

# Stability and Removal of Commonly Used Drugs in Environmental Water and Wastewater

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Abstract: Introduction: Pharmaceuticals are regarded as emerging contaminants in the environment. In recent years, their destiny and removal have piqued people's interest. Methods: Examine how well conventional wastewater treatment facilities and cutting-edge technologies (ultrafiltration and reverse osmosis) can remove specific pharmaceutical compounds from water, with a focus on the compounds' environmental status, their origin, deterioration, metabolites, and the capacities of these facilities. Results and discussion: the ability and efficacy of sophisticated treatment technologies such as membrane separation, adsorption, and AOPs (Advanced Oxidation Processes) in eliminating chosen commonly used drugs from water are explored. Batch adsorption experiments were integrated with appropriate adsorption isotherms and appropriate kinetic models to predict the final extent of pollutant removal by this method. Continuous filtration mode was also investigated. Combining filtration (using AC (Activated Carbon) and micelle-clay granule complexes) with AOPs improves the economy of treating wastewater, which contains recalcitrant PhACs (Pharmaceutical Compounds).

**Key words:** Pharmaceutical compounds, membrane technology, wastewater plants, adsorption, membrane separation, micelle-clay, AOPs.

# **1. Introduction**

The presence and destiny of anthropogenic chemical species in general, as well as PPCPs (Pharmaceuticals and Personal Care Products), in treated wastewater and the natural aquatic environment, has become a major concern [1, 2]. PhACs (Pharmaceutical Compounds) are biologically active and can be found in small amounts in the environment [1-6]. More research into their chemical stability and biological activities is needed [3-10]. They have the potential to affect people in lower quantities than many other pollutants found in the environment, which is cause for concern.

On the global market, there are currently around 3,000 and 300 active pharmaceutical compounds for

human and veterinary use, respectively [2]. ASA (Acetylsalicylic Acid), or aspirin, was first produced in 1899. Since then, paracetamol, ibuprofen, diclofenac, naproxen, ketoprofen, amoxicillin, and various other medicinal substances have been commercialized [11]. These compounds are utilized as analgesics, anti-inflammatories, anti-arthritics, and antibiotics in humans, but they are also used in veterinary medicine [12].

Some pharmaceuticals and their metabolites can be partially removed from the environment through sorption and biotic or abiotic degradation. As a result, they can end up in drinking water supplies. According to several studies, traditional water treatment processes are unable to completely remove some prescription and non-prescription drugs from water sources [13-16].

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Pharmaceuticals and their metabolites have recently been found in surface water [7, 17-23], groundwater [24-27], drinking water [21, 28-30], tap water [31], ocean water, sediments, and soil [1].

Because of the increasing use of OTC (Over-the-Counter) medicines, their presence in bodies of water is one of the most pressing topics in environmental science. Several researchers have looked into the occurrence of pharmaceuticals in rivers, groundwater, and wastewater treatment plant effluents, as well as the effectiveness of various treatment techniques for their removal. Ibuprofen, naproxen, ketoprofen, diclofenac, and bezafibrate are the most regularly used pharmaceutical chemicals in the Finnish pharmaceutical business [32], and substantial amounts of these medications are found near STPs (Sewage Treatment Plants) (Table 1). The residues of these chemicals are hazardous to the ecosystem [32].

STPs only partially remove the selected medicines, as demonstrated in Table 1. Because the medications included in Table 1 are generally polar and have low volatility, their removal by the aforementioned methods is only 60-90 percent [33]. This shows that traditional sewage treatment procedures are incapable of completely removing these chemicals.

According to Enick et al., approximately 50% of wastewater volume is generated from pharmaceutical sources around the world [34]. Pharmaceuticals carefully enter the ecosystem via municipal WWTPs (Wastewater Treatment Plants), medical centers, and solid waste disposal sites [35-39].

The elimination of PhACs during biological wastewater treatment is critical for avoiding these compounds from

Table 1Pharmaceutical concentrations and percentclearance near Finish STPs [32].

Compound	Influent (µg/dm <sup>3</sup> )	Effluent (µg/dm <sup>3</sup> )	Removal (%)
Bezafibrate	0.42	0.21	50
Naproxen	4.9	0.84	83
Diclofenac	0.35	0.26	26
Ibuprofen	13.1	1.3	92
Ketoprofen	2	0.45	78

spreading into the environment [38-40]. The majority of current wastewater treatment methods were not engineered with PhACs in mind [41-45]. According to certain research, secondary wastewater treatment techniques (such as activated sludge and membrane bioreactors) can only remove PhACs such as sulfamethoxazole, carbamazepine, and diclofenac to a limited extent. On the other hand, other chemicals including ibuprofen, naproxen, and bezafibrate were successfully eliminated [19, 41, 42, 46]. Because biological approaches are unable to provide a dependable barrier against some recalcitrant pharmaceuticals [47-51], further advanced treatment technologies must be introduced in regions where a chronic pollution problem has been identified or is expected. Furthermore, the removal of pharmaceutical residues from contaminated water has been demonstrated to be inefficient using MBR (Membrane Bioreactor) technology, ozonation, and AOPs (Advanced Oxidation Processes) [25, 52-55]. However, combining the three methods mentioned above could result in a medicinal removal solution.

## 1.1 Conventional Treatment Methods

The first technology utilized to cleanse wastewater from pharmaceutical residues was AS (Activated Sludge) technology [49, 56]. HRT (Hydraulic Retention Time), temperature, pH, DO (Dissolved Oxygen), organic load, microbial population, and the presence of hazardous heavy metals are all factors that influence the effectiveness of the activated sludge process. Because PhACs are often physiologically resistant chemicals, the AS approach has been proven to be ineffective in treating wastewater contaminated with PhACs residues [48, 55-64]. MBRs were also found to be more effective in removing medications due to their narrow pore size [65-67].

#### 1.2 Physio-Chemical Treatment Options

#### 1.2.1 Membrane Processes

For the removal of pharmaceutical residues from

contaminated water, MF (Microfiltration), UF (Ultrafiltration), NF (Nanofiltration), RO (Reverse Osmosis), electro dialysis reversal, membrane bioreactors, and combinations of membranes in series were tested [68, 69]. Because of their high pore size, MF and UF procedures are ineffective, but RO and NF are the most often used methods for drinking water purification [65]. The elimination of pharmaceutical residues by RO was shown to be very effective [69-77]. The elimination efficiency of ketoprofen and diclofenac by the NF membrane was found to be better than 90% in a pilot-size investigation [78]. In another investigation, negatively charged diclofenac was removed by RO membranes at a rate of 95% [76].

1.2.2 AC (Activated Carbon)

In tertiary treatment processes, two types of AC are used: GAC (Granular) and PAC (Fine Powder). GAC is frequently used as a traditional filter, providing a medium for both filtration and adsorption [65]. In addition to taste and odor reduction, GAC and PAC are utilized as effective materials for the adsorption of various PhACs and pesticides [79].

The Langmuir adsorption isotherm equation represents the equilibrium between aqueous and solid phase systems in AC adsorption as a reversible chemical equilibrium between species [80]. The Langmuir adsorption isotherm is based on the following assumptions: (a) all sites have the same adsorption energy; (b) adsorption occurs on localized sites with no interaction between adsorbed molecules; and (c) the maximum adsorption feasible is a complete monolayer. The adsorbent surface (solid phase) consists of fixed individual locations where adsorbate (organic pollutant) molecules can be chemically bonded [30]. Datta [81] and Cruz-Guzmá et al. [82] discovered that the adsorption of 6-APA (6-Aminopenicillanic Acid) by AC effectively removes the majority of 6-APA. Sedimentation and filtration are two pre-treatment techniques that could reduce carbon requirements. However, the high cost of active carbon, along with the costly process of regeneration, has prompted researchers to look for new low-cost materials, such as the usage of complex organoclay adsorbents.

1.2.3 Oxidation Reactions

AOPs are the most efficient procedures for removing contaminants from wastewater that are difficult to remove using traditional treatment methods. AOPs remove more material than damaging radiation alone [37,52]. In most cases, they are utilized in addition to traditional treatment approaches [83]. AOPs have been shown to be effective at removing medications in numerous studies [29, 84, 85]. Direct photolysis is not an efficient method for removing drugs from wastewater, according to reports. Photolysis using Fe (III) and  $H_2O_2$  or TiO<sub>2</sub> can, however, successfully remove the majority of pharmaceutical residues from contaminated water [86, 87].

Novel ways of treating pharmaceutically rich sewage influent have been developed to increase removal efficiency. In some circumstances, AOPs may be a better option than filtering for eliminating organic materials from wastewater [88]. AOPs work by producing highly reactive free radicals like the hydroxyl radical (OH•), which are capable of oxidizing organic molecules [89-91]. One of the most successful clean technologies for reducing/removing pollutants from wastewater and drinking water is photocatalytic oxidation. TiO<sub>2</sub> is the most commonly utilized nanoparticle in photocatalysis because it can create electronic transitions via light absorption in the near ultraviolet range. In addition, this semiconductor can be employed in a wide pH range. TiO<sub>2</sub> is also notable for its low cost, excellent photocatalytic activity, and photo-corrosion resistance. However, the nonselectivity of attack and the ability to destroy contaminants without moving them from one phase to another or concentrating them are some of the drawbacks of hydroxyl radicals [92]. AOPs have the capacity to totally and effectively mineralize most of the organics present by relying on exceptionally powerful OH radicals (oxidation potential = 2.8 V) that are produced throughout the process [93-96]. As a result of AOPs, the produced hydroxyl radical can degrade organics and other contaminants in aquatic solutions through a series of steps [96] with some exception such as tetracycline that cannot be photo destroyed.

OH reacts quicker than diffusion-controlled reactions with double and triple carbon-carbon bonds and aromatic compounds with electron-donating substituents [97]. However, the presence of hydroxyl radical scavengers, such as humic chemicals, oxidation by-products, inorganic compounds like carbonate and bicarbonate, excessive alkalinity, and high dosages of hydrogen peroxide, can reduce AOP effectiveness.

Different oxidation processes, such as photocatalysis (e.g.,  $TiO_2$ ) [98] and solar irradiation, can produce hydroxyl radicals. Combinations of UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, UV/O<sub>3</sub>-H<sub>2</sub>O, and UV/TiO<sub>2</sub> are among the AOPs currently being researched and developed in the literature [99].

Due to its capacity to eliminate refractory chemical compounds,  $TiO_2$  has recently attracted much attention [54, 100, 101]. On the other hand, the degradation of these substances may produce more dangerous intermediates [102, 103]. AOPs as a pre-treatment have been shown to improve biological therapy whereas  $TiO_2$  is used as a post-treatment to other biological, physical, and chemical treatments for complete mineralization [104].

The extension of AOPs to be effective using solar energy renders the process to be more economically feasible and affordable [105, 106].

Other research used a mixture of UV,  $O_3$ , and  $H_2O_2$  to treat municipal wastewater contaminated with various medicines [103, 107]. All of the targeted pollutants' concentrations were determined to be below detection thresholds after they were removed. Furthermore, it was discovered that adding  $H_2O_2$ 

boosted the removal effectiveness somewhat.

Doll and Frimmel [54] used a treatment method that combines photo-catalysis and microfiltration in another study. After the photo-catalytic degradation process, this integration allowed  $TiO_2$  to be separated and reused. Malato et al. [108] presented the building of a pilot plant that used a solar photo-catalytic treatment system and proposed the mechanism for the operation of these pilot plants, as well as the parameters for optimizing solar photo-catalytic reactions [109, 110].

The mechanism behind the high oxidizing power of TiO<sub>2</sub> is based on electronic transitions from its valence band to the conduction band. These transitions are caused by band gap lighting of semiconductor particles floating in the water, leaving holes in the former. These electrons and holes either migrate to the particle surface and participate in redox processes or recombine and release heat. Reduction reactions devour electrons from the conduction band, whereas oxidation reactions fill holes. Water oxidation at the valence band of TiO<sub>2</sub> produces hydroxyl radicals [111-114]. These can easily target adsorbed organic molecules or those adjacent to the catalyst's surface. For this mechanism to work, the pollutant must first be adsorbed on the catalyst's surface in order for oxidation to take place, resulting in their total mineralization at the end of the process [115] (Fig. 1).

### 1.3 Micelle-Clay Complexes as Potential Adsorbents

Montmorillonite [116] is the most commonly utilized clay in the manufacturing of organic clay. This clay has a permanent negative charge due to multiple isomorphic substitutions [117]. The cations (usually Na<sup>+</sup> and Ca<sup>2+</sup>) that can be swapped by other cations present in a solution compensate for this charge. A cation's charge causes it to be very hydrophilic and hydrated [118]. This hydration, in addition to the presence of Si-O groups in the clay, renders the mineral's surface hydrophilic.



Fig. 1 UV illumination of the TiO<sub>2</sub> solution interface and UV illumination of TiO<sub>2</sub> surface reactions.

As a result, in the presence of water, the adsorption of non-ionic, organic molecules by the clay is reduced because organic compounds, being relatively polar, cannot compete with water for adsorption sites on the clay surface. Organic cations are substituted for the cations that were initially present in the interlayers to create modified clays. Alkyl-ammonium ions are the most commonly used organic cations (such as octadecyl-trimethyl-ammonium). A central nitrogen atom is coupled to four chemical groups, including a hydrogen ion, in the molecular structure of this molecule. The charged component of the organic cation interacts with the clay via electrostatic interactions and binds itself to the surfaces of the interlayer. The clay becomes organophilic due to the aliphatic component of the molecule. The insertion of the organic cation into the interlayer causes the clay's basal distance to grow and water to be removed. The process involved is solely an exchange of cations when the cation is adsorbed to a lesser degree than the clay's CEC (Cation Exchange Capacity). The adsorption of larger loads than the CEC is due to Van der Waals forces. The organic-clay combination takes on a positive charge and is more hydrophobic than the unmodified clay when the organic cation adsorbed exceeds the CEC [119].

Surfactants have two chemical structures, one of which is water-loving or hydrophilic and the other of which is hydrophobic and consists of amphiphilic or amphipathic molecules [120]. Micelles are amphiphilic molecular aggregating in an aqueous environment. These molecules produce small "globules" in water with one hydrophobic and one hydrophilic end, with the hydrophobic parts pointing into the center and the hydrophilic ends interacting with the water. Micelles are interesting because they can sequester chemicals that are insoluble in water ordinarily. Micelle formation happens only when the concentration of amphiphilic molecules reaches a CMC (Critical Micelle Concentration) of a certain minimum [120, 121].

The micelle-clay combination is made up of an organic cation (surfactant) with a long alkyl chain that produces micelles of several nanometers in diameter spontaneously. At appropriate ratios, the micelles interact with a negatively charged clay mineral (montmorillonite) or clay, such as bentonite. The most commonly used organic cations were ODTMA (Octadecyltrimethylammonium) and BDMHDA (Benzyldimethylhexadecylammonium), both of which are quaternary ammonium cations with an alkyl chain

of 18 (ODTMA) or 16 (BDMHDA, which also has a benzene ring) [122-124].

The micelle-clay complex has different material properties than an organo-clay complex [124], which is generated by the interaction of surfactant monomers with clay. The complex has a huge surface area per weight, has substantial hydrophobic sections, and has a positive charge surplus of nearly half the clay's exchange capacity. Surfactant release from the combination is modest; a layer of AC was used to minimize released surfactant concentrations during filtration to 1 ppb or less. High temperature, salinity, and pH had little effect on filtering capacity [2-13]. Micelle-clay is good for the adsorption of anionic organic compounds, such as anionic medicines, as well as certain neutral and hydrophobic medications. The removal of anionic medicines has proven to be extremely effective. Antibiotics, painkillers, and hormones are all possible applications. Tetracyclines (tetracycline, oxytetracycline, chlortetracycline), sulfonamides (sulfamethoxazole, sulfisoxazole, sulfamethizole), amoxicillin, and cefuroxime axetil medicines were removed from water in studies [122, 125]. Diclofenac, ibuprofen, naproxen, and mefenamic acid were reported to be removed by others [71, 73, 74]. Furthermore, the statins atorvastatin, rosuvastatin, and Simvastatin, as well as dexamethasone sodium phosphate, diazepam, spironolactone, and the statins atorvastatin, rosuvastatin, and Simvastatin, were studied [75, 126].

A powdered complex was used in all of the above studies. To allow for flow, the complex held in filters had to be blended with extra sand. Undabeytia et al. [123] described a way for making a granulated complex that could be confined alone in a filter without the requirement for sand mixing. The powdered complex, with smaller particles, can be removed more efficiently by filtering than the granulated complex, but because the capacity per kg of the complex grows with its concentration, the overall capacity per weight is increased by utilizing a granulated complex [123]. Future investigations on the removal of pharmaceuticals from water and wastewater are expected to use the granulated complex. The conclusion of the filtering results and estimated capacities will be discussed in the following sections of this review.

# 2. Stability of a Number of Drugs in Pure and Wastewater

### 2.1 Ibuprofen

Despite the fact that only the S enantiomer of Ibuprofen has a pharmacological impact, a racemic combination is commonly used in commercial applications. After absorption, the inactive R (-) ibuprofen is converted into the active S (+) enantiomer by chiral inversion. As shown in Fig. 2 [127], hydroxyl-ibuprofen (2-(4hydroxyl-2-methyl propyl) phenyl) propionic acid, carboxy-ibuprofen (3-(4-(1-carboxyethyl) phenyl)-2methyl-propionic acid), and carboxy-hydrotropic acid (4-(1-carboxyethyl) benzoic acid) are the primary metabolites of Ibuprofen [127].

In the biological treatment of active sludge, ibuprofen has various transformation kinetics under different circumstances. Ibuprofen metabolites were identified, and carboxy-ibuprofen was measured [127].

However, the metabolite hydroxyibuprofen was discovered as the primary component associated with ibuprofen in the influent and effluent of a number of wastewater treatment plants. As a result, hydroxyibuprofen appears to be the most stable of the three degradation products found [71, 127]. Furthermore, Khalaf et al. [72] discovered that in aerobic situations, hydroxyl ibuprofen was generated in activated sludge, whereas carboxyhydratropic acid was formed in anaerobic settings.

#### 2.2 Naproxen

Similar to ibuprofen, naproxen (2-naphthaleneacetic acid, 6-methoxy-a-methyl-, (S)-(+) -(S)-6-methoxy-a-methyl-2-naphthaleneacetic acid) is a NSAID (Non-Steroidal Anti-Inflammatory Medication). The mechanism



Fig. 2 OH-Ibuprofen: hydroxyl- Ibuprofen, CA-Ibuprofen: carboxy-Ibuprofen, and CA-HA: carboxyhydratropic acid were the human metabolites of ibuprofen [127].

of action of NSAIDs in organisms is still a hot topic of discussion. Meanwhile, the most likely hypothesis is that the COX (cyclooxygenase) enzyme, which is the primary enzyme involved in the manufacture of prostaglandins and is responsible for pain and inflammation [127, 128], is inhibited. Prostaglandins can also cause muscle contraction and atony, which affects blood circulation and blood pressure. Prostaglandins provide protection to cells in the gastrointestinal tract (stomach, kidney, liver). Inhibition of these enzymes can cause a variety of side effects, including bleeding (one of the most important negative effects of these compounds). NSAIDs can also cause gastric ulcers and, in the case of the elderly, liver and kidney problems [129].

Naproxen stability tests were carried out in a WWTP at 25 °C by dissolving naproxen in either pure water or activated sludge. During 14 days, no chemical or biological degradation occurs, according to these investigations [74]. Furthermore, naproxen breakdown was gradual, with only one metabolite detected at low intensity after 28 days in activated sludge, resulting in a 60 percent transformation. The naproxen metabolite was identified as O-desmethylnaproxen based on its molecular anion (m/z 215), and the product ion spectra, which indicated the presence of one carboxylate group [5].

#### 2.3 Aspirin (Acetylsalicylic Acid)

Aspirin, also known as ASA (acetylsalicylic acid), is a NSAID (Non-steroidal Anti-Inflammatory Medicine) that is often used to treat minor aches and pains. It is also utilized as an antipyretic to lower fever and minimize the chance of death from a heart attack [130]. Aspirin degrades into salicylic acid in an aqueous condition, as demonstrated in Fig. 3A [11].

The conjugation of salicylic acid with glycine or glucuronic acid produced two inactive metabolites in the human body's aspirin metabolism: salicyluric acid and glucuronide ether/ester. In addition to these metabolites, gentisic acid [131, 132], which is produced by the oxidation of salicylic acid, is observed (Fig. 3B).



Fig. 3A A representation of the hydrolysis of aspirin (acetylsalicylic acid) to salicylic acid and acetic acid.



Fig. 3B An illustration of the metabolism pathway for salicylic acid.

Aspirin and salicylic acid have been observed to have the highest amounts of pharmaceuticals in water bodies in numerous regions [133]. Aspirin undergoes hydrolysis to salicylic and acetic acids after 8 days in pure water, according to aspirin stability tests in pure water and wastewater. The rate constant for the hydrolysis of aspirin in pure water was  $3.57 \times 10^{-9}$  s<sup>-1</sup> and  $8.45 \times 10^{-9}$  s<sup>-1</sup> in wastewater after five days at 25 °C. This increase in aspirin in wastewater was attributed to the wastewater's content (which includes a range of enzymes, microorganisms, and heavy metals) acting as a catalyst for such processes [134].

#### 2.4 Paracetamol

Paracetamol is a non-steroidal anti-inflammatory medicine that is currently used all over the world for pain relief and fever control [135, 136]. When taken in therapeutic doses, around 58-68 percent of paracetamol is eliminated from the body; this antipyretic medicine is freely available in most countries, even without a medical prescription. As a result, comparable to other pharmaceutical substances, paracetamol concentrations

in wastewater and water resources might be high. Paracetamol is largely safe at therapeutic levels; nevertheless, at high concentrations, it can cause liver failure, gastrointestinal sickness, centrilobular necrosis in the liver, and eventually hepatotoxic potential.

Tablets, capsules, drops, elixirs, suspensions, and suppositories are all examples of paracetamol dosage forms. It is stable at a pH of about 6, but in acidic or alkaline conditions, it degrades, and hydrolysis to acetic acid and *p*-aminophenol occurs (Fig. 4A).

Fig. 4B depicts three metabolic routes for paracetamol, including glucuronidation, sulfation, and N-hydroxylation, followed by the sulfhydryl group of GSH (Glutathione Conjugation). These three routes produce inactive, non-toxic end products that are subsequently eliminated by the kidneys. The intermediate product of the N-hydroxylation and rearrangement metabolic pathway, however, is hazardous when it reacts with proteins and nucleic acid [137]. Paracetamol solution in wastewater, on the other hand, is hydrolyzed to *p*-aminophenol after 7 days [134].



Fig. 4A The hydrolysis pathway for paracetamol.



Fig. 4B The metabolic pathways for paracetamol.

#### 2.5 Amoxicillin

The stability of amoxicillin in water containing 100 g/mL of amoxicillin was investigated at different pH levels (pH 5, pH 7 and pH 8) for water containing 100 g/mL of amoxicillin. In addition, two natural solutions were investigated: secondary effluents and tap water, both of which were kept at room temperature for 16 days and then sampled after 3, 6 and 16 days [127, 138]. Amoxicillin penicilloic acid (ADP1/2), phenol hydroxyl pyrazine (ADP6), and two more compounds, amoxicillin 20,50-diketopiperazine (ADP8/9) and amoxicillin-S-oxide (ADP3), were found as breakdown products [139].

As illustrated in Fig. 5 [140], ADP1/2 are the first products of the hydrolysis process in which the lactam

ring is opened and obtained swiftly in tap water; the other compounds, ADP4/5 and ADP8/9, are derived from ADP1/2.

The availability of the lone pair of electrons on the amine group ( $pK_a$  ( $NH_2$ ) = 7.56), which are available for nucleophilic attack on the carbonyl group to yield the diketopiperazine ring, caused ADP8/9 to form preferentially at pH 8 as opposed to pH 7 or 5; this preferential formation at relatively high pH was due to the accessibility of the lone pair of electrons on the amine group ( $pK_a$  ( $NH_2$ ) = The decarboxylation products (ADP4/5) were preferred at low pH compared to their production at higher pHs (pH 7 and 8) [141, 142].

ADP6 is the stable end product acquired through various well-known degradation procedures in the pharmaceutical sector. Its conjugated double bond is



Fig. 5 The degradation pathway of amoxicillin in an aqueous medium.

responsible for its stability, as well as its yellow color [143]. Because of the abundance of ADP1/2, which began the synthesis of the other ADPs, ADP6 was predominantly identified in tap water (pH 6.5).

# **3.** Removal of Pharmaceuticals from Water and Wastewater

Over the last few decades, the removal of micropollutants from water and wastewater has gotten much attention. Pharmaceuticals, insecticides, industrial chemicals, hormones, personal care items, and other compounds are examples of micropollutants, often known as emerging contaminants. Pharmaceuticals have been found in surface waters ranging from parts per million to parts per trillion, implying that typical STPs are ineffective in removing these substances [144, 145]. Because of their low biodegradability and high chemical stability, current wastewater treatment technologies such as those based on biological, thermal, and physical treatment processes are ineffective in eliminating or degrading tiny molecular-weight medications [146]. The increased awareness of the threat posed by toxic organic contaminants in the aquatic environment has prompted the development of advanced technologies such as membrane filtration, which consists of sequential elements such as UF (Ultra-Filtration), AC filter, and RO, as well as adsorption and AOPs [71-75].

The following sections detail the results obtained using all of the technologies used in earlier investigations, ranging from traditional treatment procedures to sophisticated technologies such as membrane filtration, adsorption, and AOPs.

# 3.1 Removal of Pharmaceuticals During Conventional Wastewater Treatment

Much prior research [147-149] has shown that drugs can find their way into the aquatic environment. One of these channels [150] is domestic wastewater, which comprises pharmaceutical drugs expelled via urine and feces either as the original compound or as metabolites. Hospital and manufacturing effluents, land applications such as biosolids, concentrated animal feeding activities, and direct discharge of pharmaceutical substances to the environment are all examples of environmental exposure pathways [151]. The majority of these paths end up in the wastewater stream, where they eventually end up at WWTPs 147]. Pathogens, organic and inorganic suspended and flocculated debris, were the primary goals of WWTPs. The majority of research found that the procedures used in WWTPs were ineffective in removing these medicines from wastewater and that, as a result, WWTPs have become a major collecting and release site for these pharmaceuticals into the environment [152]. The primary and secondary stages of a WWTP are usually present. When a better grade of released water is required for certain reasons, a tertiary treatment stage is added [153]. Physical settling or filtration are two primary treatment procedures for removing big particles from wastewater [153, 154]. Pharmaceuticals and other forms of micropollutants are primarily eliminated in primary treatment procedures by sorption on primary sludge or by absorption caused by interactions between the pharmaceutical compound's aliphatic or aromatic groups on the one hand, and the lipophilic cell membranes of sludge microorganisms on the other, or via adsorption caused by electrostatic interactions between positively charged groups and negatively charged surfaces of microorganisms and sludge [150]. Pharmaceutical chemicals were treated with a series of processes in the secondary treatment stage, including dispersion, dilution, partition, biodegradation, and abiotic transformation. The overall fall of the parent molecule, which has been linked to many distinct mechanisms such as chemical and physical

transformation, biodegradation, and sorption to solids [155, 156], is used to estimate the removal efficiency during secondary treatment. Pharmaceuticals were biologically destroyed to varying degrees after subsequent treatment, resulting in mineralization or partial breakdown (generation of by-products) [150]. In general, the transformation of the parent component into a new substance is referred to as pharmaceutical removal. As a result, it accounts for all decreases in parent compounds caused by a variety of mechanisms, such as chemical and physical transformations, biodegradation, and sorption to solid matter [157-159].

Adsorption of diclofenac and estriol to sludge particles was found to be only 28% in a similar vein [160]. Ibuprofen, naproxen, and sulfamethoxazole sorption onto solids was less than 5% in most cases [161, 162], according to Carballa et al. [128], whereas Verlicchi et al. [162] found that sorption onto solids was less than 5% in most cases [162], and Ternes et al. [159] reported about 30% sorption for mefenamic acid [163].

The investigations by Petrovic et al. [158] and Jelic et al. [163] on a set of analgesic, anti-inflammatory, and antibiotic medications in numerous countries showed regional and temporal variability in pharmaceutical concentrations in WWTP influent and effluent, with influent ranged between 0.001 to 56.94 µg/L and 0 µg/L to 5.09 µg/L effluent ranged for acetaminophen, aiclofenac, abuprofen, aetoprofen, aefenamic, aaproxen, aalicylic acid, arythromycin, aulfamethoxazole and arimethoprim. The rate of production, dosage and frequency of administration and usage, excretion rate or metabolism, environmental persistence, and elimination efficacy of wastewater treatment systems could all play a role in this variation [157, 158].

Due to variances in chemical characteristics, pharmaceutical substances are categorized according to therapeutic purposes, resulting in large variability in clearance rates within the group. The medications that were researched the most in WWTPs were NSAIDs and antibiotics. Ibuprofen, naproxen, ketoprofen, and diclofenac were found to have moderate to high removal efficiency in earlier studies [150], with average removal efficiencies of 91.4 percent, 75.5 percent, 51.7 percent, and 35.8 percent, respectively. In another study, Castiglioni et al. [164] found that ibuprofen and naproxen clearance rates were frequently higher than 75 percent and 50 percent, respectively. Diclofenac clearance rates were shown to be rather low and inconsistent in studies by Clara et al. [165], Gomez et al. [166], Joss et al. [48], and Lindqvist et al. [32] and others [28-31].

These findings show differences between WWTPs, which are most likely attributable to differences in operational characteristics. Even among chemicals that belong to the same therapeutic group, there is a wide range in biodegradability degrees. Diclofenac has a limited biodegradability (25%), according to Salgado et al. [167], but ibuprofen and ketoprofen have substantially higher biodegradability (>75%) [35]. Gros et al. [168] present results from traditional WWTP removal of certain sample NSAID medicines.

NSAIDs have a pKa value of roughly 4, indicating that they are acidic chemicals [133]. As a result, they occur in wastewater as ionic species. As a result, partitioning into sludge will contribute relatively little to overall removal, partly due to the ionized species' high-water solubility and partly due to their electrostatic repellence by the overall negative charge of sludge particles [169]. This behavior could explain why these medications are removed so slowly by conventional treatment procedures, which rely on biodegradation and sorption of micropollutants to sludge particles [155, 156]. Antibiotic removal efficiency varied among chemical classes, according to studies conducted around the world, and characterization of their behavior during the activated sludge process was difficult. This could be due to their low biodegradability and sorption capacity [163]. Sulfonamides, trimethoprim, erythromycin, azithromycin, norfloxacin, ciprofloxacin, tetracycline, chlortetracycline, doxycycline, sulfamethoxazole, and other antibiotics have all been studied in earlier

investigations; removal results have been mixed [163]. Sulfonamides and trimethoprim were partially removed by conventional WWTPs, according to Brown et al. [170] and Choi et al. [171], as well as other researchers. Trimethoprim was also removed in a modest way by Gobel et al. [172] during primary and biological treatment. By using an activated sludge technique and aerated lagoons, Karthikeyan and Meyer [173] were able to remove 43 to 99 percent of erythromycin and 68 percent of tetracycline. The removal of 50% of clarithromycin and azithromycin from three standard WWTPs was demonstrated by Kobayashi et al. [174]. According to Lindberg et al. [175], fluoroquinolone antibiotics norfloxacin and ciprofloxacin were eliminated at 78 percent and 80 percent, respectively.

The chemical and biological properties of the pharmaceutical molecule, wastewater parameters, and operating conditions all influence the removal of pharmaceuticals during wastewater treatment [150]. Hydrophobicity, biodegradability, and volatility of pharmaceuticals can all affect the clearance process. Rogers and Zhang [176] demonstrated that the hydrophobicity of a micropollutant influences its sorption by solids. The acidity of the molecule can have a significant impact on its electrostatic adsorption throughout the treatment procedure. According to Schafer et al. [177], repulsion between negatively charged chemicals and biomass in activated sludge reactors could obstruct the removal of medicinal compounds at certain pH values. Because the biodegradability of pharmaceutical compounds is largely determined by their bioavailability, the biological characteristics of the compounds have a significant impact on removal efficiency. As a result, Joss et al. [48] revealed that when micropollutants are absorbed by the cell, the convergence between the micropollutants and bacterial enzymes increases; this mechanism is mostly based on compound structure, which defines a micropollutant's resistance to biodegradation. Nonetheless, there is no evident link between chemical structure, functional groups, and elimination for several pharmacological

molecules. Camacho-Munoz et al. [178] observed that ibuprofen and ketoprofen, which have almost identical structures, had different removal behavior, with ibuprofen being removed more efficiently than ketoprofen.

Suarez et al. [179] found that the major operating parameters that affect the removal of pharmaceuticals during conventional treatment are SRT (Solid Retention Time) and HRT (Hydraulic Retention Time). The average time the activated-sludge solids are in the system is called SRT. SRT is commonly expressed in days and can affect treatment process efficacy, aeration tank volume, sludge generation, and oxygen requirements. The removal of pharmaceuticals was shown to be improved when treatment processes had long SRTs since long SRTs allow for the enrichment of slowly growing bacteria, which facilitates the build-up of growing bacteria and so increases removal efficiency [180]. Previous research supports this hypothesis; Clara et al. [165] found that extending SRTs to 10 days allowed the nitrification and denitrification processes to remove substances such as ibuprofen, bezafibrate, and natural estrogens. Suarez et al. [181] also showed a in fluoxetine, 10% increase citalopram, and ethinylestradiol elimination efficiency after increasing the SRT period. Santos et al. [182] found that when low SRT was used, it had relatively minor impacts on the elimination of several pharmaceutical substances (e.g., ibuprofen, diclofenac, naproxen, and carbamezapine). In some studies, on pharmaceutical removal during wastewater treatment, the influence of SRT was nearly ineffective for some pharmaceuticals, such as diclofenac, but it was critical in enhancing the removal of others, such as ibuprofen, ketoprofen, indomethacin, acetaminophen, and mefenamic acid [47, 48, 180]. During the treatment procedure, HRT refers to the amount of time that biodegradation and sorption are allowed to occur. Some pharmaceuticals, such as fluoxetine and some antibiotics, have less effective biodegradation at shorter HRTs [183], whereas the efficiency of elimination for others, such as naproxen, ibuprofen, acetaminophen, hydrochlorothiazide, and paroxetine, has remained stable regardless of HRT values [184]. Cirja et al. [185] found that the acidity or alkalinity of an aqueous environment might affect the removal of micro-pollutants from wastewater by changing both microorganism physiology and the solubility of micro-pollutants present in wastewater. Kimura et al. [186] found that a small change in pH could alter the elimination of several acidic medications such as ibuprofen, ketoprofen, naproxen, mefenamic acid, and clofibric acid. Because temperature can alter biodegradation and partition of pharmaceutical chemicals, the temperature of wastewater might affect the removal efficiency of traditional pharmaceuticals during wastewater treatment methods [146]. According to Nie et al. [187], the elimination of micro-pollutants can be boosted at warmer temperatures due to increased microbial activity. In contrast, a study by Hai et al. [188] found that increasing the temperature to 45  $\,^{\circ}$ C decreased the removal of micropollutants. Other research, however, assumed that the elimination of micro-pollutants was unaffected by temperature changes [189].

## 3.2 Removal of Pharmaceuticals by Adsorption

Adsorption on nanomaterials has recently been used [190], and it is also being used in drinking water facilities to purify water from contaminants, color, and odor [191]. AC, silica, zeolites, and resins are some of the most often utilized adsorbents. Ibuprofen removal was evaluated using six different adsorbents, including PAC (Powdered Activated Carbon), filtrasorb 200, GAC (Granular Activated Carbon), purolite A530E, optipore L-493, amberlite XAD-4, and amberlite XAD-7, by Sirocki et al. [192]. Batch adsorption equilibrium experiments at pH 4 and pH 7 were employed in the tests. With the exception of amberlite XAD-7, all adsorbents achieved at least 96 percent removal after 24 h, according to the findings (Table 2).

No.	Adsorbent/varied conc. (optimized according to adsorption equilibrium)	IUB initial conc.	% Removal (pH 4)	% Removal (pH 7)
1	PAC	15 mg /L	100.0	99.9
2	Filtrasorb 200 granular activated carbon GAC	15 mg /L	99.1	98.2
3	Purolite A530E	15 mg /L	99.0	95.7
4	Optipore L-493	15 mg /L	97.5	97.1
5	Amberlite XAD-4	15 mg /L	100.0	19.4
6	Amberlite XAD-7	15 mg /L	-	-

Table 2Results of ibuprofen removal during batch adsorption experiments for several adsorbents after 24 h at pH 4 and pH7 [192].

Hernandez-Leal et al. [193] also conducted a batch adsorption experiment on PAC for a collection of micro-pollutants, including personal care items, bisphenol A, and nonyiphenol, and found that these pollutants were significantly removed (more than 94 percent). Ibuprofen, mefenamic acid, naproxen, dexamethasone sodium phosphate, aspirin, salicylic acid, paracetamol, amoxicillin trihydrate, and cefuroxime axetil were among the medications studied by Khalaf et al. [71], Qurie et al. [74], Sulaiman et al. [75], Ayyash et al. [134]. Batch adsorption experiments for the medicines were carried out in these researches, with either activated charcoal or composite micelleclay adsorbents being used to assess the removal efficacy of each adsorbent. The Langmuir model was used to characterize the equilibrium interactions between adsorbents (micelle-clay complex and activated charcoal) and the adsorption isotherms of the investigated medicines in these researches. In each experiment, the adsorption capacity of each adsorbent was calculated. Tables 3 and 4 show a selection of the findings from these investigations.

Table 5 Percentage removal of tested pharmaceuticals by activated charcoal and clay micelle complex [71-75, 1]	, 134]	94.	ŁJ.
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No.	Pharmaceutical	% Removal (activated charcoal)	% Removal (micelle-clay complex)
1	Ibuprofen	99.1	90.3
2	Mefenamic acid	97.2	97.3
3	Naproxen	$\approx 25.0$	$\approx 95.0$
4	Dexamethasone sodium phosphate	34.0	91.0
5	Salicylic acid	97.6	96.8
6	Paracetamol	99.7	96.1
7	Amoxicillin trihydrate	98.5	97.5
8	Cefuroximaxetil	90.2	95.2

Table 4	Langmuir ads	orption p	arameters fo	or selected	pharmaceuti	cals on t	the micel	le-cla	ay compl	ex and	activated	charcoal	•
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Dhammaaautiaal	Langmuir parameters in micelle-clay complex			Langmuir parameters in activated charcoal		
Pharmaceutical	K (L/mg)	$Q_{\rm max}~({\rm mg/g})$	KQ (L/g)	K (L/mg)	$Q_{\rm max}~({\rm mg/g})$	KQ (L/g)
Ibuprofen	$0.64 \pm 0.03$	$62.5 \pm 0.68$	$40 \pm 2$	$0.65 \pm 0.03$	$66.7 \pm 0.35$	$43.3 \pm 1.7$
Mefenamic acid	$0.105 \pm 0.03$	$100.0\pm 0.67$	$10.5\ \pm 1.8$	$0.065 \pm 0.03$	$90.9 \pm 0.74$	$5.9\pm 1.5$
Naproxen	$0.066 \pm 0.03$	71.42	$4.7 \pm 1$	$0.067 \pm 0.03$	18.87	$1.3 \pm 0.3$
Dexamethasone sodium phosphate	2.795	652.1	1,823 ±300	0.184	103.4	19 ±2
<i>p</i> -aminophenol	$0.461  \pm 0.06$	$15.33 \pm 0.21$	$7.1 \pm 1$			
Paracetamol	$0.033  \pm 0.01$	$185.2\ \pm 9.7$	$6.1 \pm 1$	$0.035  \pm 0.01$	$129.9 \pm 1.7$	$4.5\ \pm 1$
Amoxicillin trihydrate	$0.229\ \pm 0.001$	$90.91 \pm 0.86$	$20.8\ \pm 0.4$	$0.185\ {\pm}\ 0.001$	$100\ \pm 0.35$	$18.5~\pm0.2$
Cefuroxim axetil	$0.271 \pm 0.003$	$31.25 \pm 0.65$	$8.5\ \pm 0.2$	$0.122 \pm 0.002$	$26.31 \pm 0.70$	$3.2 \pm 0.2$

<sup>a</sup> [71-75, 134].

The Langmuir equation's parameters K and  $Q_{\text{max}}$ were determined in many circumstances, and it was discovered that equivalent fits may be obtained by using big K values and small  $Q_{\text{max}}$  values, or vice versa. As a result, it is worth considering the values of the amount KQ (L/g), which were added in Table 4. Under steady-state circumstances, the micelle-clay complex outperformed activated charcoal in the adsorption of 6 of the 7 drugs evaluated. Furthermore, the micelle-clay combination outperformed activated charcoal in terms of adsorption kinetics. As a result, in the single case of Ibuprofen, where the value of KO in the case of charcoal slightly exceeds the corresponding value deduced for the micelle-clay complex (though within the estimated error), the filtration results yield a larger capacity for a filter that includes the micelle-clay complex, as discussed in the previous section.

Many parameters, including contact duration between the adsorbent and the targeted contaminants, as well as the presence of natural organic matter in water, appear to affect the removal efficacy of pharmaceuticals employing adsorption technology. The latter factor may be due to competition between these compounds and targeted pollutants for binding sites on the adsorbent, which can lead to site blockage and reduced adsorbent removal effectiveness [194]. Furthermore, other parameters such as pH, adsorbent type, adsorbate solubility in the solvent, and temperature may influence adsorption in the liquid phase [192]. Finally, the findings suggest that adsorption methods are a potential technology for the treatment of water and wastewater.

# 3.3 Removal of Pharmaceuticals Using Membrane Filtration Processes

Advanced membrane filtration technology, along with additional techniques such as adsorption, ion exchange, flocculation, and dechlorination, is used in this stage to remove more suspended particles, organic matter, nitrogen, phosphorus, heavy metals, and bacteria from water [195]. Membrane filtration technology is a separation technique that uses semipermeable membranes as filters that allow water to pass through while removing suspended particles and other compounds that collect on the membrane's surface [196]. Size exclusion, adsorption onto the membrane and charge repulsion are the three basic removal mechanisms used in membrane filtering. Membrane process type, membrane features, operating conditions, specific micro-pollutant characteristics, and membrane fouling are all elements that influence these mechanisms [197]. Because the removal of suspended or colloidal particles is reliant on the size of membrane pores (MWCO (Molecular Weight Cutoffs)) relative to that of the particulate matter, the features of semipermeable membranes are considered the main requirements for efficient separation. Other operating characteristics, such as the kind of driving force pressure, membrane chemical structure and composition, construction geometry, and feed flow type, all play a part in the membrane filtration process [198-201]. Membranes are divided into four modules: plate, frame, tubular spiral wound, and hollow fibre. The final two modules are made of organic material (synthetic polymers such as polyamide and polysulphone) and are utilized in drinking water and wastewater treatment [202]. Membrane filtration techniques can be grouped into four varieties based on the driving force used in the filtration process: MF, UF, NF, and RO. MF, UF, and RO are all done with hollow fiber and spiral wrapped [203]. External pressure, electrical potential gradient, or concentration gradient are examples of driving forces used in filtration processes. Pressure-driven forces are commonly utilized in the treatment of water and wastewater. Membranes are further categorised based on their pore sizes: MF, UF, NF, and RO. The separation properties for several pressure-driven membrane processes are shown in Table 5 [201, 204].

According to several studies, MF and UF techniques are effective in lowering turbidity in treated water, but they are ineffective in eliminating all micro-pollutants

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Membrane system Parameters	Product particle size (µm)	Retained compounds	Operating pressure, Atm.
MF Low-pressure membrane system	0.08 to 2.0	Very small suspended particles, some colloids, most bacteria	0.7 to 1.02
UF Low-pressure membrane system	0.005 to 0.2	Organic compounds > 1000 Da, pyrogens, viruses, bacteria, colloids	2.0 to 6.8
NF High-pressure membrane system	0.001 to 0.01	Organic compounds > 200 Da, some dissolved solids (i.e. multivalent ions)	5.4 to 8.5
RO High-pressure membrane system	0.0001 to 0.001	Ions, Organic compounds >100 Da	≥ 68.0

 Table 5
 Comparison between different types of pressure-driven membrane systems [203, 206].

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since membrane pore diameters are much bigger than micro-pollutant molecular sizes. The presence of NOM (Natural Organic Matter) in wastewater, which can interact with micro-pollutants and boost adsorption onto membrane polymers, was found to improve removal in these investigations [150]. Ibuprofen and estradiol were removed through a UF procedure with and without NOM, according to Jermann et al. [205]. Ibuprofen was removed insignificantly and estradiol was removed insignificantly (8%) by the hydrophilic membrane, whereas hydrophobic membranes retained much more estradiol (up to 80%) and ibuprofen (up to 80%) (up to 25 percent). Due to the low removal effectiveness of MF or UF alone, it has been suggested that they be combined with other processes such as NF or RO to improve removal efficiency. To improve the removal efficiency of micro-pollutants from municipal wastewater, Garcia et al. [206] used a combination of MF and RO. They discovered that MF could lower the amount of some chemicals by more than 50%, such as bis-(2-ethylhexyl) phthalate, and that removal effectiveness was greatly increased following RO integration, ranging from 65 percent to 90 percent for most micro-pollutants. Except for some pharmaceutical chemicals like mefenamic acid and caffeine, most PPCPs (Pharmaceuticals and Personal Care Products) were eliminated to more than 95 percent during the MF/RO treatment process, according to Sui et al. [207].

NF and RO membranes are still moderately permeable to several relatively small micro-pollutants, according to Steinle-Darling et al. [208]. Rohricht et al. [209], for example, investigated the removal of various pharmaceutical substances using two distinct types of submerged NF flat sheet modules: the results revealed a moderate removal of naproxen and diclofenac (60 percent) and a modest removal of carbamazepine. The pKa values of each chemical played a key role in the preceding situation, when naproxen and diclofenac (with pKa values of 4.2 and 4.15, respectively) were deprotonated at pH 7 and 8, whereas carbamazepine (pKa = 13.9) was not. As a result, the negatively charged membrane surface could reject naproxen and diclofenac, but carbamazepine could not be eliminated. Many medicinal chemicals can be removed by changing pH values, according to Nghiem et al. [210]. They assumed that ionized, negatively charged chemicals would be more easily removed, but uncharged compounds' physicochemical features would be more important in their removal.

Ibuprofen, mefenamic acid, naproxen, dexamethasone sodium phosphate, aspirin, salicylic acid, paracetamol, *p*-aminophenol, amoxicillin trihydrate, and cefuroxim axetil were among the previous medications studied [71, 75, 134], the WWTP included UF (Hollow fiber and Spiral wound), an activated carbon column, and a RO membrane in that order. Before entering the membrane filtering unit, spiked samples were generated by dissolving specified amounts of each medication in the secondary effluent tank (activated sludge water). The cumulative % elimination for the studied pharmaceutical substances is shown in Table 6 [71-75, 125].

### 3.4 Removal of Pharmaceuticals Using AOPs

Alternative methods such as membrane separation, adsorption technology, air stripping, and extraction technology have been used to remove resistant micro-

Pharmaceutical	HF (Hollow fiber)	SW (Spiral Wound)	AC	RO
Ibuprofen	59.8%	94.7%	98.8%	99.9%
Mefenamic acid	74.3%	94.3%	98.8%	99.5%
Naproxen	64.6%	81.9%	-	99.7%
Dexamethasone sodium phosphate	69.0%	94.0%	-	100.0%
Amoxicillin trihydrate	58.93%	90.33%	96.47%	100.0%
Cefuroximaxetil	70.90%	91.27%	96.03%	100.0%
Salicylic acid	68.7 %	79.0%	99.1%	99.6%
Paracetamol	40.5%	48.8%	98.9%	99.5%
<i>p</i> -aminophenol	71.7	88.4%	100.0%	100.0%

Table 6The sequential cumulative percentage removal of several pharmaceuticals using membrane separation technologycoupled with AC.

All of the data (Table 6) indicate that membrane filtration is an effective method for removing pharmaceuticals from water and wastewater.

pollutants from wastewater, as explained in the preceding sections. These technologies, however, are only considered phase-transfer technologies, in which micro-pollutants are transported from one phase to another rather than being destroyed [211, 212]. It has become critical to find destructive treatment strategies for stubborn organic molecules like medicines. AOPs have been presented as a potent advanced technology for the treatment of recalcitrant and hazardous organic pollutants in recent years [213].

AOPs are oxidation processes that generate highly reactive species such as hydroxyl radicals (OH) or other species with similar reactivity such as  $SO_4^{2-}$ . These radicals can react with practically all organic molecules in an aqueous solution, including medications and pesticides [214], mineralizing them and releasing CO<sub>2</sub> and inorganic ions, resulting in the elimination of target pollutants. Inorganic pollutants such as cyanide, sulfide, and nitrite can also be oxidized using AOPs [215]. The broad concept of AOPs encompasses a wide range of techniques. Depending on the number of phases involved, systems employed in AOPs are split into two broad groups: (a) homogeneous processes and (b) heterogeneous processes [216-218]. Photolysis, hydrogen peroxide and ultraviolet radiation (H<sub>2</sub>O<sub>2</sub>/UV), ozone and ultraviolet radiation (O<sub>3</sub>/UV), ozone-hydrogen peroxide-ultraviolet radiation (O3/H2O2/UV), ozone (O<sub>3</sub>) in alkaline medium, Fenton and photo-Fenton oxidation processes [219, 220]. Catalysts are commonly

used in heterogeneous advanced oxidation processes to carry out compound degradation. The pollutants are present in the aqueous phase of heterogeneous oxidation processes, whereas the catalyst is present in the solid phase [221]. Catalytic ozonation, photocatalytic ozonation (TiO<sub>2</sub>/UV/O<sub>3</sub>), and heterogeneous photocatalysis are the three primary systems in heterogeneous oxidation [222-225]. Heterogeneous photo-catalysis with semiconductors [226-228] is the most widespread and effective type of AOP used in water and wastewater treatment. Dispersed solid semiconductor particles absorb substantial percentages of the UV spectrum efficiently in heterogeneous photo-catalysis, and they create chemical oxidants in situ from dissolved oxygen or water [227]. Because of its high photosensitivity, non-toxic nature, large band gap, chemical stability, and low cost [226-230], TiO<sub>2</sub> is the most preferred semiconductor for the photo-catalytic process [228]. Table 7 summarizes the findings of two studies that looked at how different oxidation methods affected the removal of a group of medicines from liquid phase. AOPs are attractive technology because they can remove the majority of refractory organic pollutants, such as medicines and pesticides [126, 231, 232]. Brienza et al. [233] found that heterogeneous (solar/TiO<sub>2</sub>) advanced oxidation successfully eliminated the resistant anticonvulsant lipid regulator carbamazepine from secondary treated WW, which contained 53 organic pollutants.

Dhammaaaatiaal	Photolysis oxidation technology		Photocatalysis/TiO2 oxidation technology		
Pharmaceutical	% Removal	Half-life (min)	% Removal	Half-life (min)	References
Ibuprofen	8.4	-	96.7	11.6	[232]
Diclofenac sodium	95.5	70.7	97.8	54.6	[232]
Mefenamic acid	62.5	1,422.2	99.0	91.2	[232]
Dexamethasone sodium phosphate	57.1	69.0	94.0	19.8	[233]
Diazepam	$\approx 4.3$	2,048.4	M.T. 90.0	7.9	[233]
Spironolactone	M.T. 90.0	1,890	M.T. 90.0	1,188	[233]
Atorvastatin	pprox 40	301.2	M.T. 95.0	69	[233]

Table 7Percent removal and half-life  $(t_{1/2})$  for a set of pharmaceuticals during several advanced oxidation processes [230,231].

\* Pharmaceutical Conc.: 25 mg/L, TiO2: 200 mg/L.

# 4. Modelling of Filtration Results

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Simulations and predictions based on convection, adsorption, and desorption during filtration enable efficient planning of laboratory and pilot studies, as well as cost estimations [233]. The model has already been used to filter: (i) herbicides using micelle-clay, ODTMA-montmorillonite in granulated form, and a polymer-clay composite [233-235]; (ii) bacteria using powdered micelle-clay and polymer clay [236, 237], and a granulated complex [237-240]; and (iii) perchlorate using a powdered and granulated Ibuprofen [72], Amoxicillin [140], and Axetil [125] were all filtered using the model. Because the experimental data were most complete in this situation [73], the model may be shown using published results on diclofenac potassium filtration. Diclofenac potassium filtered solutions were made in tap water at concentrations of 1,000 ppm, 300 ppm, 82 ppb and 118 ppb. The focus is on filtering using the ODTMA-montmorillonite complex, which removed diclofenac potassium more effectively than other materials. Three parameters were calculated: the initial molar concentration of adsorbing sites  $(R_0 (M))$ , the rate constant of forward adsorption ( $C_1$  (M<sup>-1</sup>min<sup>-1</sup>)), and the rate constant of desorption  $(D_1 \text{ (min}^{-1}))$ . The amount of diclofenac potassium retained by the filter after filtering of 3 L of a 300-ppm solution was used to determine the first  $R_0$ . Because the adsorption sites are generally vacant at first and the effect of desorption is modest,  $C_1$  and  $D_1$  were calculated from the findings at initial and later times, respectively. The fits can be classified as simulations, with some predictions thrown in for good measure. Because the emphasis in the original work was on presenting results in which the emerging values of diclofenac were zero or rather minor, Table 8 only shows a tiny fraction of the experimental points for brevity. The capacity of the system, which included two filters in series (total length of 40 cm; 13 g of complex) for a diclofenac concentration of about 100 ppb and flow rate of 30 mL/min (a flow velocity of about 0.9 m/h), is about 8 m<sup>3</sup>/kg of complex for a diclofenac concentration of about 100 ppb and flow rate of 30 mL/min (a flow velocity of about 0.9 m/h). The capacity was estimated by dividing the filtered volume by the weight of the complex in the filter, which provided an acceptable low value of diclofenac potassium. If the filter is filled solely with granules (640 g), which corresponds to setting  $R_0 = 1$  M, the filtration results will be the same, or slightly better, if the flow rate in Table 8 (30 mL/min) is multiplied by the relevant ratio of  $R_0$  values (0.03), according to the model. Table 8 shows that after filtration of a volume of 5,000 L, a diclofenac solution (100 ppb) with a flow rate of 1,000 mL/min, which corresponds to a flow velocity of 30 m/h, the emerging concentration of diclofenac is indeed minimal (0.019 ppb). In this scenario, the capacity is 5  $m^3/(0.64 \text{ kg})$ , which is the same as the ppb values in Table 8.

Table 8Filtration of diclofenac potassium in the ppm andppb range.

Initial conc.	Vol (I)	Emerging concentration		
(ppm)	V0I. (L)	Exp.	Calc.	
1,000 <sup>a</sup>	1.1	0	0	
300	1	0	0	
300	1.5	0	0	
300	3	20 ppm	15 ppm	
300	4	Not measured	200 ppm	
Conc. (ppb)				
118	46	0	0	
82	151	0	0	

<sup>a</sup> The filters included excess sand (100/1 w/w). The weight of the active ingredient, i.e., ODTMA-Mt was 6.5 g per filter, except for this case, which was 13 g per filter (50/1 w/w). For filtration in the ppb range the results correspond to the second filter of two in series. Filtration was at room temperature. The flow rates were 2, 20 and 30 mL/min for the filtered diclofenac solutions whose concentrations were 1,000 ppm, 300 ppm and below ppm, respectively.

The parameters used in the calculations were  $C_1 = 80$  (M<sup>-1</sup>min<sup>-1</sup>) and  $D_1 = 0.001$  min<sup>-1</sup>. The values of  $R_0$  were 0.03 M except for the cases which included 13 g of complex per filter, where correspondingly the values of  $R_0$  were doubled.

Table 9 shows predictions for diclofenac potassium solution filtration at a concentration of 100 ppb, which was close to the average values in the ppb range reported by Karaman et al. [73]. In this scenario, a filter with a length of 40 cm was filled exclusively with the active material, with the same values of the kinetic parameters as in Table 8, but with  $R_0 = 1$  M. The flow rate was 100 mL/min, or around 3 m/h. This value is ten times lower than 1,000 mL/min. As a result of the lower flow velocity, the capacity is predicted to increase. The estimated data show that the emerging diclofenac concentration is 0.01 ppb (99.99 percent elimination) for the first 14,000 L filtered, corresponding to a capacity of 21 m<sup>3</sup>/kg of complex, compared to the value of 8 m<sup>3</sup>/kg for the second 14,000 L filtered (Table 8, diclofenac concentrations about 100 ppb). The two filters in series in Table 9 are filled exclusively with the active material, resulting in an increase in capacity. Rakovitsky et al. [241] demonstrated the effect of increased capacity per kg of complex for a filter filled

 Table 9
 Calculated emerging concentrations of diclofenac

 for a filtered diclofenac solution (100 ppb).<sup>a</sup>

Vol. (L)	Emerging conc. (ppb)	% Removal
14,000	0.01	99.99
16,000	0.2	99.8
18,000	1.6	98.4
20,000	8	92.

<sup>a</sup> The filters included the complex (640 g) exclusively. The flow rate was 100 mL/min. The kinetic parameters used in the calculations were as in Table 8. The value of  $R_0$  was 1 M.

completely with the active material in the purification of grey water.

It should be noted that the model can be used to simulate a solution containing many solutes, such as medications. As Nir et al. [234] point out, the observed results in this situation may imply that a given solute is eliminated preferentially at first, but the trend may alter subsequently. Another useful fact is that by lengthening the filter, the flow velocity can be increased without lowering the filter's efficiency or capacity per weight of the active component.

#### 5. Summary and Conclusion

This paper explains how water can be treated utilizing cutting-edge technology to remove carefully chosen widely used medications by membrane separation, adsorption, and sophisticated oxidation processes. Batch adsorption experiments were combined with appropriate adsorption isotherms and appropriate kinetic models to estimate the ultimate degree of pollutant removal by this method. Combining filtration with advanced oxidation processes improves the efficacy of treating wastewater containing refractory PhACs.

We surveyed and talked about different pharmaceutical removal technologies. However, research in this area is ongoing to create more effective and environmentally friendly techniques that can be used in a zero-liquid water discharge mode. The adsorbed materials regenerated by different techniques need further research to minimize their effect on the environment.

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Not applicable.

## **Code Availability**

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# **Conflicts of Interest**

The authors declare no conflict of interest.

# **Ethics approval**

Not applicable.

## **Consent for Publication**

We, the authors give consent for publication.

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