CHARACTERISTICS AND TREATMENT OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN WASTEWATER



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This report does not attempt to address the holistic management of PPCPs nor any current or future policy decisions related to these chemicals. The discussion herein is not exhaustive in describing the extent and effects of PPCPs, but rather introduces this complex class of chemicals which may pose newly identified or re-emerging risks to human health, aquatic life, or the environment, along with technologies that can be used to treat them at wastewater treatment plants (U.S. EPA, 2022a). This report was developed to support EPA's Searchable Clearinghouse of Wastewater Technology (SCOWT) and to encourage the use of EPA funds for emerging contaminants projects.

Introduction

Pharmaceuticals and personal care products (PPCPs) encompass a diverse group of chemicals, including all drugs (prescription and over the counter) and non-medicinal consumer chemicals (i.e., fragrances in lotions and soaps, ultraviolet [UV] filters in sunscreens) (U.S. EPA, 2013). PPCPs vary in their intended applications and chemical composition, making it challenging to monitor and treat these compounds. When detected in wastewater or the environment, PPCPs are usually present at low concentrations (parts per billion or trillion). Even at low concentrations, however, PPCPs may have adverse effects on aquatic organisms, including effects on antibiotic resistance, endocrine disruption, and bioaccumulation (Dhangar & Kumar, 2020). The PPCPs most studied in wastewater include analgesics (pain relievers), antihypertensives (blood pressure medications), psychoactives, antibiotics, hormones, stimulants, UV filters (sunscreen), and fragrances due to their high consumption volume and persistence in the environment.

Conventional municipal wastewater treatment facilities (WWTFs), defined as facilities using solids removal (primary treatment) and biodegradable organics removal (secondary treatment), are not currently designed to specifically target PPCPs. However, primary and secondary treatment can partially remove many PPCPs to varying degrees depending on the physicochemical properties of specific PPCPs, treatment operational variables, and climatic conditions. There are additional physical, chemical, and biological wastewater treatment technologies that can treat PPCPs. These technologies may be most appropriate for moderate- to large-scale facilities with more sophisticated operator capabilities and resources to support the operation, maintenance, and monitoring of PPCP removal technologies. This technology brief aims to provide preliminary information on the treatment of PPCPs in municipal wastewater and inform the initial identification of PPCP treatment technology. An important first step to discussing technology options is to understand the characteristics of PPCPs that make them resistant to removal in conventional WWTFs.

EXAMPLES OF PHARMACEUTICALS

- Blood pressure medications
- Bactericides
- Antimicrobials
- Growth promoters
- Animal drugs
- Hormones

EXAMPLES OF PERSONAL CARE PRODUCTS

- UV filters (sunscreen agents)
- Detergents
- Preservatives
- Insect repellents
- Cosmetics



Characteristics and Treatment of Pharmaceuticals and Personal Care Products (PPCPs) in Wastewater | August 2024

PPCP Sources and Effects

One of the primary ways that PPCPs enter the environment is through municipal WWTF effluent. Municipal WWTFs are not designed to treat these contaminants but receive them continuously. Many studies link the presence of PPCPs in surface water to effluents from WWTFs that are not designed to remove PPCPs (Al-Baldawi et al., 2021; Dhangar & Kumar, 2020; Tarpani & Azapagic, 2018; Tijani et al., 2013; U.S. EPA, 2013). Pharmaceuticals from residential sources are introduced to the municipal system through two primary mechanisms: 1) through the improper direct disposal of unused or expired medications to the sanitary sewer and 2) as waste following the

incomplete metabolization of pharmaceuticals in the body (Al-Baldawi et al., 2021). Personal care products (e.g., soaps, cosmetics, fragrances) are discharged into municipal wastewater through regular household activities such as bathing and laundry (U.S. EPA, 2009). This technology brief does not focus on additional pathways for PPCPs to enter the environment such as through hospital-specific wastewater, pharmaceutical manufacturing wastewater, or agribusiness.

The presence of PPCPs in the environment may pose both an environmental and public health concern. Some PPCPs have been shown to bioaccumulate in aquatic organisms such as fish (U.S. EPA, 2013). PPCPs can also cause behavioral changes in aquatic organisms (Brodin et al., 2014). Long-term exposure to some PPCPs has been correlated with endocrine disruption in fish and humans, leading to hormonal abnormalities and cancer (Tijani et al., 2013). Antimicrobial resistance is also a significant concern. As pathogens and bacteria are exposed to PPCPs such as antibiotics, they develop drug resistance, which may inhibit the treatment of certain pathogenic diseases (Kumar et al., 2023). Preventing and reducing the release of PPCPs to the environment protects both human health and the environment.

Source Control

Source control is the most effective means to keep PPCPs out of wastewater and the environment. Best management practices such as sewer bans and drug take-back programs help to reduce the amount of PPCPs that enter municipal wastewater. This technology brief is focused on how to treat and remove PPCPs once they are already in the wastewater.

More information on how EPA is reducing the amount of hazardous waste pharmaceuticals entering our waterways.

Photo Credit: Lance Cpl. Kirstin Merrimarahajara for the United States Marine

Chemical Properties and Considerations for Monitoring

PCPPs are a category of chemicals defined by their intended use, not their chemical properties. This leads to variability in the behavior of PPCPs and the effectiveness of different wastewater treatment technologies for PPCPs. For example, compounds that have a high tendency to sorb onto solid material are likely to be adsorbed onto sludge and may be effectively removed through conventional treatment methods. Table 1 provides a few examples of PPCPs and their chemical properties. When addressing a chemical of concern in a community or WWTF, the unique properties of that chemical should be identified before determining the best treatment option.

ions



EPA has developed and validated **Method 1694** for 74 PPCPs and **Method 1698** for 27 steroids and hormones in water, soil, sediment and biosolids.

More information on EPA analytical methods for PPCPs.

Compound	Application	Probability Compound Will Dissolve in Water ^b	Probability Compound Will Dissociate into Smaller Molecules ^c	Probability Compound Will Adsorb onto Solid Material ^d	Probability Compound will Biologically Degrade ^e
Galaxolde	Fragrance	Low	—	High	Low
Fluoxetine	Antidepressant	Moderate	High	Moderate	—
17β-Estradiol	Hormone	Low	High	Moderate	High
17α- Ethinylestradiol	Hormone	Low	High	Low	Moderate
Roxithromycin	Antimicrobial	Low	High	Low	Low
Trimethoprim	Antimicrobial	High	Moderate	Low	—
Triclosan	Antimicrobial	Low	Moderate	Moderate	—

Table 1. Chemical properties of select PPCPs.^a

^a This table contains summarized information from Table 2 in Suarez et al., 2008 and Table 1 in Ohoro et al., 2022. Categories assigned are based on numerical ranges provided in the reference table and should only be used to compare the characteristics of each compound to the others in this table.

^b Solubility in water, s.

^c Dissociation constant, pKa.

^d Octanol-water partition coefficient, K_{ow}.

^e Pseudo first-order degradation constant, k_{biol}.

If you would like more detailed information on what chemical characteristics these constants describe, please see "<u>Physiochemical Properties and Environmental Fate</u>" in *A Framework to Guide Selection of Chemical Alternatives* (National Research Council, 2014).

Conventional Treatment

This section provides a brief discussion of the treatability of PPCPs using conventional wastewater treatment, which is defined here as only primary and secondary treatment. Conventional treatment is not designed to remove PPCPs but may have the co-benefit of removing select PPCPs without the addition of tertiary treatment processes. Figure 1 summarizes how PPCPs move through a WWTF and how they can potentially be treated and removed. Compounds that are likely to sorb onto solids, such as fragrances, are readily removed in For more information on conventional wastewater treatment, see <u>How</u> <u>Wastewater Treatment</u> <u>Works... The Basics</u> (EPA 833-F-98-002).

conventional treatment at efficiencies between 60 and 90 percent (Suárez et al., 2008). Compounds that are unlikely to sorb and are resistant to biodegradation, such as the antiepileptic drug carbamazepine, are removed at 0 to 45 percent efficiency (Suárez et al., 2008).

The goal of primary treatment is to remove settleable matter and solids. PPCPs that readily dissociate or adsorb are likely to be removed during primary treatment. Just as with other suspended particles, the removal of PPCPs may be enhanced by the addition of chemical coagulants or flocculants (Suárez et al., 2008). This may lead to some removal of less sorbent PPCPs, but mainly improves the removal of sorbent compounds.

In secondary treatment, bacteria break down organic matter and adsorbent compounds sorb onto biological floc. Actual PPCP removal during secondary treatment depends on several factors, such as biomass concentration, the type of process used, operating conditions such as solids retention time and hydraulic retention time, and local conditions such as temperature and sunlight intensity. The success of removal also depends on PPCP compound chemical characteristics and the extent of biotic degradation and adsorption onto solids (Blair et al., 2013). Most pharmaceuticals are designed to be resistant to biodegradation and thus do not easily degrade in conventional activated sludge processes (Kumar et al., 2023). Studies on PPCP removal in activated sludge treatment plants report inconsistent removal rates across study locations. For example, fragrances were removed at 50 to 75 percent efficiency and hormones were removed at 49 to 99 percent

PPCPs in Biosolids

The presence of PPCP compounds in biosolids is one of the potential routes of human and ecological exposure. To date, EPA has found 243 PPCP compounds in biosolids through nine biennial reviews of public literature and three national sewage sludge surveys (Richman et al., 2022; U.S. EPA, 2022b). These compounds, in addition to the other chemicals that have been found in biosolids, will be evaluated for risk by EPA. Chemicals that present risk above EPA's level of concern may be regulated in biosolids.

efficiency in two different case studies of PPCP removal in activated sludge treatment (Suárez et al., 2008). This is likely due to differences in operating conditions (with the intent to improve secondary treatment) between systems, such as dissolved oxygen levels, sludge age, and overall wastewater characteristics (Yang et al., 2011). The complex nature of PPCPs further limits the removal efficiency of secondary treatment. While research suggests that conventional treatment may have the co-benefit of removing some PPCPs, conventional treatment alone may not be capable of treating all the PPCPs that may be present in a WWTF's influent.

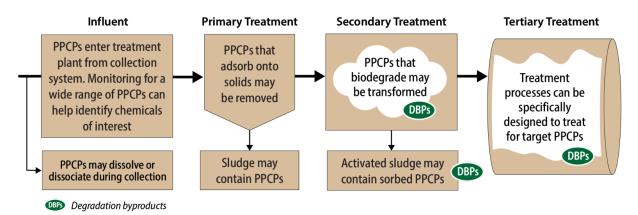


Figure 1. How PPCPs move through a WWTF (DBPs: degradation byproducts).

Potable Reuse

As natural water resources in some areas become increasingly stressed, potable reuse may be an effective option to increase drinking water availability. The advanced technologies needed to treat wastewater for potable reuse have the co-benefit of removing PPCPs. Those exploring potable reuse should consider the potential for targeted treatment of PPCPs.

The sections that follow describe a few of the technologies available for PPCP treatment in wastewater. There is limited research on these technologies operating at full scale where PPCPs are specifically monitored, but evidence at the pilot- and lab-bench scale indicates that these technologies are likely to achieve greater removal of PPCPs than conventional treatment alone at full scale. The removal efficiencies presented are likely dependent on the characteristics of the influent and concentration of each PPCP discussed. A table summarizing the applications, considerations, and performance of these technologies is provided at the end of this document.

Adsorption Technology

Description

Adsorption is sometimes called "phase-changing technology" because it removes dissolved organic and inorganic compounds from wastewater by adhering them to binding sites on a solid adsorption media. As seen in Figure 2, contaminants like PPCPs can be removed from wastewater through adsorption to sorbents like activated carbon. Advanced adsorption media is specifically sourced and designed to be more effective than the adsorption that occurs in conventional primary treatment. The most common adsorption media is activated carbon, either in a granular (GAC) or powdered (PAC) form, because of its high efficiency relative to other adsorbents (Baskar et al., 2022). GAC is often used in a bed form, where the

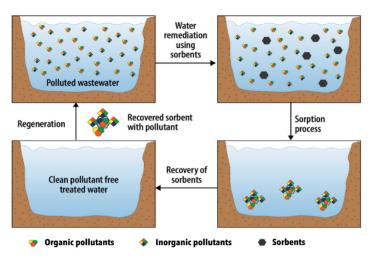


Figure 2. Illustration of the removal of wastewater contaminants using sorbent (Baskar et al., 2022).

adsorption media remains in place while wastewater flows through it, while PAC is fed into the waste stream and must be removed along with other sludge solids (U.S. EPA, 2000).

Over time, binding sites on the adsorption media are filled and the material becomes unable to remove additional dissolved compounds. When used in a bed form, adsorption media can be backwashed to remove adsorbed particulates, but the spent media will eventually need to be removed and replaced (U.S. EPA, 2000). Spent adsorption media can be regenerated through various methods, including solvent washing, sonication, and most commonly, thermal treatment (Baskar et al., 2022). Regeneration may need to occur off site at a different facility. Solid adsorption media can be regenerated multiple times but does become less effective with each regeneration.

Applicability

Adsorption technology is available in a variety of configurations, making it easier to integrate into existing facilities. The type of adsorption media a facility uses can be tailored to the needs of the system and the targeted PPCP compounds. Highly soluble PPCPs that are unlikely to sorb onto solids will not be efficiently removed with adsorption. An additional treatment step prior to GAC, such as filtration or use of additional GAC columns, would further reduce organics in the water that would otherwise bind to the adsorbent media and occupy binding sites needed for PPCP removal (Snyder et al., 2007).

Considerations

Advantages of Adsorption Technology	Disadvantages of Adsorption Technology
 Adsorption technology removes a wide range of PPCPs. Adsorption technology does not form potentially harmful degradation products. GAC media can be backwashed, regenerated, and reused. 	 Adsorption technology does not degrade PPCPs; they remain in their original form. GAC systems must be monitored and backwashed frequently to prevent clogging and breakthrough. GAC media regeneration requires significant energy and may need to be done off site. GAC media regeneration produces a concentrated waste stream that must be handled appropriately.

Performance

Several laboratory-scale studies of activated carbon using spiked aqueous solutions have shown removal efficiencies of more than 90 percent for four nonsteroidal anti-inflammatory drugs, three antibiotics, and caffeine (Dhangar & Kumar, 2020). This technology has shown similar efficiencies at full scale surface water treatment and water reuse plants, but efficiencies can vary greatly between systems (Snyder et al., 2007). The source of the adsorption media affects the removal efficiency of PPCPs. In one study at the laboratory scale using aqueous solutions, acetaminophen had a greater than 90 percent removal efficiency when using activated carbon from a wood source, but only 60 to 87 percent removal efficiency when using activated carbon from herbaceous plants (Dhangar & Kumar, 2020). It can be helpful to do bench-scale testing with samples from the WWTF of interest to ensure that the most appropriate adsorption media is selected for installation.

Oxidation Technologies

Description

Oxidation is a chemical process in which chemical agents react with target pollutants and oxidize them into a different chemical that is distinct from but related to their parent compound. The oxidation processes include chlorination, photolysis (UV radiation), and ozonation; each of these are defined by the agent used to initiate the process (Dhangar & Kumar, 2020; Kumar, 2023). Ozone is a strong chemical oxidant that can be used to treat a variety of organic pollutants, including PPCPs, and can be combined with other physical or chemical agents in advanced oxidation (Ikehata et al., 2008). Each of the oxidants in these processes react either directly or indirectly (i.e., through their degradation products) with the chemical structure of PPCPs to break them down, as outlined in Figure 3.

Some chemical agents are more effective than others; for example, ozone is a much stronger oxidation agent than chlorine or UV. These chemicals are also used for conventional wastewater disinfection but are applied at a lower dose than is required to oxidize complex chemicals such as PPCPs. Unfortunately, oxidation does have the potential to form

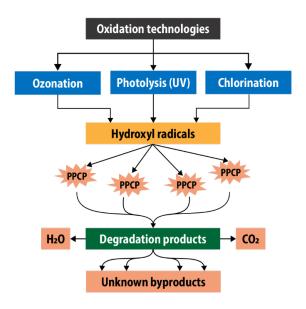


Figure 3. Diagram of oxidation processes (modified from Krishnan et al., 2021).

harmful byproducts along with non-harmful byproducts (Dhangar & Kumar, 2020). There is little information on the presence and effects of the degradation products of oxidized PPCPs because there are no EPA-validated analytical methods to detect or analyze them.

Applicability

Oxidation technology is appropriate for moderate- to large-scale facilities with the capacity for chemical handling. It is best used after secondary treatment to reduce the competing species in the process water that could also be oxidized by the chemical agent. Decisions on which oxidation process(es) to use for PPCP removal are based on several factors, including the facility's overall treatment goals and the specific pollutants within the water to be treated. Regardless of which oxidation process is used, when the chemical agent is applied at a higher dose or for a longer contact time, a wider range of PPCPs are oxidized at a higher rate. The chemical agent dose or reaction time applied is expected to be higher than that required for standard disinfection (Paucar et al., 2018).

To choose the most appropriate chemical agent, facilities must consider the balance between their performance goals and the risk of creating harmful byproducts. Chlorination is not as effective and has greater challenges than photolysis and ozonation; chlorination is also likely to form harmful byproducts (Dhangar & Kumar, 2020). Photolysis is most effective when paired with a photosensitizer such as hydrogen peroxide and can effectively degrade many PPCPs, including antibiotics, analgesics, and hormones (Ngumba et al., 2020). Ozone is a strong oxidant that can degrade many PPCP compounds, including antibiotics, hormones, and beta blockers, but it is energy intensive to produce (Dhangar & Kumar, 2020). Ozone decomposes rapidly and must be generated on site (U.S. EPA, 1999). Byproducts of ozonation include bromate and nitrosamines (such as N-nitrosodimethylamine [NDMA]), which have been classified as probable human carcinogens and are not related to the presence of PPCPs (Lim et al., 2022).

Considerations

Advantages of Oxidation Technologies	Disadvantages of Oxidation Technologies
 Oxidation technologies effectively degrade	 Chemical transformation of PPCPs can form
resistant PPCPs. Oxidation technologies chemically transform,	potentially harmful degradation products that are
not simply phase change, PPCPs. Oxidation technologies treat for pathogens and	challenging to monitor. Byproducts of the oxidant itself may be potentially
metals (Tarpani & Azapagic, 2018). Oxidation technologies produce no additional	harmful. Chemical agents may need to be produced on site
waste stream.	and may be energy intensive. Chemical agents can be hazardous to handle.

Performance

A laboratory scale study of UV photolysis on municipal wastewater effluent containing six PPCPs showed removal efficiencies of over 90 percent for two antibiotics and one antiviral, all of which strongly absorbed UV light (Ngumba et al., 2020). The removal efficiencies of the other two antivirals and one antibiotic that did not strongly absorb UV light all increased with the addition of hydrogen peroxide but remained at or below 70 percent removal (Ngumba et al., 2020). Ozonation is highly effective and effectively removes most types of PPCPs, especially hormones, at an efficiency of 90 to 100 percent (Dhangar & Kumar, 2020). However, ozonation is less effective on compounds without reactive groups in their chemical structure, such as ibuprofen (Suárez et al., 2008).

Case Study: Pilot Scale Test of Ozonation at Different Doses and Contact Times (Paucar et al., 2018)

Conventionally treated municipal wastewater effluent was used as feed wastewater in this laboratory study performed at the pilot scale. Three 35-liter stainless steel ozone reactors were connected in series to model full-scale ozone treatment with ozone monitors placed before and after each reactor. Operating conditions of the ozone treatment unit, including ozone dose (1 to 9 milligrams per liter) and contact time (five to 15 minutes), were analyzed for their PPCP removal efficiency.

Thirty-seven PPCPs were detected in the feed wastewater effluent, including antibiotics and anticonvulsants. All 11 antibiotics detected in the feed wastewater were degraded to concentrations that could not be detected when treated at the highest ozone dose and longest contact time. The anticonvulsant carbamazepine was degraded to undetectable levels at the lowest ozone dose and medium contact time. The other anticonvulsant detected, primidone, was one of the three chemicals that was resistant to ozone (i.e., not removed below the limit of detection) even at the highest ozone dose and longest contact time. The other ozone-resistant chemicals were DEET, an insect repellant, and ketoprofen, an analgesic. All three of these ozone resistant chemicals, though not removed below the limit of detection, were still significantly reduced (92 to 99 percent) at the highest ozone dose, showing that even the most resistant PPCP compounds can be removed significantly using ozone.

Membrane Technologies

Description

Membrane separation processes remove PPCPs through size exclusion, electrostatic repulsion, and adsorption. High pressure pushes water and molecules with low molecular weight through the membrane while solid particles and molecules with high molecular weight remain behind in a concentrated waste stream (Dhangar & Kumar, 2020). Nanofiltration (NF, pore size ~1–10 nanometers) and reverse osmosis (RO, pore size <1 nanometers) membranes vary in pore size, charge, molecular weight cut-off, and hydrophobicity/hydrophilicity, which influence the

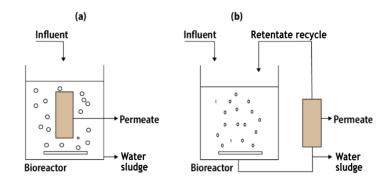


Figure 4. MBR system in (a) submerged and (b) sidestream configurations (Melin et al., 2005).

removal efficiency of specific PPCPs (Couto et al., 2018; Loganathan et al., 2023). The PPCPs themselves exist in a range of properties (e.g., size, charge, hydrophobicity), so it is not possible to generalize their performance based on membrane type or PPCP compounds in general.

Membrane bioreactors (MBRs) combine microfiltration (MF, pore size 0.1–1 micrometers) or ultrafiltration (UF, pore size 0.01–0.1 micrometers) with biological treatment. Figure 4 provides schematics of the two primary configurations of MBR systems. As with NF and RO membranes, water is forced across the membrane surface, but instead of a pressurized system, MBRs use a vacuum so that the water outside is at ambient pressure (U.S. EPA, 2007). The microbes at the membrane surface then work to biodegrade the retained compounds and transform them into smaller, less harmful compounds (Kumar et al., 2023).

MBRs work well for PPCPs that sorb onto solids and PPCPs that biodegrade. MBRs are less effective on dissolved trace organic compounds, including PPCPs, that are unlikely to biodegrade or sorb and may pass through the membrane pores. The addition of advanced membrane size exclusion methods, such as RO, increases PPCP removal when used in combination with an MBR (Wang et al., 2018). A downside of membrane technologies is that they form a concentrated waste stream that contains the contaminants removed from the water that were not biodegraded.

Applicability

Membrane separation processes effectively remove low molecular weight organic pollutants, such as PPCPs, from wastewater (Couto et al., 2018). Membranes and MBRs can be added to a conventional treatment system as a tertiary treatment step or MBRs can replace secondary biological treatment (U.S. EPA, 2007). The integration of an MF or UF membrane with a biological reactor in an MBR system allows for an increase in the solids retention time, resulting in improved efficiency in removing trace organics such as PPCPs (Couto et al., 2018).

Proper operation and maintenance are essential to avoid membrane obstruction and fouling. Regular cleaning with chemicals such as bleach or citric acid also helps to avoid clogging (U.S. EPA, 2007). Most MBR systems use an air-scour technique which blows air around the membrane to reduce material buildup on the pore surface (U.S. EPA, 2007). Membrane technology requires the management of concentrated waste streams consisting of PPCPs extracted from the wastewater along with other pollutants (Kumar et al., 2023). This concentrated effluent can be challenging to treat or dispose of in a way that mitigates ecological ramifications.

Considerations

Advantages of Membrane Technologies	Disadvantages of Membrane Technologies
 Membranes technologies do not alter the chemical structure of PPCPs, thus avoiding the production of potentially harmful byproducts. Membrane technologies have small footprint requirements. Membrane technologies can be used to treat other emerging contaminants, not just PPCPs. Membrane technologies make minimal use of dangerous chemicals. MBRs combine physical and biological removal of PPCPs. 	 Membrane technologies can have issues with clogging and fouling if improperly operated. RO/NF membranes create concentrated waste streams that must be disposed of or treated appropriately. Membrane technologies are complex to operate and maintain.

Performance

UF and RO were studied in combination at the pilot scale using conventionally treated secondary effluent (Snyder et al., 2007). The UF unit did not achieve significant PPCP removal and was used mainly as pretreatment for the RO unit. All 21 PPCPs identified in the secondary effluent, besides caffeine, were removed at over 90 percent efficiency using the UF/RO system (Snyder et al., 2007). Many PPCPs, including carbamazepine (anticonvulsant), DEET (insect repellent) and meprobamate (antianxiety) were removed at over 99 percent efficiency with the UF/RO system (Snyder et al., 2007).

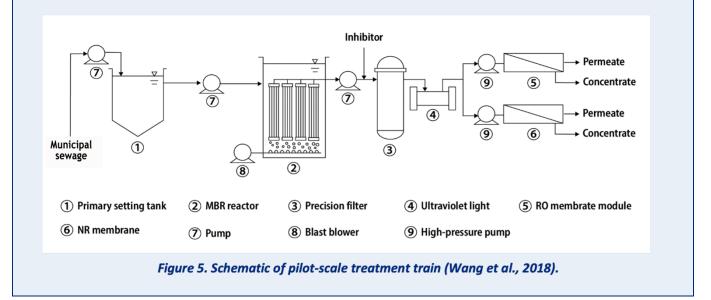
Pilot scale testing of an MBR system was performed on primary effluent from a municipal WWTP. Four membrane modules with a pore size of 0.2 micrometers were in operation during the study (Snyder et al., 2007). Several compounds were removed at 85 to 95 percent efficiency, including caffeine, carbamazepine (anticonvulsant), gemfibrozil (cholesterol medication), and hydrocodone (analgesic) (Snyder et al., 2007). Other compounds, such as ibuprofen and the antianxiety medication meprobamate, increased in concentration through the MBR (Snyder et al., 2007). Some trace organic contaminants may increase through an MBR due to potential precursor compound transformation in the wastewater treatment process.

Case Study: Integrated Membrane System for Municipal Wastewater (Wang et al., 2018)

This pilot-scale system treated municipal sewage using a primary settling tank prior to treatment in an MBR reactor using an MF membrane. The MBR reactor was followed by a precision filter (to remove suspended solids), UV light, and either RO or NF. The full treatment train is outlined in Figure 5. Twenty-seven PPCPs were detected in the raw wastewater and were monitored throughout the system.

Removal efficiency across the 27 contaminants was variable and highly dependent on their chemical characteristics. Removal efficiency through the MBR system alone was high for the hormone estriol (95 percent) and caffeine (88 percent) but was lower for the anticonvulsant carbamazepine (41 percent) and the beta blocker metoprolol (47 percent). The MBR system showed limited removal of hydrophilic PPCPs and those resistant to biodegradation. The downstream use of a smaller pore size NF/RO membrane more effectively removed these types of compounds. The combination of the MBR and NF membrane removed 13 of the 27 compounds to below their detection limit, while MBR and RO membrane removed 20 of the 27 compounds to below their detection limit. Using MBR and membrane filtration in combination can target a wide range of PPCP compounds and remove them effectively.





Constructed Wetlands

Description

Constructed wetlands mimic natural wetlands but are specially designed to meet treatment goals. As shown in Figure 6, several removal pathways occur in constructed wetlands, including biodegradation, sorption, and chemical oxidation (Al-Baldwai et al., 2021). The most effective mechanisms of PPCP removal in constructed wetlands are plant absorption and microbial degradation. Plants are primarily responsible for biodegradation in the form of phytodegradation. In phytodegradation, plants and their associated root microbes convert both inorganic and organic contaminants to less toxic forms, including complete mineralization to nontoxic inorganic end products (e.g., carbon dioxide, water) (Al-Baldwai et al., 2021). If PPCPs become embedded in plant tissues, they are rendered unattainable and will not return to soluble forms. Pretreatment of wastewater is needed to remove competing compounds that the plants may prefer, such as sucrose (Al-Baldwai et al., 2021). Unlike biodegredation, sorption and chemical oxidation mainly occur in the soil matrix where there are binding sites for PPCPs to sorb to and chemicals that could potentially oxidize them as well (Dhangar & Kumar, 2020).

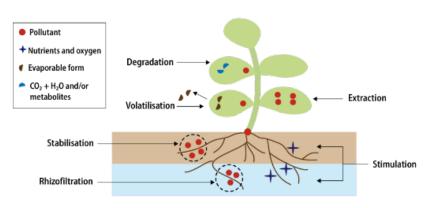


Figure 4. Major phytoremediation processes (Al-Baldwai et al., 2021).

Applicability

Constructed wetlands have low energy requirements, have simple operation and maintenance requirements, and are environmentally friendly. However, they do require a large footprint and are highly climate dependent as the activity of microbes decreases significantly in colder months (Kumar et al., 2023). They require occasional maintenance to remove built-up solids and exhausted biomass (Kumar et al., 2023).

The flow regime of wastewater through the constructed wetland is a critical design element in addition to the appropriate plant and soil substrate. Horizontal flow, vertical flow, and subsurface/surface flow are examples of regimes that could be used (Al-Baldwai et al., 2021). All flow regimes must provide a long hydraulic residence time such that there is ample contact time between microbes, substrates, and the contaminants. Over time, the accumulation limit of the plants is reached, and they must be harvested. These plants could potentially be used in compost or biofuels, however, the recalcitrance of PPCPs through different treatments and their pathways of rerelease are still within the research phase and more studies are needed (Al-Baldwai et al., 2021).

Considerations

Advantages of Constructed Wetlands	Disadvantages of Constructed Wetlands
 Constructed wetlands have low energy requirements. Constructed wetlands are simple to operate and maintain. 	 Constructed wetlands have large land requirements. Constructed wetlands are climate dependent. Constructed wetlands are prone to clogging issues. It is difficult to monitor removal pathways in a constructed wetland. Constructed wetlands necessitate the harvesting and disposal of vegetation which may contain PPCPs.

Performance

The performance of constructed wetland systems is highly dependent on their design and function, especially since these factors can vary widely between systems. The growth and activity of plants and microorganisms are significantly affected by water, soil, and air temperatures (Hu et al., 2021). A full-scale study of a constructed wetland treating municipal wastewater in Spain reported ibuprofen removal at 42–99 percent and caffeine removal at 83–96 percent, whereas a full-scale study of a constructed wetland treating wastewater in the Czech Republic reported ibuprofen removal at 55 percent and caffeine removal at 84 percent (Al-Baldwai et al., 2021). In the Spain study, ibuprofen was assumed to be aerobically biodegraded, as was caffeine in the Czech Republic study. In constructed wetlands, it can be difficult to know which degradation pathway a chemical has taken because there are several possibilities.

Case Study: Full-Scale Application of Integrated Conventional, Membrane, Adsorption, and Oxidation Treatment (Yang et al., 2011)

Combining processes to treat PPCPs takes advantage of the different mechanisms specific to each process that are synergistic or complementary. The following case study is an example of this principle in action. The F. Wayne Hill Water Resources Center (WRC) is an advanced water reclamation plant that employs several of the technologies described above to treat approximately 60 million gallons per day of municipal wastewater. The WRC's treatment process consists of conventional treatment (primary clarification and activated sludge treatment) followed by membrane microfiltration, activated carbon adsorption beds, and ozonation, as seen in Figure 7.

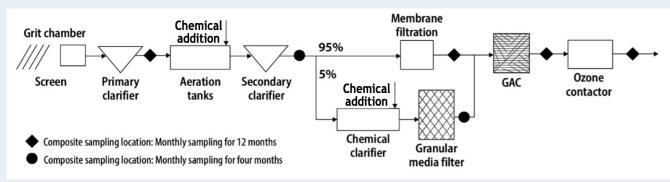


Figure 7. Schematic diagram of the wastewater reclamation plant (Yang et al., 2011).

Sixteen PPCPs were monitored throughout the WRC to determine which treatment units were removing specific compounds. Acetaminophen, ibuprofen, and caffeine were removed at over 99 percent removal efficiency in the activated sludge treatment. The concentration of DEET was reduced by several orders of magnitude after passing through activated sludge treatment and membrane microfiltration, but was largely unaffected by the GAC and ozone. Two antibiotics and one anti-inflammatory that were resistant to biological treatment were removed by GAC. One antibiotic that increased in concentration through the GAC on average showed 88 percent removal efficiency through the ozone contactor. Only DEET, caffeine, an antibiotic, and an anticonvulsant were detected consistently in the final effluent. Except for one antibiotic and one anticonvulsant, which were reduced in concentration by about 50 percent, all compounds were removed at an efficiency of over 95 percent between the primary effluent and the final effluent.

Implementing tertiary treatment after the conventional treatment steps improves removal beyond what can be achieved by clarification and activated sludge treatment. What isn't removed in those initial steps is targeted more specifically in adsorption and ozonation treatment units. A multi-step approach that incorporates a combination of processes removes a range of PPCPs. Note that this study did not include an analysis of the sludge handling, which is critical when designing PPCP wastewater treatment decisions.

Call for Projects! Interested in piloting one of these technologies at your facility or have a different project planned to address PPCPs in your area? We'd love to hear from you!

To learn how to have your project featured in EPA's Searchable Clearinghouse of Wastewater Technology (SCOWT), contact EPA (<u>cwsrfEC@epa.gov</u>) to provide project details. Contributing information about your project helps EPA build a library of case studies to serve as examples for future projects. Be a part of advancements in the treatment and removal of emerging contaminants.

Pharmaceuticals and Personal Care Products (PPCPs) Treatment Technology Summary Table

(Note: This table is not comprehensive and is intended to be complementary to this technology brief.)

Treatment	Targeted PPCP Type(s)	Advantages	Disadvantages	Performance	Operation and Maintenance Considerations
Conventional Treatment Further reading: Suárez et al., 2008	Non-targeted treatment.	Does not require changes to the current system. Removal can be enhanced with coagulants/flocculants.	Not designed to specifically target PPCPs.	Primary treatment: fragrances (60–90% removal); carbamazepine (0– 45% removal). Secondary treatment: fragrances (50–75% removal); hormones (49–99% removal).	Sludge is likely to contain PPCPs and should be properly used or disposed of.
Adsorption Technologies Further reading: Baskar et al., 2022; Dhangar & Kumar, 2020; Kumar et al., 2023; Snyder et al., 2007; Suárez et al., 2008; Tarpani & Azapagic, 2018; U.S. EPA, 2000; Yang et al., 2011	Some PPCPs likely to sorb onto solids.	Removes a wide range of PPCPs. Granular activated carbon (GAC) media can be backwashed, regenerated, and reused. Does not form potentially harmful degradation products.	GAC systems must be monitored and backwashed frequently to prevent clogging and breakthrough. GAC media regeneration requires significant energy and may need to be done off site.	Laboratory scale: >90% removal of select PPCPs. Full scale: more variable, system dependent. Dependent on adsorbent media, can be targeted to specific compounds.	Media regeneration and replacement required (for GAC). Solids removal and handling required (if using powder).

Treatment	Targeted PPCP Type(s)	Advantages	Disadvantages	Performance	Operation and Maintenance Considerations
			GAC media regeneration produces a concentrated waste stream that must be handled appropriately. Adsorption technology does not degrade PPCPs; they remain in their original form.		
Oxidation Technologies Further reading: Dhangar & Kumar, 2020; Kumar et al., 2023; Ngumba et al., 2020; Paucar et al., 2018; Suárez et al., 2008; Sui et al., 2013; Tarpani & Azapagic, 2018; Tijani et al., 2013; U.S. EPA, 1999; Yang et al., 2011	Dependent on type of chemical agent used. Effective on PPCPs resistant to sorption and biodegradation.	Effectively degrades resistant PPCPs. PPCPs are chemically transformed, not simply phase changed. Also treats for pathogens and metals (Tarpani & Azapagic, 2018). Produces no additional waste stream.	Chemical transformation of PPCPs can form potentially harmful degradation products that are challenging to monitor. Byproducts of the oxidant itself may be potentially harmful. Chemical agents may need to be produced on site and may be energy intensive. Chemical agents can be hazardous to handle.	Ultraviolet (UV) photolysis: >90% for two antibiotics and one antiviral. Ozonation: >90% removal of most PPCPs, especially hormones. Dependent on chemical agent, can be targeted to specific compounds.	Chemical handling may be required, especially if generated on site.

Treatment	Targeted PPCP Type(s)	Advantages	Disadvantages	Performance	Operation and Maintenance Considerations
Membrane Technologies Further reading: Dhangar & Kumar, 2020; Kumar et al., 2023; Snyder et al., 2007; Tijani et al., 2013; U.S. EPA, 2007; Wang et al., 2018	PPCPs likely to sorb onto solids. PPCPs likely to biodegrade.	Membranes do not alter the chemical structure of PPCPs, thus avoiding the production of potentially harmful byproducts. Small footprint requirements. Can be used to treat other emerging contaminants, not just PPCPs. Minimal use of dangerous chemicals. Membrane bioreactors combine physical and biological removal of PPCPs.	Issues with clogging and fouling if improperly operated. Reverse osmosis/nanofiltration creates a concentrated waste stream that must be disposed of or treated appropriately. Complex to operate and maintain.	Pilot scale: 85–95% removal of several different PPCPs. Laboratory scale: high removal of hormones and triclosan, low removal of pesticides and pharmaceuticals.	Regular air-scouring of membranes is required to remove adhered solids. Regular chemical cleaning is needed to reduce fouling.

Treatment	Targeted PPCP Type(s)	Advantages	Disadvantages	Performance	Operation and Maintenance Considerations
Constructed Wetlands Further reading: Al- Baldawi et al., 2021; Dhangar & Kumar, 2020; Kumar et al., 2023	PPCPs likely to sorb onto solids. PPCPs likely to biodegrade.	Low energy requirements. Simple operation and maintenance.	Large land requirements. Climate dependent. Prone to clogging issues. Difficult to monitor removal pathways. Harvesting and disposal of vegetation which may contain PPCPs is required.	Full scale, Spain: 42– 99% removal of ibuprofen, 83–96% removal of caffeine. Full scale, Czech Republic: 55% removal of ibuprofen, 84% removal of caffeine.	Regular solids removal is required to reduce clogging. Removal and disposal of biomass is required.

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