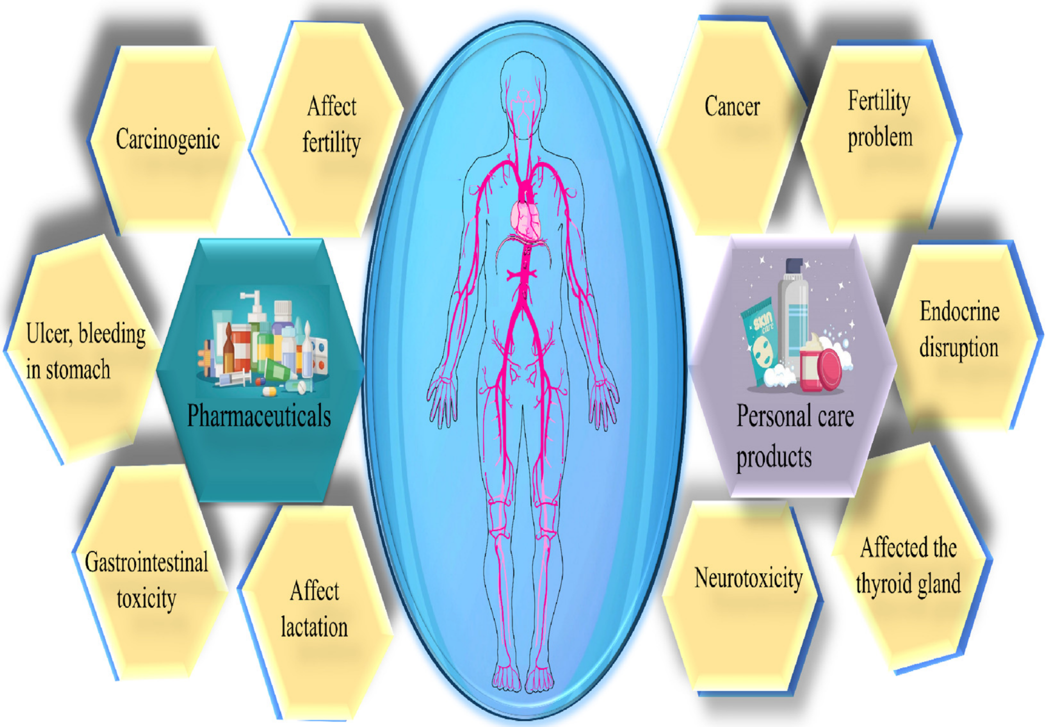

Fig. 2. Health impacts of PPCPs and emerging contaminants on human.

disruption, and neurotoxicity (Anerao et al., 2022a). Brominated compounds are inflammatory agents (neuroprotective, impermeable) that can cause pulmonary and endocrine cancers (O'Connor et al., 2022). Hexabromodiphenyl and tetrabromodiphenyl ethers can lead to mitochondrial and DNA damage, endocrine disruption, hormonal imbalance, and these ultimately impact the neurodevelopment (Surana et al., 2022). Decabromodiphenyl ether is a carcinogen that impairs fertility, thyroid function, growth and neuronal mechanisms, which ultimately impair the fetal brain formation (Zhao et al., 2018). Therefore, brominated flame retardants lead to implanted or genetic abnormalities by immune cell disruption and hormonal imbalance (estrogen, androgen, progestatic, thyroid) (O'Connor et al., 2022). On the other hand, exposure to phthalates can lead to premature birth and spontaneous abortion (Das et al., 2021). Additionally, exposure to chemical pesticide compounds can cause behavioral changes and hormonal implications: ovarian tumor, reduced sperm production, shrinkage of eggshells, thyroid disorders, etc. (Sun et al., 2020). A study on the genome of mice and bacteria has found the musk "xylol", a widely used synthetic fragrance (absorbable by human tissues), to be potentially neurotoxic and carcinogenic (Saggioro, 2021).

However, correlating the exposure to these contaminants and their direct impacts (similar causes and effects) on human health is complex, particularly field observations involving multiple species at different levels (Sridharan et al., 2022). Nevertheless, the tensile properties of these contaminants make them hazardous to the environment and health (Kumar et al., 2022a,b). For instance, bisphenol A is a neurotoxin that impairs cell division in flora and fauna (Jafari et al., 2021). Perchlorates, even at low concentrations, inhibit the development of thyroid and brain in living wellbeing through the infected mothers (gestational exposure) (Knight et al., 2018). Moreover, certain chemicals like perfluorochemicals (PFCs) can inhibit metabolic processes involved in cell wall formation for protein transfer. Studies on model animals have shown that fetal exposure to phthalates can impair male reproductive organs and lead to cognitive impacts. Phthalates can also impact the health of livestock: hepatic, renal, mammoid, and thyroid insufficiency (Das et al., 2021). More concerning hazards include partial deafness, fetal deformity, delayed adolescence, sperm quality reduction, persistent thinking, memory and behavioral issues, thyroxine disorder, etc. (Rathi and Kumar, 2021; Bai and Acharya, 2017).

3.3.2. Impact on environment/ecosystem

Growing concern has been expressed regarding the environmental and ecological effects of PPCPs, much like the effects on human health (Chaturvedi et al., 2021). PPCPs may exist with other co-pollutants in the surrounding environment and, as a result, even at low quantities, they can adversely affect the environment and ecosystem (Oluwole et al., 2020). Antibiotics are frequently used in animal husbandry for preventative the growth of harmful microbes, and their excessive use leads to the environmental genetic selection of more dangerous microbes (Awasthi et al., 2022b). Numerous pathogenic species, including bacteria, have been shown to develop induced drug resistance as a result of antibiotic exposure. Steroid hormones used as birth control, contraception, and sex enhancers frequently disrupt the endocrine system or function as anti-androgenic ligands (Surana et al., 2022; Katibi et al., 2021). Endocrine disruption that has negative impacts on some vertebrate species, including fish, mollusks, and other aquatic animals, by inducing sterilization, the imposition of sex organs, and feminization (Oluwole et al., 2020). For example, Solé et al. (2003) found that fish feminization and decreased infertility were produced by the presence of the sex hormones such as estrogen and progestogens at concentrations nearly 1.0 g/L. Even at a low dose of 5 g/L, diclofenac produces negative health impacts on rainbow trout. On the other hand, zebrafish exposed to a cocktail of acetaminophen, carbamazepine, gemfibrozil, and venlafaxine at doses ranging from 0.5 to 10 g/L showed effects such tissue degradation, a decrease in embryo production, and an increase in embryo mortalities (Galus et al., 2013; Schwaiger et al., 2004). It has also been noted that exposure to endocrine-disrupting contaminants in the aquatic environment can alter the activities and functions of various physiological traits in some non-target aquatic vertebrate by modulating the hypothalamus-pituitary-gonad, hypothalamus-pituitary-thyroid, and hypothalamus-pituitary-adrenal systems (Archer et al., 2017). The endocrine systems of non-target vertebrate residing in

WWTP effluent may also be adversely affected by naproxen and ibuprofen, which are frequently not removed from WWTPs. For instance, the Japanese Medaka fish (*Oryzias latipes*) showed delayed hatching when treated to 0.1 g/L of ibuprofen (Oluwole et al., 2020). According to earlier research, veterinary diclofenac may have a harmful impact on the variety of birds, including steppe eagles and vultures in South Africa and India, respectively (Zhang et al., 2022). The UV sunscreen ingredient benzophenone-3 is dangerous for coral reef conservation in Hawaii and the US Virgin Islands and poses a threat to the ability of coral reefs to adapt to climate change (Downs et al., 2016).

According to Martins et al. (2017), exposure to triclosan and 4-methylbenzylidene camphor resulted in developmental abnormalities (up to 3 %) in frog embryos and negative impacts on the early phases of frogs' lives. Inducing oxidative stress and apoptosis in the marine copepod (*Tigriopus japonicus*) may also cause 4-methylbenzylidene camphor to be harmful to development, reproduction, and even life (Chen et al., 2018). According to the risk assessment, 4-methylbenzylidene camphor can seriously endanger marine ecosystems and crustaceans at environmentally relevant concentration (Chen et al., 2018). Other findings indicate that the freshwater insect (caddisfly) can be adversely affected by benzophenone-3 and 4-methylbenzylidene camphor in ecologically relevant concentration (Campos et al., 2017). Polycyclic and neuromuscular chemicals inhibit (long-term) membrane-resistance structures powered by specific carrier proteins in certain marine invertebrates like *Mnemiopsis* sp. Triclosan and its degradation products (like methyl triclosan) can accumulate in the fatty cells and tissues of fish and harm marine biodiversity. Overall, PPCP residues are frequently found in marine animal tissues, although the trophic transfer of these substances within the food web is still poorly understood (Reyes et al., 2021). The ecotoxicity and environmental hazards of the PPCPs in wastewater can be biologically assessed by novel sophisticated methods linking "omics" (Kumar and Kumar, 2022; Scaria et al., 2020). The detailed discussion on PPCPs remediation technologies have been provided below.

4. Remediation technologies

4.1. Physical

There are various technologies available to remove PPCPs and emerging pollutants from aquatic streams as summarize in Table 4. However, physical treatment techniques do not involve biological and chemical agents, and hence removes pollutants without altering their biochemical properties (Ahmed et al., 2021). Various physical processes are being used in the WWTPs for the removal of PPCPs: adsorption, membrane filtration, sedimentation, etc. Sedimentation involves the removal of suspended solids by gravity, which is less efficient as some of the PPCPs are hydrophilic in nature (Zhang et al., 2022). Fig. 3 representing the conventional wastewater treatment operations. Therefore, the present review focuses mainly on the application of membrane filtration and adsorption for the removal of PPCPs from aquatic media.

4.1.1. Membrane technology

As the conventional treatment methods like activated sludge, sand filtration, coagulation and flocculation cannot effectively remove PPCPs, further efficient industrial treatment technologies have been developed: adsorption, ozonation, enhanced oxidation, membrane separation, etc. (Vieira et al., 2020; Huang et al., 2021). Membrane technology is a physical technique that involves filtration of wastewater and able to remove diverse size ranges (micro to nano) of contaminants via specialized membranes with diverse filtration characteristics (hydrophobicity, surface charge, pore size) to facilitate the contaminant removal. Novel high-pressure membrane technologies like nanofiltration, reverse osmosis, etc. have been applied to remove emerging pollutants (Saidulu et al., 2021). These techniques have also been employed at commercial scale for treatment and recycle of drinking water and removal of ECs from contaminated surface water. There are a few more membrane techniques for potentially treating ECs like electrodialysis, distillation, and forward osmosis, etc., though not applicable on a large scale. However, with growing research, membrane techniques like reverse osmosis (RO) have been developed to provide a suggestively better and effective removal rate (99 %) for pollutants (Dhangar and Kumar, 2020). Integration of membrane distillation with an enzyme bioreactor has shown effective degradation (90–99 %) of 13 phenolic and 17 non-phenolic pollutants (Ensano et al., 2019; Saidulu et al., 2021). Electrodialysis reversal can be applied for emerging ionized contaminants. Pharmaceutical drugs can be removed by employing nanofiltration (NF) membranes with sieving, electrostatic repulsion, and adsorption (Gogoi et al., 2018), which is a promising choice to treat diverse range of ECs. Studies on the treatment of pharmaceutical compounds including anti-inflammatory or inflammatory drugs, H_2 receptor antagonists, antipsychotics, antibiotics (fluoroquinolone, nitroimidazole, macrolides, sulfonamides), platelet activators and inhibitors have reported RO employing bioactive membranes to achieve efficient (99 %) removal (Ensano et al., 2019; Pathak et al., 2018; Saidulu et al., 2021).

Table 4
Summarizing the various techniques to remove emerging pollutants and PPCPs.

Treatment method	Emerging pollutant	Pollutant concentration (μg/L)	Removal efficiency (%)	Removal mechanisms	Reference
Wetland system	Acetaminophen	3.50	99	Biodegradation and sorption	Guedes-Alonso et al. (2020)
	Bisphenol A	3.50	99	Biodegradation and sorption	Guedes-Alonso et al. (2020)
	Diclofenac	0.77	89	Biodegradation and sorption	Guedes-Alonso et al. (2020)
	Triclosan	0.15	79	Phytoremediation	Ahmed et al. (2021)
	Tonalide	0.54	90	Phytoremediation	Ahmed et al. (2021)
Adsorption	Amoxicillin	1–20	93.5–99	Biosorption	Langbehn et al. (2021)
	Coumestrol	1–20	93.5–99.0	Adsorption and photocatalytic degradation	Zhang et al. (2021)
	17a-Ethinyl estradiol	100	92.4	Ionic exchange and hydrophobic partitioning	Smiljaníc et al. (2020)
	Estrone	100	96.9	Ionic exchange and hydrophobic partitioning	Smiljaníc et al. (2020)
	Estriol	100	90.4	Ionic exchange and hydrophobic partitioning	Smiljaníc et al. (2020)
	Equilin	100	94	π–π interactions, dispersion interactions, electron donor-acceptor, and hydrogen bonds	Lima et al. (2019)
	Daidzein	1–20	92.0–98.4	Adsorption and photocatalytic degradation	Zhang et al. (2021)
	Paracetamol	30	100	π–π interactions, dispersion interactions, electron donor-acceptor, and hydrogen bonds	Lima et al. (2019)
Advanced Oxidation and UV/ Chlorine Processes	Benzotriazole	1	73	Catalytic degradation	Rathi and Kumar (2021)
	Carbamazepine	1	90	Catalytic degradation	Huang et al. (2021)
Thermophilic bioreactor with membrane distillation	Atrazine	5	98	Biodegradation and membrane filtration	Saidulu et al. (2021)
	Clofibric acid	5	100	Biodegradation and membrane filtration	Ensano et al. (2019)
	Gemfibrosil	5	100	Biodegradation and membrane filtration	Saidulu et al. (2021)
	Propoxur	5	100	Biodegradation and membrane filtration	Saidulu et al. (2021)
	Primidone	5	100	Biodegradation and membrane filtration	Saidulu et al. (2021)

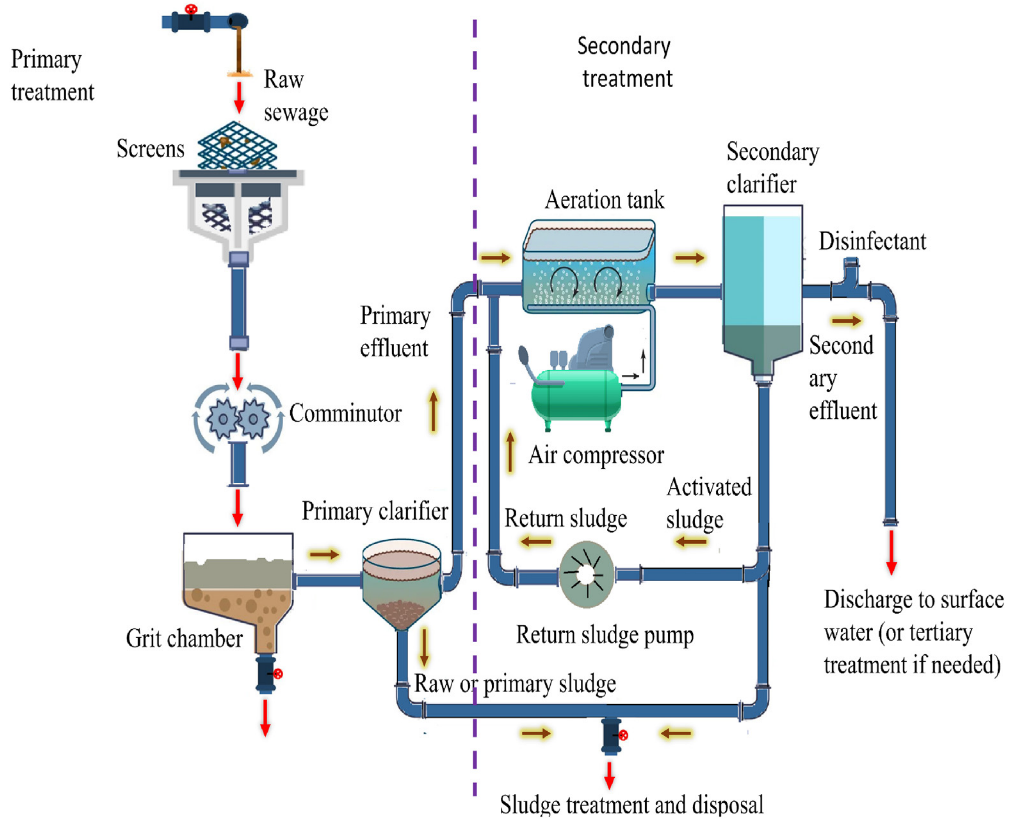

Fig. 3. Schematic representation of conventional wastewater treatment operations.

Therefore, physical treatments like membrane filtration and adsorption are more efficient than chemical or biological methods for contaminant removal. Nevertheless, further research and refabrication are needed to apply these techniques at a large scale for treating a wide spectrum of PPCPs and ECs. Moreover, after treatment, disposal of the remaining stream of contaminants is a huge challenge as there would be two distinct effluents (the diluted and the concentrated ones) to be disposed separately (Khan et al., 2020). These residual contaminants need to be degraded integrating other sustainable techniques. Studies report improved detention and degradation efficiency for integrated approaches. For instance, physical techniques, when combined with chemical oxidation, have increased removal efficiency and limits the disposal issues (Rosman et al., 2018).

4.1.2. Adsorption

In adsorption, chemical compounds are extracted from liquid phase and transferred to solid phase. In various environmental compartments, adsorption occurs as a natural course of mechanism. In WWTPs or during the effluent discharge, the pharmaceuticals (or any target compound) interact with the solid and liquid phases. A solid substance called adsorbent is used to attract the contaminant (adsorbate) (Urtiaga, 2021; Taoufik et al., 2019; Dhangar and Kumar, 2020), which is an effective method to segregate the contaminants in a diluted stream (trace levels). It also allows efficient recovery, recycle and multiple reuses of the adsorbent (Urtiaga, 2021) (Fig. 4). Adsorption occurs in three stages: (1) External (film) diffusion: the contaminant (adsorbate) transfers to the surface of the adsorbent; (2) porous diffusion: the adsorbate migrates from the surface to the pores of the adsorbent; (3) surface reaction of the adsorbate: the adsorbate adheres (fixes itself) to the pores of the adsorbent. Though this recent technology is recognized as the best available technique to remove PPCPs, treatment or disposal of the adsorbate (adhered chemicals) and renewal of the adsorbent are a few challenges to be addressed (Baskar et al., 2022). However, the versatility (can be used for various applications), ease of operation (simplicity) and less susceptibility (the adsorbents are usually insensitive to toxic chemicals) make this adsorption technique an effective and promising approach for wastewater treatment (Yaashikaa et al., 2019). The available studies have explored the feasibility of adsorption techniques for the removal of diverse range of ECs from various sources: drinking water, wastewater from perfume products, paper industry, pharmaceuticals, sludge, fertilizers, silt and soil, etc. Many sorbents have been investigated: mineral substance, metal-organic complexes, biochar, zeolites, polymers, activated hydrochar, AC, graphene, carbon nanotubes, organic carbon complexes, clay mesoporous nanocomposites, activated composite carbon materials, etc. (Kumar et al., 2022a,b; Baskar et al., 2022; O'Connor et al., 2022). Various nanocomposites have been exploited as potential adsorbents for ECs in WWTPs (Bolan et al., 2022). AC is a common adsorbent to remove antibiotics and other organic chemicals via non-specific scattering, i.e., van der Waals interactions between molecules. Electrostatic interactions occur between the surface charge group of AC and the oppositely charged ionic or polarized antibiotics. Hence, AC is a promising adsorbent to remove a wide array of charged and hydrophobic pharmaceutical compounds from water. A wide range of materials can be utilized as adsorbents: AC from minerals, plants or animals; fly ash, organic or ion exchange resins, carbon nanotubes, chitosan, etc. The cost involved in development, application and regeneration of the adsorbent must be considered and linked with its efficiency and regeneration capacity in order to understand the cost-effectiveness of the process (Baskar et al., 2022). From the economic aspect, "low-cost adsorbents" are always preferred, which are abundantly available naturally, from waste or as by-products (from manufacturing) that require little to no processing. The processing cost can offset the procurement cost of the final materials (Yaashikaa et al., 2019). Thus, thorough cost analyses are required to estimate the feasibility. There are many sustainable sources for low-cost adsorbents: animals, plants, bark, clays, keratin, hair, fruit leftovers, mosses, algae, etc. The levels of various emerging pollutants like bisphenol A, 17-estradiol, fluoroquinolone acids, and 17-ethynylestradiol, have been consistently rising in wastewater over the last few years. Powdered AC is a potential

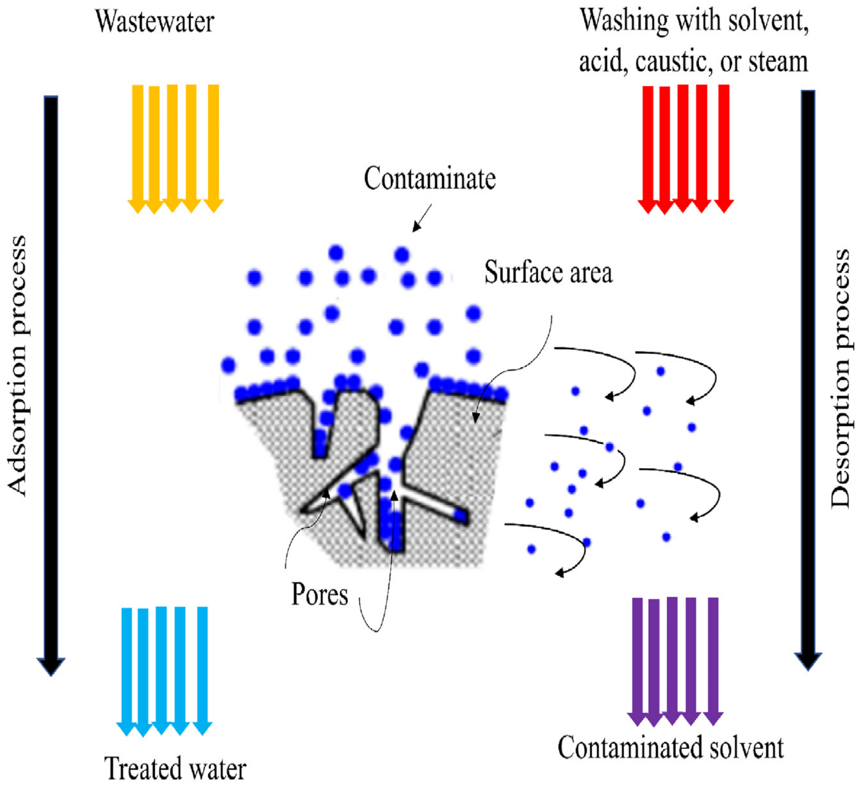

Fig. 4. Adsorption and desorption processes of wastewater contaminates.

adsorbent for salicylic acid, caffeine, gallic acid, diclofenac, clofibric acid, floxacins, and ibuprofen. However, due to the increased pore size and surface area, biochar can achieve a significantly higher (5–30 % than powdered AC) removal of benzophenol, 17-estradiol, bisphenol A, and benzotriazole (Patel et al., 2019). Natural clay can potentially adsorb trimethoprim and amoxicillin. Zeolites can potentially remove fluoroquinolone and enrofloxacin, where the adsorption of enrofloxacin can be enhanced by 50 % by adding ammonia (increase from 50 to 200 mg/L) (Iervolino, 2020). At temperatures from 5 to 35 °C, fluoroquinolones can be effectively removed (99 %) using modified zeolites with TiO_2 (0.3 g). Hence, adsorption is a viable option for wastewater treatment because of the low adsorbent cost and ease of use. Before choosing the precursors, a few factors need to be considered: material accessibility, hazard, pore diameter, oxygen and carbon content, thermal properties, thermal stability, resistance to abrasion, which indicate the chemical, morphological, textural and structural characteristics of the suitable adsorbent. A few commonly characterization methods have been employed to characterize the adsorbents include Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) zeta potential, scanning electron microscopy (SEM), and nitrogen physisorption, point of zero charge (PZC) (Quesada et al., 2019; Zhang et al., 2020).

4.2. Chemical

Biological treatment can effectively remove the majorly targeted EC depending on the operating parameters and wastewater characteristics. However, chemical treatment like chemical oxidation processes is employed as novel polishing techniques to further enhance the removal efficiency (Xiaohong and Chongchen, 2021; Yu et al., 2020). Usually, chemical treatments mineralize the contaminants into innocuous (less hazardous) or a biodegradable state by transforming them into inorganic compounds (Surana et al., 2022). However, many external chemicals need to be utilized: metal oxides, hydrogen peroxide (H_2O_2), chlorine, ozone, metal-based catalysts, along with external agents: sun (UV radiation), ultrasound, gammas, and electric current (Priya et al., 2022; Masud et al., 2020). There are two different methods for chemical oxidation: conventional oxidation and advanced oxidation.

4.2.1. Conventional oxidation

A few methods of conventional oxidation are the Fenton process, chlorination, ozonation, and photolysis. Bromine and chlorine (less reactive species) can influence the removal of ECs. Studies have reported that a contact period of 1 h (60 min) can significantly eliminate naproxen (95 %), EE2 (100 %), and diclofenac (100 %), while the removal efficiency was lower (34–83 %) for triclosan, bisphenol A, ketoprofen, nonylphenol, and ibuprofen under the same conditions (Zhang et al., 2020; Leng et al., 2020). Increased contact time and doses of chlorine can increase the removal of contaminants. Yet, due to the possible sub-product generation (during the disinfection process) and low mineralization, this process is not generally preferred (Fenyvesi et al., 2020). When iron (Fe) is added, hydrogen peroxide reactions (the Fenton process) releases hydroxyl radicals (Xiaohong and Chongchen, 2021), which makes the Fenton process viable due to the non-toxicity and easy availability of Fe. However, it generates $Fe(OH)_3$ sludge and is less efficient in contaminant removal (than the oxidation process) (Scaria et al., 2020). Nevertheless, introduction of catalysts (or even light sources) can improve the contaminant removal (Ahmed et al., 2017). Photolysis process treats and degrades the ECs with intense UV radiations (Du et al., 2021). There are two major methods of photolysis: direct (photon directly adsorbed by contaminants) and indirect (photon indirectly adsorbed to contaminants: photosensitizers like H_2O_2) photolysis. UV photolysis (direct) is more effective than H_2O_2 (direct) (Ahmed et al., 2017, 2021). Drugs, antibiotics, and pain relief products can be removed by direct photolysis. In order to enhance the biodegradability, ozonation (powerful oxidant) is a common treatment employed in WWTPs, which practically removes (90–100 %) various forms of ECs as O_3 oxidizes with aromatic rings in the PPCPs (Zhao et al., 2021; Ahmed et al., 2017). Still, it is an infeasible, energy-intensive and highly expensive process owing to the production of O_3 is tedious and energy-demanding. Moreover, treatment and control of the oxidative metabolites and free radicals (hinders the treatment) formed in this reaction are a major challenge, and hence need to be researched and explored further (Meng et al., 2021).

4.2.2. Advanced oxidation processes (AOPs)

AOPs are advantageous and effective than the previously discussed methods. AOPs, either individually, or in integration with other techniques, can increase the degradability of various drugs in water (Rathi and Kumar, 2021). Particularly, the biological oxidation phase is advantageous in several ways, though a few higher chemicals are difficult to degrade. AOPs can be applied before, after or together with biological treatment. AOPs have shown efficient removal (80–90 %), which is further enhanced when integrated with other techniques (90 % removal) like nanofiltration, coagulation, Fenton's reaction, electrocatalytic oxidation, UV radiation, sonolysis, ozonation (Ahmed et al., 2021; Rathi and Kumar, 2021). Hydroxyl radicals can be generated through UV radiation. Studies have reported that new WWTPs and drinking water management systems that employ AOPs to be highly effective and successful. Hydroxyl radicals, though not catalysts, are powerful oxidizing agents that can oxidize the target organic pollutants. However, the characterization of the wastewater to be treated is crucial for any successful treatment approach (Gogoi et al., 2018). Organic pollutants like desethylatrazine, carbamazepine, sulfamethoxazole, iopamidol, diclofenac, 17-ethinylestradiol, benzotriazole and tolyl triazole can be effectively removed by UV- or chlorine-mediated advanced oxidation. Major drugs and other ECs in wastewater can be removed by AOP with ozone. Various PPCPs and drugs like diclofenac, acetaminophen, and ketorolac can be removed using AOPs using heterogeneous solar photocatalysis with TiO_2 (Taoufik et al., 2019; Pandian et al., 2021). Various AOP strategies have been examined for water treatment. AOPs are highly efficient in the removal of impurities by facilitating degradation (Karimi-Maleh et al., 2020), generally employing techniques like photocatalytic oxidation, ozonation, sonolysis, or integration of these approaches (Mathur et al., 2021). AOPs have overcome the limitations and tiresomeness of conventional oxidization processes (ultrasonic treatment, ferrate, photocatalytic, Fenton processes by solar or electric energy) (Dhangar and Kumar, 2020). Arsenic, estrogen and several emerging pollutants can be removed using ferrate (FeO_4^{2-}), a strong oxidant and disinfectant. ECs can be ozonated and coagulated using Fe^{6+} and Fe^{3+} respectively. However, high preparation costs make these techniques expensive and infeasible, which need to be addressed by the future research. Electro-Fenton process can prevent the limitations of the conventional Fenton process, by electrochemically generating H_2O_2 under controlled conditions in situ (Mirzaei et al., 2017). Via generating more oxygen radicals, pollutant degradation and Fe^{2+} production can be accelerated when the electro-Fenton process with UV radiation is combined with the photoelectron-Fenton process. Metoprolol, atendol, tetracycline, acetaminophen, sulfamethoxazole, triclosan, and propranolol can be removed (even at complex or high concentrations) from wastewater effluents using AOPs. However, high operational and maintenance costs are a major drawback of one of the Fenton processes (Mirzaei et al., 2017). This method operates under wide pH conditions for contaminant removal. Photo-Fenton technique could effectively remove (95–100 %) different contaminants except triclosan (Rathi and Kumar, 2021; Ahmed et al., 2017; Mirzaei et al., 2017). UV-mediated photo-Fenton process is more advantageous and effective than solar photo-Fenton process. There are other AOPs-based techniques: anodic oxidation and sonochemical irradiation (ultrasound irradiation). A study has reported effective degradation (70 %) of 23 different emerging pollutants using sonochemical irradiation (Mirzaei et al., 2017). The degradation is facilitated by the breakdown of conjugation bonds in the chemicals.

4.3. Biological

Microbial biodegradation pathways are the most widely used methods of biological treatment of ECs (Zhou et al., 2022). During degradation, organic compounds of high molecular weight are broken down into simpler compounds, which ultimately get biomineralized to inorganic molecules (water, CO_2) by microbes like microalgae, bacteria and fungi (Sooriyakumar et al., 2022; Zhao et al., 2021). During decomposition, microbes utilize these organic compounds for their growth and proliferation (Awasthi et al., 2022a). However, biodegradation gets limited when the toxic organic chemicals inhibit the microbial metabolism and multiplication (Maddalwar et al., 2021), and the microbes require a “co-substate”, which are additional external nutrient or electron acceptor sources (N and P) (Ahmed et al., 2021). Various factors like operation settings, physicochemical properties and biological persistence of the target contaminant, treatment techniques used, etc. influence the contaminant degradation rate (Kumar et al., 2021d). Biological treatments can be conventional or non-conventional depending on the removal efficiency, maintenance, operation, treatment issues, wastewater characteristics, etc. (Ahmed et al., 2017).

4.3.1. Conventional treatment

Conventional treatment consists of a combination of physical, chemical, and biological processes and its treatment efficiency governed by the primary removal methods: biological metabolism and mineralization (Dhangar and Kumar, 2020). Some of the conventional methods include trickling filters, activated sludge, nitrification, moving bed biofilm reactors, biological AC, bacteria, fungi, microalgae treatments. Ahsan et al. (2018) reported efficient removal of ECs in water by microalgae and fungal-based biological treatment. While the endocrine disruptors and PPCPs were degraded effectively (95–100 %), pesticides could not be degraded under the same conditions. Therefore, additional research needs to explore the integration of conventional biological treatment with other biologically active processes (BAP) to enhance pesticide removal. BAP perform adsorption and biodegradation concurrently upon interactions with microbes, contaminants, dissolved oxygen, and granular activated carbon (GAC) (Hena et al., 2021). Though some chemicals (beta-blockers, pesticides, medications) could be removed in this process, it was less effective for some organic compounds (E3, PPCPs, medications, bisphenol A, and octylphenol). Therefore, this technique needs to be integrated with other technologies as hybrids to accelerate the contaminant removal. Anaerobic, aerobic, and facultative microbiological methods facilitate sludge removal in all sewage treatment facility (three-fourth of all), where the suspended particles absorb some energy from the ECs. Though biodigesters, lagoons, stabilization ponds, bioreactors could not degrade PPCPs and a few beta-blockers, the degradation of ECs and pharmaceutical were acceptable (though low). The overall removal of contaminants was based on facultative anaerobic-aerobic process. However, these processes demand a long time for sludge retention, which is disadvantageous (Karimi-Maleh et al., 2020; Zhao et al., 2021). The universal primary removal mechanism for ECs is biodegradation in an aeration tank, which is implemented as the activated sludge process (ASP) (Pérez-Lemus et al., 2019; Karimi-Maleh et al., 2020). The ASP treatment has been found to have a low removal efficacy (>65 %) for medicines, while outstanding efficacies for PPCPs (>78 %), endocrine disruptors (>75 %) and surfactants (>95 %) (Guedes-Alonso et al., 2020). Therefore, to accelerate the removal of ECs and to improve the efficiency, ASP can be integrated with other biochemical or AOP methods. More research on improving the efficiency of trickling filters is required as their removal efficiency was lower (70 %) than that of ASP (>85 %). Similarly, extensive research is needed on the moving bed biofilm reactors for EC treatment (Rathi and Kumar, 2021; Karimi-Maleh et al., 2020; Ahmed et al., 2017). The ECs like oxybenzene, bisphenol A, ketpfenac, galaxolide, salicylic acid, tonalide, ibuprofen, metronidazole, and benzophenone can be removed by the processes of nitrification and denitrification, though the removal of other organic pollutants is incomplete (Ahmed et al., 2017). Anyway, high removal efficiency can be achieved by integrating this technique with MBR (Racar et al., 2020).

4.3.2. Non-conventional treatment

Non-conventional treatment is considered as an advanced and integrated technology in which oxidation and sorption along with biodegradation takes place in a single system. A few instances include artificial wetlands, MBR, and biosorption (Racar et al., 2020). Here, the microbes are immobilized using biomass, biomass oxidation or adsorbents, which has become a common biological treatment process adopted recently (Kumar et al., 2021a) (Fig. 5). Hence, the contact between the microbial biomass and the contaminants are enhanced by this technique. Microbes or other biological materials are used for biosorption; however, the microbes must be alive for high efficiency (López-Ortiz et al., 2018). A vast array of ECs like naprox, 17-estradiol-17-acetate, gemfibrozil, ibuprofen, 4-tert-octylphenol, triclosan, bisphenol A, and pentachlorophenol can be removed by biosorption (Ahsan et al., 2018). High-quality effluents devoid of emerging pollutants can be produced through MBR (Ahsan et al., 2018). MBRs limit the organic compounds by physical retention at the membrane surface by limiting the migration of high molecular weight compounds, which are then subjected to microbiological biodegradation. In comparison to ASP, MBR may be more effective in contaminant removal due to the twin mechanism of sorption followed by biodegradation. MBR can remove beta-blockers, PPCPs, pesticides, medicines, and endocrine disruptors from wastewater. Propylparaben (92 %), atendol (97 %), salicylic acid (99 %), triclosan (99 %), beta-blockers (70–80 %), and other drugs (75–95 %) can be efficiently eliminated by MBR (Patel et al., 2019). However, a few pesticides are not removed effectively in MBR and ASP. However, there are many disadvantages and limitations in MBR like higher costs (than ASP), operational problems, membrane obstruction and fouling, poor removal of ECs. Integrating MBR with ozonation and membrane filters (RO, ultra, nanofiltration), AOP, or other physicochemical treatment systems can minimize these limitations and enhance the removal efficiency for ECs (Priya et al., 2022).

4.3.3. Constructed wetland

Constructed wetlands (CWs) are sustainable built aquatic plant-based systems for reliable and effective wastewater treatment. Due to their ability, low cost, easy maintenance, simple operation, and environmental friendliness have resulted in their worldwide implementation as an alternative to WWTPs (Ávila et al., 2021; Ilyas and van Hullebusch, 2020). Natural wetlands are “living filters” that recover the water quality by becoming ecotones (transitional zones) between water and land. These techniques are extensively exploited to remove total suspended solids, biological oxygen demand (BOD) and contaminants like phosphates, organic compounds (pharmaceuticals, pesticides), and metal ions (Matamoros and Bayona, 2006). CWs have been built to treat pharmaceuticals (Ávila et al., 2021; Ilyas et al., 2020; Nguyen et al., 2019). CWs can replace secondary WWTPs, or utilized to polish effluents from WWTPs (Almuktar et al., 2018). A major drawback of CWs is the lack of studies on the fate and removal pathways (step-by-step) of the target pollutants (Barya et al., 2020; Guedes-Alonso et al., 2020). As the concentrations of only influent and effluent are estimated at present to examine their performance (Reyes-Contreras et al., 2012).

Wetland systems usually do not achieve complete removal of pharmaceuticals, and hence, the efficiency is usually similar to sludge and WWTPs (Zhang et al., 2014; Li et al., 2014; Camacho-Muñoz et al., 2012). CWs can adequately remove (70 %) sulfa drugs, salicylic acid, caffeine, paracetamol, and tetracycline (Li et al., 2014). In plant-based aquatic systems, there is simultaneous occurrence of biological and chemical processes. A few of those processes include microbial degradation, plant uptake, sorption, volatilization, sedimentation, photodegradation, and

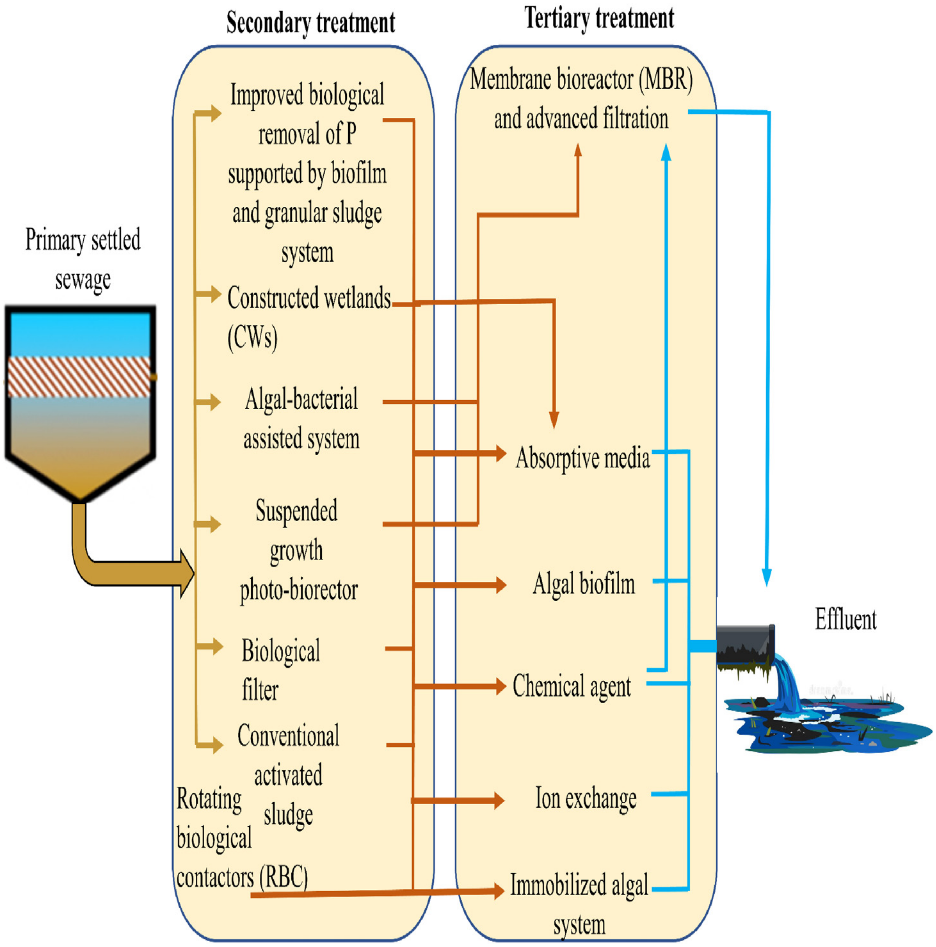

Fig. 5. Schematic representation of integrated biological treatments of wastewater (adapted and modified from Ahmed et al. (2021)).

accumulation (Zhang et al., 2014). Design and operational factors in CWs decide the degradation rates. A few influential factors for the removal of pharmaceuticals include the wetland configuration, presence of vegetation, soil matrix or substrate, depth of bed, plant diversity (types and number of species), mode of loading (continuous or batch operational mode), organic and hydraulic loading rates (Ávila et al., 2013; Pedescoll et al., 2011). Different designs of wetland are effective for different types of pharmaceuticals, and hence, configuration is an important factor for wetland design.

Trimethoprim, salicylic acid, carbamazepine, sulfadimethoxine, sulfamethoxazole, clarithromycin, naproxen, doxycycline, and ketoprofen can be effectively removed by horizontal subsurface flow constructed wetlands (HSSF-CWs), but ibuprofen and amoxicillin are poorly removed (Li et al., 2014). HSSF-CWs, surface-flow constructed wetlands (SF-CWs), lagoons, and ponds can be integrated to form hybrid CWs, which can improve the overall removal efficiencies (Chen et al., 2016; Li et al., 2014). Ibuprofen, salicylic acid, diclofenac, and naproxen are more efficiently removed by vertical subsurface flow constructed wetlands (VSSF-CWs) than other CWs, possibly due to shorter hydraulic retention times, better conditions in unsaturated flow for oxygenation, and the low sensitivity towards overloading conditions (Matamoros et al., 2007). Only a few studies exist on the use of VVSF-CWs for treatment of pharmaceuticals, and hence, it is unestablished if it is actually advantageous than the other types of wetlands.

Phytoremediation, which plays a key role in CWs, is significantly dependent on the plant uptake, bioaccumulation, and translocation of the contaminants to their own internal systems for cellular detoxification (Bhanse et al., 2022; Hassan et al., 2021; Barya et al., 2020). Initially, the plant root uptake of pharmaceuticals was believed to be influenced (directly proportional) by the values of log K_{ow} (Chuang et al., 2019). However, recent studies have shown that the uptake of some pharmaceuticals do not depend on their hydrophobicity or log K_{ow} values (Calderón-Preciado et al., 2012). A model-based study has proposed that hydrophilic compounds tend to have high root uptake and translocation (Zhang et al., 2013). Several transformations occur in the contaminants after uptake and translocation: (1) chemical modification (oxidation, reduction hydrolysis); (2) conjugation (combines with glutathione, amino acids or sugars); (3) compartmentation and sequestration (contaminants converted to their conjugates, accumulated in cells (vacuoles), adhered to lignin and cell walls) (Patel et al., 2019; Prasad et al., 2022).

For the removal of pharmaceuticals in CWs, photodegradation has been suggested to be the chief pathway (Ilyas and van Hullebusch, 2020; Ilyas et al., 2020). However, a study in Spain reported that in a free water surface constructed wetland (FWS-CW), the degradation of recalcitrant diclofenac and ketoprofen to be primarily mediated by photodegradation (Llorens et al., 2009). Later, photodegradation was confirmed as the chief mechanism for the breakdown of ketoprofen (Matamoros et al., 2012). The removal of contaminants is highly dependent on the irradiation and temperature. In comparison to the winter period, significantly higher removal of pharmaceuticals can be achieved in summer due to increase temperature and intense irradiation, leads to photodegradation (Li et al., 2014).

4.4. Emerging and hybrid treatment technology

One of the aims of the present study has been to explain how the novel treatment techniques can address the limitations of the conventional approaches to treat the emerging pollutants in water.

Combined biological treatment integrates biodegradation with photocatalysis, which is renewable, eco-friendly, low-cost option for wastewater treatment. The major components here are the biofilm (microbes), permeable carriers and photocatalysts (Priya et al., 2022). The core paradigm that integrates photocatalysis with biodegradation is the photocatalyst over a porous membrane that converts complex xenobiotic pollutants into degradable forms (Jafari et al., 2021; Yu et al., 2020). Emerging pollutants can also be removed using electrochemical approaches. Effective degradation of pollutants can be aided by Fenton reaction (Mirzaei et al., 2017). Non-imprinted polymers with can also help managing merging contaminants from effluents. Mainly anaerobic digestion is the major process that biodegrades most of the ECs. One of the modern anaerobic digesting technologies is the anaerobic membrane bioreactor, which has a high device stability and vast microbial communities. Emerging pollutants undergo better anaerobic decomposition in the membrane system of anaerobic bioreactor than in the conventional anaerobic digestor, thus significantly increasing the biogas production. Recently, anaerobic membrane bioreactors have been employed to treat atmospheric pollutants, which provides practical data for enhancing their performance and efficiency to treat ECs (Saidulu et al., 2021). Ozonation cycle has been widely employed to treat toxic organics and disinfection of water and wastewater. However, the ozonation phase is less effective in oxidation and ozone consumption. These limitations may be overcome by a recently popular technique, catalytic ozonation (Xiaohong and Chongchen, 2021). In order to minimize the hazards of emerging pollutants on the public health and environment, biological wastewater treatment is preferred, which employs microorganisms to degrade the toxic compounds. However, bio-based treatment process has several limitations such as low inefficiency, high cost, and lack of specificity. The advantages and limitations or drawbacks of several available treatments for emerging pollutants have been represented in Table 5. For biological treatment, the inherent tolerance and potential of microorganisms to grow in contact with the contaminants and to degrade them are critical aspects for a successful field application (Zhang et al., 2020).

For efficient adsorption of PPCPs, hybrid synthesis is a promising method to fabricate and activate novel adsorbent materials (Dotto and McKay, 2020). For effective removal of emerging pollutants, a hybrid system can be applied using AC, carbon adsorption, ultrasonic irradiation, and membrane ultrafiltration (Table 6). Ultrafiltration followed by AC adsorption can efficiently remove ECs. The recent incorporation of biochar-based composites into AOPs has significantly benefited the catalytic degradation and adsorption processes (Rathi and Kumar, 2021; Anerao et al., 2022b; Kumar et al., 2022a,b). carbon-based nanocomposites have been commonly utilized as adsorbents in wastewater treatment (Madima et al., 2020). However, despite these advantages, nanomaterials, owing to their tiny size, can also enhance the toxicity of the conventional products. Nanoparticles can easily interact with the biotic and abiotic components, with host aggregation leading to bioaccumulation, biomagnification, and consequently biotransformation in the human body via environmental chemical exposure (Pesqueira et al., 2020).

In order to enhance the medicinal adsorptive properties of graphene, innovative compounds are incorporated into graphene-based nanoparticles. Photocatalysts can be combined with electromagnets and coated on fiber optics, and the membrane vessels can be integrated with the adsorbents to improve the water treatment by photocatalysis (Wang et al., 2021). For an efficient adsorption, AC in an iron-packed form can be enriched with activated procedure (Rathi and Kumar, 2021; Yaashikaa et al., 2019). A few nanocomposites for organic pollutant treatment include inorganic nanomaterials and carbon-based nanomaterials. Adsorption, degradation, and oxidation are the most widely applied nanoparticles-based methods to remove organic pollutants (Leng et al., 2020; Kumar et al., 2022a,b). Nanobiochar, which is fabricated by mechanized crushing and top-down approach along with conventional methods, can be utilized to eliminate highly toxic components including antibiotics and fertilizers from water (Kumar et al., 2020b; Abhishek et al., 2022). Studies have reported *Dendro* nanobiochar to be a highly efficient nanomaterial for removing emerging pollutants by a great partition coefficient (Karthik and Philip, 2021). Magnetic support to the nanoparticles can provide convenient and accelerated magnetic isolation. Interactions of magnetic nanoparticles with the biomaterials can potentially increase their adsorption capacities (Rao et al., 2021). Magnetic AC can effectively remove (96.77 %) paracetamol and amoxicillin and paracetamol from aqueous solutions (Khan et al., 2020).

Table 5
Pros and cons of various treatment methods applied for treating PPCPs and emerging contaminants containing wastewater.

Treatment process		Pros	Cons	Reference
Physical processes	Adsorption	♦ Depending on the contaminants to be removed, versatile adsorbent materials are available. ♦ Waste materials can be used to create adsorbents and remove a wide range of ECs.	♦ Contaminant disposal issues in the concentrated solid phase. ♦ Occurrence of organic suspended particles.	Ahmed et al. (2017); Langbehn et al. (2021)
	Coagulation	♦ Decreases the turbidity induced by suspended particles.	♦ Sludge formation in large quantities.	Ahmed et al. (2017)
	Nanofiltration	♦ Effective for wastewater and saline water treatment. ♦ Useful for removing dyes and pesticides.	♦ Membrane fouling. ♦ High energy consumption. ♦ Issue of waste disposal.	Urtiaga (2021)
	Reverse osmosis	♦ EDCs and PPCPs Are removed effectively. ♦ Effective at getting rid of pathogens.	♦ Disposal of toxic waste products from wastewater treatment. ♦ Less porosity results in a removal of pharmaceuticals that is less effective.	Ahmed et al. (2017)
	Ultra/Micro Filtration	♦ Designed specifically to remove heavy metals.	♦ High operational cost. ♦ Only partially successful in eliminating ECs.	Ensano et al. (2019)
Chemical processes	Advanced Oxidation Processes (AOPs)	♦ ECs are removed with high efficiency. ♦ Suitable for sterilization. ♦ Pollutants are degraded in a short period of time.	♦ Production of reactive oxygen species.	Iervolino (2020)
	Ozonation	♦ Reduces turbidity caused by suspended particle sedimentation. ♦ High levels of ECs are eliminated when H_2O_2 is present.	♦ Effective at getting rid of micropollutants. ♦ Formation of beneficial by- products.	Ahmed et al., 2017 Mathur et al. (2021)
	Photo-Fenton and Fenton	♦ UV radiation has the ability to mineralize and break down ECs.	♦ Huge sludge production. ♦ The number of anions in treated wastewater is significant.	Iervolino (2020)
	Photocatalysis (TiO_2)	♦ Degradation occurs to persistent organic pollutants in the environment. ♦ The rate of the reaction is accelerated by the use of a catalyst. ♦ TiO_2 catalyst is inexpensive, chemistriically stable, and simple to extract	♦ The cost of the process is increased using artificial UV lights. ♦ It is challenging to separate and reuse photocatalytic particles in a slurry suspension.	Mathur et al. (2021)
	Sonochemical	♦ Effective in fully degrading and mineralizing EC. ♦ Pollutants are quickly degraded.	♦ Bubble size and the presence of hydroxide radicals have an impact on the process. ♦ Finding the ideal ultrasonic frequency to correlate all the characteristics is difficult.	Mathur et al. (2021)
Biological processes	Activated sludge	♦ Cheaper and easy to operate than alternative treatments. ♦ Eco-friendly treatment.	♦ Eliminating beta blockers and medications has a lower impact. ♦ Difficult for increased COD load (>4000 mg/L).	Xiaohong and Chongchen (2021)
	Algal reactors/ponds	♦ Recovered biomass can be applied as fertilizer. ♦ It produces exceptional wastewater with little acute toxicity risk from ECs.	♦ Degradation of ECs is less efficient. ♦ Ineffective in colder regions.	Pandian et al. (2021)
	Constructed wetlands	♦ Low cost and energy consumption. ♦ Pathogens, insecticides, PCPs, and estrogens are effectively eliminated.	♦ Problems with solid entrapment and clogging are brought on by increased silt development. ♦ Leads to the development of biofilms and chemical precipitation.	Ahmed et al. (2021)
	Trickling filters (Biofilm reactor)	♦ Energy efficient. ♦ Cost effective.	♦ High costs of maintenance.	Pérez-Lemus et al. (2019)

5. Challenges and economy associated with remediation technologies of PPCPs

Discharge of ECs into water sources is a major environmental challenge of this century. The global population explosion has led to an increased demand for freshwater and drinking water sources. Rapid urbanization and population increment have increased the global volume of wastewater from industrial and domestic sources (Choudhary et al., 2020). Moreover, besides climate change, the never-ending industrial development and agricultural land expansion have created a huge demand and pressure on the

Table 6
Hybrid treatment methods through coupled physical, chemical, and biological techniques for the removal of PPCPs and emerging pollutants.

Specification	Treatment process	Target PPCPs	Removal mechanisms	Removal efficiency (%)	References
Progressive treatment	Powdered activated carbon coupled with + submerged membrane filtration	Nonylphenol ethoxylates	Coagulation, filtration, adsorption, biodegradation	75	Nguyen et al. (2021)
	Ultrafiltration with powdered activated carbon (UF/PAC)	*17α-ethynylestradiol (EE2)*	Filtration, adsorption	80	Katibi et al. (2021)
Physical + chemical treatment	Dual-pulse ultrasound + electrochemical degradation (US-ECD)	Nitrobenzene	Electrochemical degradation	80	Xia et al. (2014)
	Fenton + Sonication	Ibuprofen	Sonolysis and sono-Fenton oxidation	59	Adityosulindro et al. (2017)
	GAC + Fenton	Carbamazepine	Fenton oxidation, filtration	49.39	Dwivedi et al. (2018)
Physical + biological treatment	NF + RO	Estrogen		73–85	Tan Xin (2004)
	RO + MBR	E2, E1	Filtration	99.60, 99.40	Surana et al. (2022)
	GAC + MBR	E1, E2, E3, EE2, BPA, triclosan, ibuprofen, 4-tetra-butylphenol, 4 n-nonylphenol	Filtration	100	Goswami et al. (2018)
Chemical + biological	Biological treatment + Photo-Fenton	Pharmaceuticals	Biodegradation, Photo-Fenton oxidation	95	Perini et al. (2018)

freshwater sources for cities, industries and agriculture, leading to the global water scarcity. The mismanagement and improper control of wastewater sources have adverse impacts on the environment and humans as the development of town attracts investors and population, which adds pressure on the capacity of these urban areas to meet the basic needs of the migrating population (Ambika et al., 2022). Especially in residential areas, unplanned or improper management of wastewater (industrial and domestic) is a serious threat to the environment and health of neighboring communities. Hence, it is important to develop community awareness along with advanced, sustainable, cost-effective, and high-performance systems for wastewater handling and treatment (Patel et al., 2019; Kumar and Kumar, 2022). Though the development of feasible and efficient wastewater treatment technologies is a tedious and challenging task, it is the need of the hour due to the noticeable impacts of ECs on the biota and ecosystems.

Besides legislation and policy governance, effective wastewater management also depends on the socio-economic and regional conditions. It is tedious and extremely difficult to develop a universal method for contaminant disposal from wastewater stream. In the last few decades, various technologies have been reported and commercialized for wastewater treatment: physical, chemical, and biological (Nie et al., 2020; Kumar et al., 2020a). Each of them has their own pros and cons along with challenges: environmental impact, cost-efficiency, feasibility, effectiveness, sludge production, operational difficulty, and practicability. Therefore, it is important to identify the best method to serve the purpose under specified conditions. Theoretically, these technologies can eliminate emerging pollutants. However, the industrial effluents are complex and contain various types of pollutants altogether, and hence, these methods or technologies cannot achieve complete removal of emerging pollutants (Patel et al., 2019). Hence, practical removal of ECs at the lowest possible cost can be achieved by combining two or more techniques to attain the optimal water quality.

Various methods reported in the literature dealing with preliminary, primary, secondary, tertiary, and advanced wastewater treatment rarely includes cost estimation and large-scale feasibility of the developed techniques. The available literature on pharmaceutical chemicals mainly focused on site-specific treatment methods or treatment of a specific contaminant from the effluent, and hence do not address real-time conditions. Various factors like processing requirements, electricity cost, labor cost, construction cost, other local issues, recycling and lifetime issues, and availability decide the individual cost. Therefore, the cost factor is different for any treatment facility is different at different locations, and hence, the same cost estimation methods cannot be applicable. The cost of a particular adsorbent is influenced by various aspects: availability, lifetime issues, recyclability, and other processing requirements (Baskar et al., 2022), which is unfortunately not addressed by the available literature. Even the cost for precursors of the chosen adsorbents varies at different countries or regions. Moreover, cost reduces if some byproduct (from any prevailing industry) can be utilized as an adsorbent. For instance, biochar from pyrolysis (biorefinery industry) is an inexpensive value-added coproduct (Kumar et al., 2020b, 2021b). Selection of a suitable adsorbent in WWTPs critically depends on the evaluated cost or planned budget (de Andrade et al., 2018; Banerjee et al., 2017; Chakraborty et al., 2018). The capacity of an adsorbent is an important aspect to be considered for the comparative evaluation of various adsorbents. For instance, if a suitable adsorbent is available for a 3-fold higher price but a 5-fold higher capacity, then it is the most appropriate and cost-efficient when all the considerations are equal (de Andrade et al., 2018). The following factors need to be included for the cost analysis for adsorbents: activation, carbonization, size reduction, and collection. Other factors that influence the cost of adsorbents include adsorbent reusability, recovery, cost, and availability (Baskar et al., 2022; Chakraborty et al., 2018). Moreover, the treatment cost of WWTPs increases due to these pharmaceutical compounds reducing the effluent mineralization by 20 % (Durán et al., 2018).

The available data on the adsorbent cost estimation to treat pharmaceuticals in wastewater is limited. Usually, adsorption is less expensive than any other technique (Ahmed et al., 2015). However, these expenses can be further lowered by utilizing sustainable adsorbents from waste products at lower cost. Moreover, affordability and efficiency of the adsorption process also depend on the target pollutant, nature of the wastewater and the additional pollutants present. The cost factor becomes interdependent when adsorption systems are integrated into a multistep WWTP or sewage treatment plant. Based on the amount and type of the adsorbent required, water treatment with adsorption costs around 10–200 USD per million liters of wastewater, which makes it more economically feasible in comparison to other techniques like RO, ion exchange, electrolysis, electrodialysis, which may cost around 450 USD per million liters under similar conditions (de Andrade et al., 2018; Chakraborty et al., 2018). Modern and efficient techniques like AOPs extensively demands expensive chemicals (Durán et al., 2018) and energy (Monteil et al., 2019), which ultimately leads to a high treatment cost. Therefore, integration of chemical techniques with biological processes has been recently suggested to decrease the expenses (Ahmed et al., 2021). There are other emerging technologies of lower operational cost like solar-photo-Fenton method and solar radiation-based wastewater treatment, which are promising. Moreover, ferrioxalate-aided methods operate at neutral pH (~7), which further decreases the operational cost (Durán et al., 2018). Solar energy-powered technologies for wastewater treatment using photovoltaic panels are interesting and promising from environmental aspect, which makes this an interesting evaluation from economic perspective.

Studies have reported the following expected costs (approximated) for different adsorbents: bagasse fly ash (0.02 USD/kg), red mud (0.025 USD/kg), MOF (HKUST-1) (20 USD/kg), biochar (2.65 USD/kg), MOF (MIL-101) (5 USD/kg), bentonite (0.072 USD/kg), chitosan (16 USD/kg), chitosan-based bioadsorbents (8–10 USD/kg), ion exchange resins (150 USD/kg), commercial ACs (20–22 USD/kg) (de Andrade et al., 2018). These costs may vary with treatment conditions, local availability, regeneration, disposal, and the precursors used (natural, synthesized, byproduct, waste). The low production cost of biochar makes it a feasible and excellent adsorbent to replace GAC and other traditional adsorbents for water treatment. For instance, biochar can achieve 20 % higher removal of sulfamethoxazole than GAC and activated biochar (Lin et al., 2017). Therefore, biochar is a potential adsorbent for removing pharmaceutical compounds from wastewater. The cost may further drop if the availability is increased by utilizing biochar as a byproduct from the processes for syn gas and biooil/biofuel production (Rathour et al., 2022; Ambika et al., 2022; Kumar et al., 2021c). The application of biochar as an absorbent can also be exploited for carbon sequestration and agriculture (soil amendment, conditioning) (Bolan et al., 2021; Ding et al., 2023; Mishra et al., 2021).

6. Initiatives, policies and strategies for PPCPs management

In order to enhance the efficacy of drugs, their half-life in the body is increased by imparting biological stability to the drugs during manufacture, which in turn, make them resistant to biodegradation (recalcitrant) and prolong their environmental persistence. Pharmaceutical compounds, being xenobiotics, can permeate cell membranes and lead to toxic impacts to the aquatic biota and public health. Therefore, stringent policy and governmental regulations are immediately required to control the entry of pharmaceutical compounds into different ecosystems. Strict standards for effluent are also required for hospitals, clinical labs, and manufacturing locations globally along with appropriate disposal practices for unused, expired and waste pharmaceutical products. Inclusion of sustainable processes to reduce the pharmaceuticals in the WWTP effluents is the needed. A few national regulatory approaches have been made by the governments of different countries (Glassmeyer et al., 2017; Furlong et al., 2017; Lopez et al., 2015; Murata et al., 2011; Barnes et al., 2008), but international standards have not been established yet. Minimizing and controlling the release of pharmaceutical chemicals are the best approaches to regulate the presence of PPCPs in the environment. However, sustaining and implementing standard guidelines regarding effluent streams along with regulating and monitoring the point sources (industries, hospitals, WWTPs) are the only way to achieve this. For large-scale pollution, segregation and remediation of effluents from industrial and hospital effluents can contribute to a sustainable solution (O'Brien and Dietrich, 2004). The environmental concentrations of pharmaceuticals have been set as 0.01 and 1 μg/L as per the standards of the European Union and the United States Food and Drug Administration (USFDA) respectively (Patel et al., 2019).

The release of pharmaceuticals into the environment can be controlled only by regulating their source and return programs. The major elimination pathway for the PPCPs from the human system is urinal excretion. As human urine can contain significantly higher concentrations (100–500 times) of PPCPs than wastewater (O'Brien and Dietrich, 2004), source segregation of urine from the other household wastewater followed by immediate treatment are ideally desired, which is however impractical and expensive. Therefore, major emphasis is placed on their mitigation in WWTPs and sewage treatment systems, which may lead to reduced effluent discharge of nutrients (like phosphate and ammonium) along with the pharmaceuticals (Escher et al., 2006). The volume of pharmaceutical compounds released from domestic effluents can be regulated by enforcing return programs for pharmaceutical waste (mainly unused, expired drugs) (Bound and Voulvoulis, 2005). A few countries like Spain, Canada, and the USA have already issued national guidelines dealing with the proper disposal of such unutilized and expired pharmaceuticals. Disposal of unused, and out-of-date (expired) or unwanted pharmaceutical products have been included in the guidelines of the United States federal prescription for drug disposal (ONDCP, 2007). British Columbia (Canada) and Spain have a collaborative pharmaceutical return program wherein the pharma industries are required to collect the unused and out-of-date drugs (EMA, 2004). Some countries like The Netherlands, Germany, and Switzerland incinerate the municipal solid waste, which significantly decreases the pharmaceuticals subsequently migrating from municipal solid waste to landfills and agro-ecosystems (Doerr-MacEwen and Haight, 2006). At present, there are advanced technologies like adsorption, advanced oxidation, and ultrafiltration, which can achieve >95 % removal of PPCPs. The accumulation of these harmful chemicals in the environment can be minimized by designing ecofriendly “green” pharmaceuticals with no bioaccumulation and reduced toxicity and environmental persistence. A system for classification of environmental impacts of pharmaceuticals termed “PBT index” has been developed in The Stockholm County Council of Sweden. The PBT index is the totality of the values for toxicity, persistence, and bioaccumulation of the pharmaceuticals, ranked on a scale from 0 to 3, where 0 is the most ecofriendly and 3 is the most hazardous (Gunnarsson et al., 2009). In order to encourage more ecofriendly pharmaceuticals, physicians should discourage the use of drugs with high PBT index.

Conclusion and prospects.

Available studies have established that PPCPs and other ECs can cause significant impacts in humans and fauna (livestock) even at very low concentrations. However, the primary sources of PPCPs are drugs, skin care and personal hygiene products, most of which are unavoidable in day-today life. Nevertheless, identification of these compounds at trace concentrations requires tedious pretreatment (filtration, extraction) and derivatization processes along with sophisticated equipment like LC-MS and GC–MS. As the conventional systems for wastewater treatment cannot remove ECs, additional treatments are required which include membrane technology, constructed wetlands, enhanced oxidation, adsorption, etc. As most of these are expensive techniques, adsorption, a simple technique, is preferred for its convenience and low-cost. However, the efficiency solely depends on the right selection of suitable adsorbents. Additional advancements in the technologies have led to the development of efficient hybrid treatment methods (biodegradation along with physical adsorption, coupling photocatalysis). Recent research advances on these hybrid systems have led to crucial breakthroughs like modified adsorbents and nanoadsorbents which could be combined with other treatment methods. The use of combining MBR treatment with RO or NF membrane treatment as well as use of biochar and zeolites as adsorbent in later stage could be a potential approach for treatment of PPCPs containing wastewater. These recent advancements have overcome various limitations associated with adsorption, and hence adsorption has emerged to be a promising technique to remove PPCPs and other ECs.

Ecotoxicity, clinical impacts and persistence of emerging pollutants in the environment demand more advances in research and water treatment technologies to prevent their release into various ecosystems. Every year, novel pharmaceutical products come to the market, and hence, the possible environmental interactions and impacts of each of them need to be explored. A few recommendations are listed as follows:

- Advanced techniques and analytical methodologies for sensitive, accurate and real-time detection of environmental PPCPs must be developed.
- Research on PPCPs needs to monitor and focus on the rapidly developing industrial nations for potential environmental implications.
- Stringent legislative and regulatory standards need to be implemented for effluent release, with special focus on the point sources such as hospital and industries.
- Strict regulatory standards must be developed and implemented for micropollutants in drinking water and wastewater streams.
- Development, manufacture and advanced applications of pharmaceutical industries must adhere to sustainable and greener technologies.
- More research is needed to understand the clinical and ecotoxic impacts of chronic exposure to micropollutants on humans and biota.
- Pilot-scale implementation of eco-friendly, effective and cost-efficient remediation technologies for PPCPs need to be developed and implemented.
- In addition to advanced remediation techniques in WWTPs, effective strategies must be developed to minimize the environmental release of PPCPs.
- Finally, technoeconomic and life cycle assessment of the PPCPs treatment technologies are required before their widespread implementation in order to determine their economic viability and environmental effects.

CRediT authorship contribution statement

Manish Kumar, Ph.D: Conceptualization, writing-original draft, editing, validation, and supervision: **Srinidhi Sridharan, M.Tech**: Writing-original draft, editing, validation, and visualization; **Ankush D. Sawarkar, M.Tech:** Writing-original draft, validation, and editing; **Adnan Shakeel, Ph.D**: Writing-original draft, editing; **Prathmesh Anerao, M.Tech**: Writing-original draft, editing; Giorgio Mannina, **Ph.D**: Writing-original draft, editing, validation, and visualization; **Prabhakar Sharma, Ph.D**: Writing-original draft, editing; **Ashok Pandey, Ph.D**: Conceptualization, writing-original draft, editing, validation, visualization, and supervision.

Data availability

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

Declaration of competing interest

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

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