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Review

Recent Advances in Biofiltration for PPCP Removal from Water

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Abstract: As emerging pollutants, pharmaceuticals and personal care products (PPCPs) in water have attracted more and more attention because of their harmfulness to the ecosystem and human health. Due to the perpetual input from sewage/wastewater effluents, landfill leachates, urban/agricultural runoff, etc., PPCPs in the aquatic environment are generally "pseudo-persistent". Conventional filtration in the water treatment process cannot effectively remove PPCPs, while biofiltration, a synergistic combination of adsorption and biodegradation, is an effective upgrade method that has received great attention and application in recent years. This paper systematically reviewed the principle of biofiltration and its efficiency in the removal of PPCPs. The important operational parameters influencing biofiltration performance such as filter media, temperature, backwash conditions, empty bed contact time, etc. were summarized. In addition, the limitations and prospects of the current research on biofiltration were also pointed out.

Keywords: PPCPs; biofiltration; activated carbon; biodegradation; empty bed contact time

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1. Introduction

In recent years, the emergence of pharmaceuticals and personal care products (PPCPs) has garnered increasing attention due to pollution concerns [1,2]. PPCPs constitute a large and diverse group of chemicals, including human/veterinary drugs and chemical consumer products, as well as additives and inert ingredients utilized in their production and processing. These chemicals include a range of items such as antibiotics, hormones, anti-inflammatory drugs, antiepileptic drugs, blood lipid regulators, β-blockers, contrast media, and cytostatic drugs for pharmaceuticals; and antimicrobial agents, synthetic musks, insect repellants, preservatives, and sunscreen UV filters for personal care products (Table 1) [3]. Of the pharmaceutical group, antibiotics have received special attention for their wide application in human therapy and livestock agriculture, which contain several subgroups, such as macrolides (e.g., erythromycin and roxithromycin), sulfonamides (e.g., sulfamethoxazole and sulfadimethoxine), and fluoroquinolones (e.g., norfloxacin and ciprofloxacin) [4]. Persistent exposure to antibiotics can result in the emergence of antibiotic-resistant bacterial strains and antibiotic resistance genes (ARGs), posing risks to public health [5]. Hormones, particularly steroid estrogens, constitute one of the most extensively studied pharmaceutical groups, and the most concerned and studied hormones include estrone (E1), estradiol (E2), estriol (E3), and ethinylestradiol (EE2) [4]. The hormones released are thought to be linked to the endocrine-disrupting effects observed in polluted water bodies [6]. Other pharmaceutical groups include analgesics and anti-inflammatory drugs (e.g., diclofenac and ibuprofen), antiepileptic drugs (e.g., carbamazepine and primidone), blood lipid regulators (e.g., clofibrate and gemfibrozil), β-blockers (e.g., metoprolol and propanolol), and contrast media (e.g., iopromide and diatrizoate) [4]. Among personal care products groups, triclosan and triclocarban stand out as the two typical antimicrobial

agents frequently detected in the aquatic environment. Triclosan and triclocarban possess toxic effects and bioaccumulation on various aquatic organisms [7]. The synthetic musks encompass nitro musks (e.g., musk xylene and musk ketone) and polycyclic musks (e.g., galaxolide and toxalide) which have been detected in different kinds of environmental media, exhibiting chronic toxicity and endocrine-disrupting effects [8]. The regularly detected ingredient in insect repellents is N,N-diethyl-m-toluamide (DEET). Parabens serve as typical preservatives, while 2-ethyl-hexyl-4-trimethoxycinnamate (EHMC) and 4-methyl-benzilidine-camphor (4MBC) are commonly used components in sunscreen UV filters [9]. These UV filers have been reported to show joint effects on zebrafish embryo development, leading to an increased risk of death [10].

Table 1. Classification of PPCPs.

	Groups	**Representative Compounds**
Pharmaceuticals	Antibiotics	Clarithromycin, erythromycin, sulfamethoxazole, sulfadimethoxine, ciprofloxacin, norfloxacin, and chloramphenicol
	Hormones	Estrone (E1), estradiol (E2), and ethinylestradiol (EE2)
	Analgesics and anti-inflammatory drugs	Diclofenac, ibuprofen, acetaminophen, and acetylsalicylic acid
	Antiepileptic drugs	Carbamazepine and primidone
	Blood lipid regulators	Clofibrate and gemfibrozil
	β-Blockers	Metoprolol and propanolol
	Contrast media	Diatrizoate and iopromide
	Cytostatic drugs	Ifosfamide and cyclophosphamide
Personal care products	Antimicrobial agents/disinfectants	Triclosan and triclocarban
	Synthetic musks/fragrances	Galaxolide (HHCB) and toxalide (AHTN)
	Insect repellants	N,N-Diethyl-m-toluamide (DEET)
	Preservatives	Parabens (alkyl-p-hydroxybenzoates)
	Sunscreen UV filters	2-Ethyl-hexyl-4-trimethoxycinnamate (EHMC) and 4-methyl-benzilidine-camphor (4MBC)

PPCPs play an essential role in people's daily lives, and public health events such as the coronavirus disease 2019 (COVID-19) pandemic can result in their significant influx into the environment within a short time frame [11]. Numerous studies showed that PPCPs had been detected in surface, ground, and drinking waters, and more than one-third of these PPCPs had been proven to be or likely to be persistent, migratory, and toxic [12,13]. An increasing amount of PPCPs in the environment threaten the ecosystem and human health. For example, the existence of antibiotics contributes to the elevation of microbial resistance, potentially leading to the emergence of drug-resistant bacteria. Diclofenac has been reported to disrupt the biochemical functions of rainbow trout, resulting in tissue damage [14]. Fluoroquinolone antibiotics, particularly ciprofloxacin, were demonstrated to produce genotoxicity in hospital wastewater [15]. Therefore, implementing a suitable water treatment process to mitigate PPCP levels is crucial for the safeguarding of drinking water and the corresponding water resources.

Currently, the conventional water treatment process relies upon coagulation and flocculation followed by filtration and disinfection [16]. Coagulation/flocculation can help remove PPCPs in the water; however, filtration and disinfection have very limited capacity for the removal of PPCPs. Moreover, residual PPCPs in the water can also react with disinfectants to form carcinogenic disinfection by-products (DBPs), especially nitrogenous

DBPs [17]. Upgrading or strengthening the filtration process is an effective strategy to control the concentration level of PPCPs.

Filtration is the removal of particles from the water phase by passing the water through a granular or porous media [18]. Filtration has limited adsorption capacity for the dissolved organic matter, which will be lost when the media become saturated [19]. To enhance and extend the removal capacity of filtration for dissolved organic matter including PPCPs, changing non-biological patterns to biological patterns to form biofiltration is an effective and feasible approach, which combines both biosorption and biodegradation functions, providing many benefits for water treatment [20]. Different from the biological filter process in sewage treatment, biofiltration is often used for drinking water purification. Recently, more and more studies have demonstrated the efficacy of biofiltration on PPCP removal, so a comprehensive understanding of the biofiltration process and its removal efficiency and mechanism on PPCPs is essential. In this review, we summarized the principle and application of biofiltration in removing PPCPs, aiming to evaluate the efficacy of the different types of biofilters, analyze the influencing factors of operation, and establish a theoretical foundation for future applications.

2. Source and Occurrence of PPCPs

2.1. Source of PPCPs

There are many ways for PPCPs to enter the environment, and sewage/wastewater discharge is one of the most important sources, including domestic sewage, hospital wastewater, pharmaceutical wastewater, breeding wastewater, etc. [21] (Figure 1).

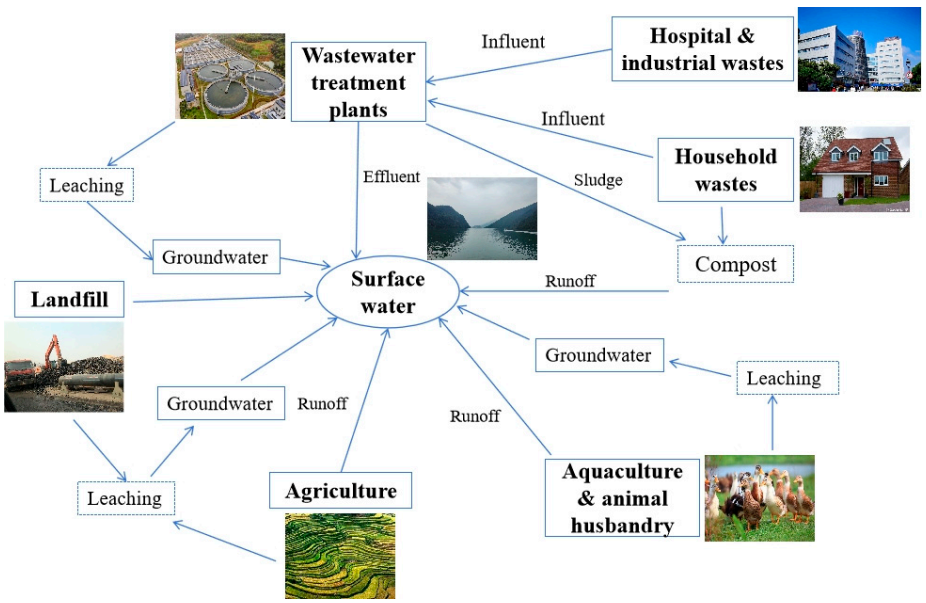

Figure 1. Major routes of PPCPs entering the environment.

PPCPs in domestic sewage primarily include human and animal drugs, and personal care product discharge. Following absorption by the human or animal body, only a portion of drugs undergoes complete metabolism, and the remainder is expelled into the environmental medium through excreta and urine. Studies have found that 50–90% of the drugs taken by humans/animals will enter the environment through excretion [22]. In recent years, the abuse of antibiotics has escalated. In 2014, the World Health Organization (WHO) issued the "Antimicrobial Resistance: Global Report on Surveillance" which indicated that antibiotic resistance had become a problem in all the regions of 114 countries globally [23]. As a kind of emerging chemical pollutant, after entering the environment, antibiotics will cause microorganisms to produce another emerging biological pollutant, i.e., ARGs, posting greater risks to animal and human health.

The wastewater from hospitals and the pharmaceutical industry is another important source of PPCPs. There are diverse and substantial quantities (~10,000 types) of human and livestock drugs in the market [24]. China is a major global producer of pharmaceuticals, and more than 1600 kinds of bulk drugs have been produced in recent years, with an annual production capacity exceeding 2 million tons [25]. With the development of the pharmaceutical industry, the environmental pollution caused by pharmaceutical wastewater is becoming more and more serious. According to the data statistics in 2022, the wastewater discharge from the pharmaceutical industry reached 572.1 million tons per year in China, accounting for 3.9% of the wastewater discharge from all the industries [26]. Antibiotic residues, antibiotic production intermediates, and unreacted raw materials are the most prevalent PPCPs in wastewater discharge. Although there are corresponding discharge standards for the pharmaceutical industry, certain drugs are still difficult to degrade after treatment. These drugs with potential toxicity and high concentrations may find their way into municipal sewage networks or directly into natural water bodies.

In the operation process of a hospital, the wastewater produced with direct or indirect infectivity, toxicity, and other harmfulness is complex in composition, involving a variety of biological, chemical, or radioactive pollutants. Hospital activities have been demonstrated as a relevant source of PPCPs due to the extensive use of medications with a centralized mode [27]. In most countries, hospital effluents are discharged without prior treatment and into municipal wastewater networks where they are treated with other effluents [28]. In the last decade, over three hundred PPCPs were found in hospital wastewater, including their metabolites and derivatives [29]. Therefore, hospital wastewater usually is associated with a danger to public health safety due to its high concentration of PPCPs.

Breeding wastewater is another important source of PPCPs entering the environmental medium. In the farming industry, it is common to use antibiotics to address livestock diseases, and livestock excreta are usually utilized as plant nutrients, resulting in the entry of antibiotics into the soil, and eventually into the surrounding surface water environment [30]. Wu et al. found that the content of PPCPs was higher in the water bodies around farms in rural areas than in other areas [31]. Due to a lack of knowledge about antibiotic safety and the inadequate management of antibiotic use, a large amount of breeding wastewater containing antibiotics has been discharged into surface waters, resulting in moderate and high risk in some rural locations.

Besides the above sources, landfills and agriculture are also important sources of PPCPs in the environment. Landfill leachate containing expired drugs is also a source of PPCPs [32]. The non-degraded components of pesticides used in agriculture can enter the surface water with surface runoff.

Various types of wastewater containing PPCPs converge at the wastewater treatment plants (WWTPs). Given the wide variety and recalcitrant feature of PPCPs, the current secondary treatment process based on the activated sludge method cannot completely remove PPCPs, resulting in the detection of PPCPs in the effluent of WWTPs and re-entering the environment, even the water resources [3]. Due to the perpetual input, PPCPs in the aquatic environment are generally "pseudo-persistent" with a relatively stable concentration [33]. Therefore, drinking water treatment plants (DWTPs) face ongoing risks from PPCPs.

2.2. Occurrence of PPCPs

PPCPs exhibit a widespread distribution in the environment and have been identified in surface water sources worldwide, with concentrations ranging from ng L^{-1} to ug L^{-1}. Table 2 summarizes the concentrations of PPCPs detected in water sources across the globe, as reported in recent years.

Notably, antibiotics are the most frequently detected PPCPs, which is attributed to their extensive production and use globally. Following closely are anti-inflammatory drugs, which are widely employed to treat pain and inflammation. Generally, water systems with detected PPCPs are predominantly found in eastern China and developed countries in

Europe and America. This distribution may be closely linked to the developed economy and relatively high population density in these regions. Given that China is one of the largest producers and consumers of PPCPs, detections have been reported in major surface water sources in China, including Taihu Lake, Liao River, and Honghu Lake along the eastern coast. Moreover, although there are few pathways for PPCPs to enter groundwater, PPCPs have been also detected in groundwater in China, especially in the riverbank and vicinity of municipal landfills [50,51].

Table 2. Occurrence of some PPCPs in surface water.

Compound	Category	Highest Concentration (ng L^{-1})	Source (River/Lake)	References
Oxytetracycline (OTC)	Antibiotics	2796.6	Honghu Lake, China	[34]
Erythromycin (ERY)	Antibiotics	2834.4	Liaoning section of Liao River, China Beiyun River, China Central and lower Yangtze River, China Taihu Lake, China	[35–37]
Roxithromycin (ROX)	Antibiotics	741.0	Beijing urban surface water, China Baiyangdian Lake, China Taihu Lake, China	[35,36]
Ciprofloxacin (CIP)	Antibiotics	414.0	The urban area of Beijing and the Liaoning section of Liao Rivers, China	[35,38]
Difloxacin (DIF)	Antibiotics	250.2	Honghu Lake, China	[34]
Amoxicillin	Antibiotics	622.0	River Taff/Ely, UK River Warta, Poland Wascana Creek, Canada	[39,40]
Azithromycin (AZM)	Antibiotics	24.0	Iberian River, Spain	[41]
Sulfamethazine	Antibiotics	1920.0	Llobregat River, Spain	[42]
Ofloxacin	Antibiotocs	990.0	The urban area of Beijing and the Liaoning section of Liao Rivers, China	[35,38]
Ibuprofen	Anti-inflammatory drug	11.0	Msunduzi River, South Africa	[43]
Keroprofen	Anti-inflammatory drug	57.0	Msunduzi River, South Africa	[43]
Clofibric acid	Blood lipid regulator	9.0	Freshwater Swiss lakes, Switzerland	[44]
Caffeine (CAF)	Central nervous system stimulant	9785.0	Beiyun River, China Jiulong River, China Liuxi River, China	[45–48]
Amphetamine	Illicit drugs	50.0	Llobregat River, Spain Olona River, Spain	[49]

In addition to differences in spatial distribution, PPCPs also have obvious differences in temporal distribution. The study found that in Luoma Lake in China, there were significant differences in PPCP concentration and risk to aquatic organisms in different seasons, which might be due to differences in water quantity in different seasons [52]. It was also found in Qinzhou Bay that the concentration of most PPCPs was higher in winter than in summer, which may be related to precipitation and water temperature in different seasons [53].

3. Mechanism of Biofiltration Technology

Biofiltration utilizes microorganisms to attach and grow on the surface of the filter material or packing to form biofilms. Upon contact with the biofilm, the pollutants in the water are adsorbed and transformed by the microorganisms, and the water is purified (Figure 2). Biofiltration is widely employed for water purification at present.

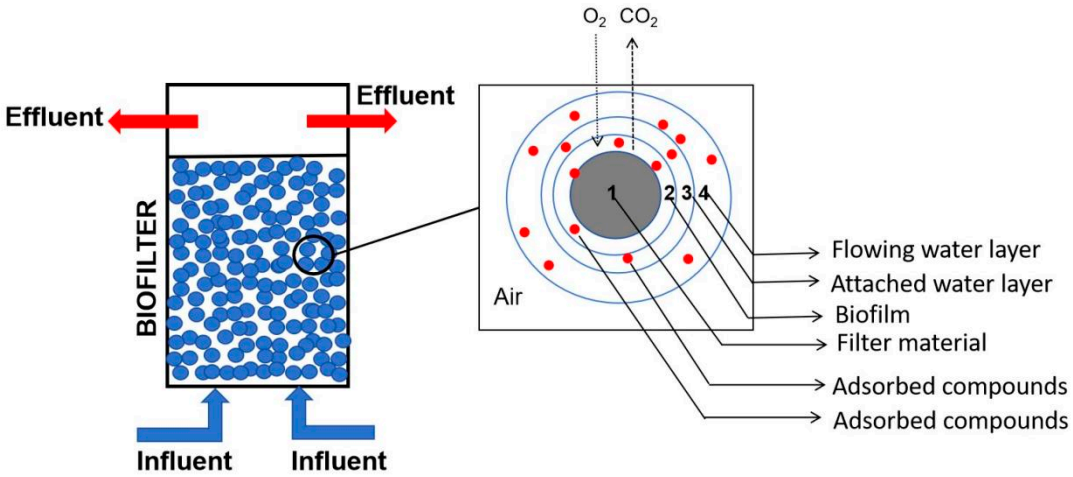

Figure 2. General mechanisms of biofiltration.

The microbial species in biofilm mainly encompass bacteria and fungi, such as *Nitrosomonas*, *Nitrobacter*, filamentous fungi, etc., which play crucial roles in the oxidative decomposition of organic matter [54]. Additionally, protozoa and micro-metazoa are also present in biofilm, which play important roles in improving effluent quality [55]. The outermost layer of the biofilm structure consists of aerobic and facultative microorganisms, where organic matter is decomposed by the microorganisms through aerobic metabolism [56]. The microorganisms inside are in an anaerobic state because the oxygen has been consumed, and here the organic matter is decomposed through anaerobic metabolism.

Some of the critical microorganisms for the treatment process of biofiltration are slow-growing, residing on the inner layer of the biofilm by establishing a stable gradient of substrate concentration. In contrast, fast-growing heterotrophic organisms inhabit the outer layers [57]. This mechanism ensures the protection of internal microorganisms from being washed away by the water flow.

The removal of pollutants in water by biofilm is a multi-process, involving the turbulent diffusion of pollutants in water, the diffusion and transfer of pollutants in the interface, and the oxidation and decomposition of organic matter via the metabolism of microorganisms [58]. Oxygen from the air is also diffused with water flow and transferred into the aerobic layer of biofilm for microorganisms to respiration. Ultimately, organic matter undergoes conversion into inorganic matter, achieving the purification of water. In the process of biofiltration, in order to acquire enough dissolved oxygen, bottom aeration has been usually used for (1) keeping the gas/water ratio = (4–6):1, providing enough dissolved oxygen (>1 mg/L) and maintaining the growth of aerobic microorganisms and exerting their biological oxidation function; (2) providing enough air wash intensity (≈14 L/(m^2·s)), achieving periodic air/water backwash and surface wash for saturated fillers. Although molecular sieve oxygen generation aeration can disperse oxygen more effectively and save energy consumption, due to the limited hydraulic strength, it can not effectively form a turbulent environment and can not effectively realize the backwash of the filler, so its practical application is limited.

Compared with macromolecular organic matters, the overall removal effectiveness for PPCPs through conventional filtration is generally limited due to their small molecular weights, complex structures, strong biological activities, and low concentrations. However, due to the strong biodegradation function, biofiltration can be effective in removing a range

of organics (both hydrophilic and hydrophobic, specifically amines, aliphatic aldehydes, phenols, pharmaceuticals, pesticides, algae metabolites, and algal toxins) and inorganics (e.g., inorganic nitrogen and phosphorus species, iron, and manganese) [59]. Therefore, biofiltration was identified as a cost-effective option to control the risks of PPCPs.

4. Efficiency of Biofiltration on PPCP Removal

Biofiltration has been used in Europe for purifying surface water to effectively reduce turbidity and cholera bacteria in drinking water since the early 1990s. However, the importance of biofiltration in drinking water treatment was noticed only after it was found to benefit in reducing the DPBs, PPCPs, and other emerging organic contaminants (EOCs) a few decades ago [17,60,61]. Since entering the 21st century, biofiltration has a growing prominence in drinking water treatment. Typically, a DWTP comprises two main biofiltration processes including biological granular activated carbon filtration (BAC) and biological sand filtration (BSF), which are applied together with coagulation, flocculation, sedimentation, and disinfection steps in various combinations [62]. Recently, biofiltration processes have been widely used to remove PPCPs in drinking water [63]. It is necessary to summarize the PPCP removal efficiency of these processes.

4.1. Biological Granular Activated Carbon Filtration

Adsorption on activated carbon (AC) stands out as a well-established technology widely employed in water/wastewater treatment plants for the removal of various organic matters with various and unique advantages including low cost, high adsorption capacity, and easy disposal [64–66]. According to the size of activated carbon particles, it is divided into granular activated carbon (GAC) and powder activated carbon (PAC), both of which have been evaluated for the adsorption of micropollutants [67]. Both PAC and GAC can remove PPCPs from water. A pilot scale investigation showed that less dose is needed for PAC compared to GAC in order to achieve the same removal efficiency due to the high adsorption capacity, surface chemical properties, pore structure, and particle size of PAC [68]. However, compared with PAC, GAC is to be more environmentally friendly with the ability of being easy to be recycled and reused, and not easy to cause secondary pollution.

In order to ensure the safety of drinking water, GAC has been widely used for the advanced treatment of contaminants in surface water. For example, Kim et al. found that the removal rate of PPCPs in drinking water (including ibuprofen, caffeine, etc.) by GAC was as high as 99% [69]. Grover et al. also used GAC to remove some PPCPs [70]. The results showed that GAC had a good removal effect on some PPCPs such as mebeverine, indometacin, and diclofenac, and the removal rate could reach 99%.

Natural organic matter (NOM) can diminish the PPCPs' adsorption onto the AC through direct adsorption competition and pore blocking [71–73]. In order to figure out which of the two mechanisms is more dominant, de Ridder and co-workers carried out adsorption batch experiments using NOM-preloaded GAC [74]. Higher hydrophobic NOM preloading resulted in up to 50% lower pharmaceutical removal compared with higher hydrophilic NOM preloading, indicating NOM competition may influence pharmaceutical removal more than pore blocking. Another report indicated NOM severely affected the breakthrough time of non-ionic pharmaceuticals compared to ionic pharmaceuticals in GAC filter operation [75].

However, Yu et al. gave the opposite conclusion based on the adsorption tests of two pharmaceuticals (naproxen and carbamazepine) and an endocrine-disrupting compound (nonylphenol) on GAC; adsorption capacity reduction by NOM preloading was most severe for the acidic naproxen, followed by the neutral carbamazepine and then the more hydrophobic nonylphenol [76]. The surface NOM can add an additional mass transfer resistance layer and thus reduce film diffusion for PPCPs. In addition, when a layer of NOM has been adsorbed on GAC, the surface becomes negatively charged due to NOM coverage, with increasing negative charge at higher NOM loading [77]. This may promote electrostatic repulsion, further reducing the film diffusion of anionic PPCPs.

Besides the bench-scale experiments, numerous pilot- or full-scale studies have been conducted on the removal of PPCPs by the AC process. Cyr et al. carried out a pilot-scale study on the removal of thimerosal, an organic mercury compound, from pharmaceutical wastewater using two 30 min EBCT GAC columns in series [78]. The GAC system showed excellent performance with 99.8% removal efficiency of the mercury from the wastewater.

Due to the refractory behavior of PPCPs in the conventional treatment processes at WWTPs, researchers began to consider GAC as a post-treatment process to remove PPCPs residues from treated wastewater. Recently, the IVL Swedish Environmental Research Institute initiated a pilot study to treat PPCP residues from WWTP effluents by GAC [79]. The GAC system can remove 90–98% of the PPCP residues from WWTP effluents, and estimated total costs are comparable to ozone treatment and lower than for the other methods with the same efficiency. Together with advances in GAC characteristics/regeneration and the production of renewable GAC, GAC is a promising method that can help meet future demands for PPCP control in water or wastewater treatment.

The feasibility of GAC for PPCP removal has also been confirmed in a full-scale plant in Swindon, UK [70]. A significant reduction in the concentrations of steroidal estrogens (>43–64%) and many other pharmaceuticals such as mebeverine (84–99%) was observed in the post-GAC effluents. In the practical operation of GAC, regular regeneration is critical for the excellent removal of PPCPs. A full-scale GAC plant with non-regenerated filters displayed no removal of target PPCPs [80]. This may be caused by the accumulation of NOM competing for available adsorption surface area and sites and blocking the pores [81].

Moreover, there are few reports on the removal of PPCPs by the BAC process, which integrates both sorption and biodegradation. The microbial activity may enhance the removal of easily biodegradable PPCPs, such as naproxen and ibuprofen. Wang et al. reported that the coupling of BAC biofilter with ultrafiltration (UF) could be a promising process for the treatment of river water contaminated by PPCPs [82]. By using this BAC-UF process, the average removal of total PPCPs reached 47.84%, especially anhydroerythromycin, sulfachloropyridazine, sulfadiazine, trimethoprim, and caffeine. Chen et al. investigated the removal efficiencies of PPCPs in secondary effluents from WWTPs by a combination of BAC filtration, ozonation, and ceramic membrane filtration [83]. The total removal efficiency of PPCPs reached 98.5%. Generally, compared with GAC filtration, there have been fewer studies on the removal of PPCPs by BAC. The formed biofilm increases the acid/base reactivity of the activated carbon surface that may greatly influence the adsorption of ionic PPCPs. Therefore, more work have to be undertaken regarding the BAC process for the removal of PPCPs.

Based on the research on biofiltration, improved biofilters have been developed to control PPCPs more effectively. Fu et al. implemented two parallel trains of two-stage biofiltration, i.e., a sand/anthracite (SA) biofilter coupled with a GAC post-filter contactor to control the levels of PPCPs in drinking water in a DWTP [17]. The results showed that the biofiltration process could effectively remove PPCPs with an average removal of 53.4%, where the GAC contactor played the dominant role to remove 48.1% of the total PPCPs.

4.2. Biological Sand Filtration

BSF mainly relies on the cultivation of attached biofilm on the surface of quartz sand filter material, and the removal effect on pollutants is enhanced through the adsorption and biodegradation of the biofilm [84]. The BSF process is a new process that increases the biochemical effect of quartz sand surface on the basis of the sand filter process to improve the removal effect on pollutants. This process mainly completes the degradation of pollutants through two ways, respectively, the surface retention effect of the sand filter material and the surface biodegradation effect. The adsorption performance of the filter material and the adsorption and degradation performance of the microorganism on the attached membrane are fully utilized [85].

Because the BSF process has a good effect on the removal of pollutants, researchers believe that the effluent water quality can reach a better standard through this process [86,87].

By controlling reasonable process conditions, BSF can achieve denitrification and nitrogen removal effects while reducing turbidity, suspended solid (SS), dissolved organic matter, ammonia nitrogen, and other pollutants in the discharge water. Therefore, BSF has been used for the advanced treatment of drinking water in waterworks and tailwater in WWTPs [88]. According to the filtration fate, the BSF can be classified into either slow sand filtration (SSF) or rapid sand filtration (RSF). In recent decades, these types of BSF have been demonstrated to show great potential in removing emerging organic pollutants including PPCPs [63].

4.2.1. Slow Sand Filtration

SSF mainly uses the top filter membrane to hold back suspended solids, and at the same time exerts the purification effect of microorganisms on water quality, with the characteristics of low water production, slow filtration speed (<10 m d^{-1}), and large land occupation [89]. Figure 3 shows the schematic representation of an SSF filter. The lower part of SSF has a drainage system, and the upper part of the drainage system is successively paved with a supporting gravel layer and a sand filter layer. The raw water with low turbidity enters the filter from the upper part of the filter, passes through the sand filter layer and the supporting layer, and flows out from the drainage system. A thin, slimy, gelatinous biofilm, called schmutzdecke (German), grows at the top of the sand layer and plays an important role in water purification [63].

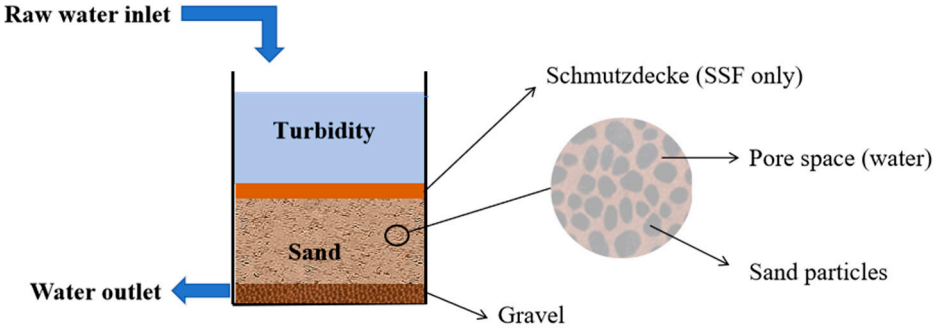

Figure 3. Schematic representation of an SSF filter.

Some research published the removal effect of SSF on PPCPs from contaminated water including wastewater effluents, surface water, and tap water. The removal effect of different PPCPs varies significantly. Ibuprofen, as one of the typical PPCPs, is one of the most widely used non-steroidal anti-inflammatory drugs (NSAIDs) at present. Some studies have shown that ibuprofen could be removed effectively through SSF [90,91]. The proportion of removal has been reported to be higher than 90%. Except for ibuprofen, some other PPCPs have also been reported to be removed through SSF. Mònica et al. reported that SSF reactors can remove micro-pollutants from WWTP effluent [92]. For instance, when the empty bed contact time (EBCT) is in the range of 0–60 h, the removal of seven micropollutants (diclofenac, propranolol, iopromide, iohexol, imeprol, tebuconazole, and propiconazole) in the SSF reactor met the first-order kinetics. With the hydraulic loading rate of 0.012 m^3 m^{-2} h^{-1}, the reactor removed 41, 94, 58, 57, and 85% of the diclofenac, propranolol, iopromide, iohexol, and imeprol, respectively.

Although the SSF exhibited a significant removal effect on PPCPs, there have been some differences between laboratory-scale and pilot/full-scale experiments. In most cases, the pilot/full-scale tests achieved relatively lower PPCP removal than laboratory studies [63]. For instance, laboratory-scale SSF removed about 20% of the carbamazepine from WWTP secondary effluent [93], whereas another pilot study reported that 0% of the carbamazepine was removed from surface water [94]. The main reason for the different removal effects can be the difference in inlet water quality, initial concentrations, and operational conditions [63]. Further investigations on PPCP removal are required at various experimental scales to improve these limitations for pilot/full-scale tests.

4.2.2. Rapid Sand Filtration

Compared to SSF, the filtration fate of RSF increases to 8–10 m h^{-1}. Besides the filtration rate, there is another huge difference between RSF and SSF is that RSF generally lacks a biofilm layer on the filter media (schmutzdecke) and is primarily used to remove large suspended solids through physical processes [63]. However, some studies found that despite tolerating the condition of the oligotrophy and frequent flushing, microorganisms attached to the surface of quartz filter sand also contribute to the removal effect on organic micropollutants in RSF including PPCPs.

Generally, the effect of RSF on the removal of organic matter, microorganisms, and chroma is not as good as that of a slow filter due to a shorter contact time within the RSF system. Zearley et al. studied the degradation of 34 micropollutants through RSF from tap water [91]. At a filtration rate of 2.4 m h^{-1}, only 2.4% of sulfamethoxazole was eliminated. In comparison, Gijn et al. studied the removal rate of organic matter through SSF from WWTP secondary effluent [93]. Generally, the effluent organic matter removal was negatively correlated to the flow rate in the sand filter. At a filtration rate of 1 L d^{-1}, 20–60% of sulfamethoxazole was eliminated.

Similar to SSF, there also have been some differences between laboratory-scale and pilot/full-scale experiments through RSF. For instance, triclosan, one of the antibiotics commonly used in personal care products has been studied both by small- and large-scale RSF. Zearley et al. reported that the average removal of triclosan was $\geq$ 90% with a filtration rate of 1.2 m h^{-1} through a laboratory-scale SSF [91]. Nakada et al. studied the removal of selected PPCPs including triclosan through a full-scale RSF [95]. The results showed that the efficiency of the removal of triclosan was 25.2–52.5% with a filtration rate of 110 m d^{-1}.

4.3. Benefit and Cost Analysis for Biofiltration

It is necessary to consider a benefit and cost analysis for the biofiltration of PPCPs. Sun et al. found that the use of activated carbon adsorption also had some negative effects. The activated carbon reached the adsorption saturation state and the adsorption efficiency was greatly reduced after operation for a period of time [48]. In addition, after the completion of the adsorption process, the recovery and reuse of activated carbon will increase the cost. The AC technology is simple and the operation cost is low, and the adsorption and removal of PPCPs are rather effective; however, it is different to separate carbon powder and water. Therefore, it is necessary to choose an effective filtration method to control the pollution of AC to water treatment equipment. These shortcomings can increase the cost of equipment operation to a degree.

Compared with AC, BSF has shown advantages such as cost-effectiveness (relatively cheaper operation/maintenance costs), configuration simplicity, low chemical and electricity requirements, and practical compatibility [63]. Some natural biomass materials can be used as filtration media. Zaman et al. reported a simple and inexpensive water purification method developed using natural coagulant (Moringa seed powder) and antibacterial agents (scallop powder) followed by bio-sand filtration.

5. Influencing Factors of Biofiltration on PPCPs

5.1. Filter Media

In early biofiltration, materials such as gravel, steel slag, and coke were used as filter materials, and later plastic and GAC gradually became the main media of biofiltration. As the inhabits for microorganisms, the media plays an important role in the normal operation of biofiltration. Different filtration media demonstrate varying efficiencies for PPCP removal. Paredes et al. comparatively assessed sand and GAC biofilters as post-treatment technologies of secondary effluents for the removal of 18 organic micropollutants (OMPs) [86]. The results showed that biotransformation was crucial for the elimination of OMPs in sand biofilters and the filtering material did not affect the biological activities in biofilters. Xu et al. investigated the removal of five antibiotics (amoxicillin, clarithromycin, oxytetracycline, sulfamethoxazole, and trimethoprim) in sand, GAC, GAC sandwich, and

anthracite/sand biofiltration systems [96]. Results showed that the target antibiotics were substantially removed (>90%) by GAC-associated biofilters and partially removed (≤20%) by sand alone and anthracite-sand biofilters. Li et al. reviewed the progress of sand and sand-GAC filtration technologies in removing PPCPs [63]. The combination of sand and GAC filtration with different models (serial, dual, and sandwich filters) significantly enhanced PPCP removal.

Yapsakli et al. evaluated the effect of GAC selection on the biodegradation of dissolved organic carbon (DOC) [97]. The study compared thermally activated carbon (Norit 1240) and chemically activated carbon (CAgran) performance. It indicated that biodegradation, measured as DOC removal, was significantly higher in the thermally activated carbon columns (~72% removal) compared to the chemically activated carbon (~47%). The greater ability to retain these biodegradable compounds led to increased DOC removal. Consequently, it was concluded that the choice of filter material is crucial in BAC systems [98]. This research underscores that filter media with greater adsorption capacity are likely to exhibit higher removal of PPCPs.

5.2. Backwash Conditions

Backwash condition is one of the key factors to determine the smooth operation of biofiltration. Insufficient filter material washing may cause bonding issues, leading to the failure of process operation. In addition, temperature also influences the formation of biomass. Liu et al. studied the performance of anthracite and GAC biofilters under various temperature and backwash conditions [99]. The backwash conditions considered were backwash water without a disinfectant, water with chlorine, water with chloramine, and the effect of air scouring. Temperature variations covered low temperatures (5 °C) and high temperatures (20 °C). The study examined various combinations of conditions and assessed the performance of the filter in removing acetate, formate, formaldehyde, and glyoxl. It was found that air scours under collapse-pulse conditions did not have a significant effect on biodegradation. For the GAC media, only a combination of low temperature combined with chlorinated backwash water exhibited minor detrimental effects on removing the biodegradable compounds. This is because both conditions are unfavorable in the development of biomass. The low temperature and presence of chlorine had a more pronounced effect on glyoxl removal, as it is less readily biodegradable. All the other combinations of conditions had nearly no effect on biodegradation [99]. For the optimal removal of organic material, it is advisable to avoid chlorine in backwash water during periods of low water temperature.

5.3. Empty Bed Contact Time

An important parameter in the removal of NOM is the EBCT. Seredyńska-Sobecka et al. studied the effect of EBCT on NOM removal by measuring UV254 absorbance removal, total organic carbon (TOC) removal, color removal, and COD removal [100]. The data revealed that longer EBCTs (10–23 min) resulted in more effective NOM removal compared to shorter EBCTs (2–5 min). The effect of EBCT was also studied on the removal of micropollutants, including PPCPs. The longer EBCT (15.8 min) resulted in a greater removal efficiency of PPCPs than the shorter EBCT (7.9 min) [91]. Thus, a longer EBCT proves to be advantageous in the removal of PPCPs.

5.4. Other Parameters

Several other parameters were also considered and investigated for their impact on PPCP removal. The age of filter media has a certain effect on the removal efficiency of PPCPs. In an experiment conducted by Paul et al., raw PAC was employed to remove triclosan, oxybenzone, fluoxetine, and fluoranthene with the removal rates of 98%, 97%, 95%, and 95%, respectively [67]. However, the researchers observed a substantial decrease in the removal rate of used PAC, attributed to the gradual adsorption saturation of PAC over time, ultimately leading to a loss of adsorption capacity for PPCPs [67]. Pre-filter

treatment is an important factor to enhance the treatment performance of the biofiltration process. For instance, pre-ozonation has been identified as a strategy to enhance the removal effectiveness for PPCPs. Lin et al. demonstrated that a combination of pre-ozonation with GAC could effectively remove PPCPs [101]. In this study, the researchers found that some pharmaceuticals with N=C double bonds, pyrrole rings, or the phenol ring were all susceptible to chemical attack by ozone, which was beneficial for improving the removal efficiency of GAC on PPCPs. Other studies consider the effect of microbial parameters such as microbial community composition [102], flow velocity [17,103], and the accumulative state of biofilm [104]. Though the precise effects of these factors remain unclear, their consideration is deemed important in the operation of biofiltration-related processes.

6. Summary and Prospect

As a type of emerging pollutant, PPCPs have a relatively low concentration level but are widely distributed in the environment. Due to their diverse nature and discernible biological effects, PPCPs have garnered global attention. In this review, the sources and occurrences of PPCPs in natural water bodies are systematically summarized, which are of importance for the effective management of PPCP discharge from their origins. As illustrated above, the spatial and temporal distribution of PPCPs displays variations, which are closely related to population density, drug use habits, and the development level of the pharmaceutical industry in different regions. Consequently, targeted control measures for PPCP discharge are essential in key regions. Further exploration into the migration and transformation of PPCPs within environmental media can furnish the scientific foundation for the enhanced control of PPCP concentrations in the environment.

Current PPCP removal techniques encompass physical, chemical, and biological methods, each boasting its merits and demerits. Biofiltration technology, seamlessly integrating adsorption and biodegradation, stands out as a prevalent approach for PPCP elimination. Within this domain, activated carbon-based biofiltration technology is an ideal choice for the removal of PPCPs. GAC filtration has been proven to be stalwart in DWTPs for PPCP removal. However, drawbacks including elevated infrastructure and operational expenses, susceptibility to toxins such as nitrite, and vulnerability to sudden pollution load persist in the GAC treatment process. How to further reduce infrastructure investment and operating costs, especially reducing the cost of activated carbon regeneration, will become the focus of future research. The BAC process can exert the synergistic potential of biochemical and physicochemical treatment, extending the working cycle of activated carbon, significantly enhancing the treatment efficiency, and refining the effluent quality. Yet, BAC grapples with issues like micropore blockage by activated carbon, a narrow pH application range for influent water, and suboptimal resistance to impact loads.

In the biofiltration process, the factors that affect the removal efficiency of PPCPs involve the type of filter media, temperature, backwashing conditions, pre-filter treatment, etc. Fine-tuning these parameters holds the key to enhancing the removal efficiency. The combination of pre-ozonation and activated carbon has emerged as a potent strategy in numerous WWTPs for tackling PPCPs. Despite the considerable body of research on PPCP removal by GAC and/or BAC process, there are lingering gaps in the current understanding, warranting improvements in the following aspects:

(1) A large number of studies have shown that the GAC process can be used alone or in combination with other processes as the mainstream process for removing PPCPs in biofiltration. Its removal efficiency for different types of PPCPs is diverse, which is related to the properties of the PPCPs themselves, including octanol/water partition coefficient, chemical topological structure, biodegradability, etc. Therefore, for different types of PPCPs, it is very important to choose the appropriate conditions to maximize the efficiency of the biofiltration process.

(2) Generally, the interplay between adsorption and biodegradation within BAC processes introduces a dynamic equilibrium for the removal of PPCPs. However, recent studies highlight a fascinating nuance: this equilibrium is not always maintained.

Specifically, when using the BAC reactor to tackle non-steroidal anti-inflammatory drugs such as diclofenac, it was found that the biodegradation rate of drugs in BAC appears significantly lower than in a standalone BAC bacterial suspension [83]. This phenomenon implies that the removal of certain drugs by BAC involves more than a mere cumulative effect of biodegradation and activated carbon adsorption. Instead, it suggests the existence of competing mechanisms between biodegradation and adsorption, prompting a deeper exploration into the microbiological intricacies during the BAC process.

(3) In general, the disposal of sludge generated by biological processes is a concern. For the biofiltration process, the generation of sludge is relatively low, while the removal mechanism mainly uses the biofilm grown on the carrier for biological oxidation. In order to control the overgrowth and blockage of the carrier biofilm, backwashing should be performed regularly. For serious cases, pre-chlorination or adding hydrogen peroxide can also be used to remove the overgrown biofilm and reduce the loss of water head. The ultimate disposal of sludge generated by the biofiltration process could be also a direction worthy of attention in the future.

(4) Currently, the forefront of research on the removal of PPCPs by biofiltration revolves around three primary avenues: identifying potent degrading bacteria, pinpointing adsorption media, and devising synergistic combinations. However, one notable knowledge gap exists: the microbial degradation mechanism, particularly the intricate correlation between functional genes and the degradation process at a genetic level, remains insufficiently explored. Metagenomics and metatranscriptomics emerge as powerful tools for mapping microbial community structure and function profiles, and can also help construct transformed enzymatic metabolic pathways for PPCP degradation during the BAC process.

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