Methods for Removal of Ceftriaxone from Wastewater

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Ceftriaxone is a type of antibiotic used to treat a variety of bacterial illnesses. The presence of pharmaceuticals in surface water and wastewater poses a threat to public health and has significant effects on the ecosystem. Since most wastewater treatment plants are ineffective at removing molecules efficiently, some pharmaceuticals enter aquatic ecosystems, thus creating issues such as antibiotic resistance and toxicity.

Keywords: antibiotics ; ceftriaxone ; wastewater

1. Methods Used for Removal of Antibiotics from Wastewater

The selection of the method for wastewater treatment depends on the characteristics of the wastewater and features such as costs, feasibility, efficiency, practicability, dependability, impact on the environment, sludge production, difficulty in operation, pretreatment demands, and the formation of potentially dangerous by-products which characterize the relevant method ^[1]. The potential of various techniques to remove antibiotics from wastewater systems has been investigated. Among those techniques are constructed wetlands, biological treatment, advanced oxidation processes (AOPs), and membrane technology ^[2].

1.1. Constructed Wetland

A constructed wetland (CW) wastewater treatment system utilizes the combined influence of microbes, plants, and soil to remove the pollutants from wastewater. The wastewater is treated through microbial decomposition, adsorption, plant uptake, ion exchange, co-precipitation, and filtration ^[3]. The suitability of CWs for the elimination of some pharmaceuticals and personal care products (PPCPs) has recently been studied ^[4].

Diclofenac, ibuprofen, naproxen, ketoprofen, salicylic acid, triclosan, sulfamethoxazole, carbamazepine, clofibric acid, atenolol, and caffeine are some of the pharmaceuticals that have been investigated in constructed wetlands ^{[5][6]}. The average removing efficiencies of constructed wetlands are 93% (monensin), 89% (ofloxacin), 87% (oxytetracycline), 83% (sulfapyridine), 80% (caffeine), 79% (salicylic acid), 72% (atenolol), 72% (furosemide), 69% (doxycycline), 68% (codeine), 67% (diltiazem), 64% (acetaminophen), 62% (naproxen), 57% (ibuprofen), 56% (metoprolol), and 51% (sulfadiazine) to some studied pharmaceuticals ^[Z]. Several studies have shown that physico-chemical decomposition, photodegradation, adsorption by wetland soil and plants, and biodegradation (microbial activity) comprise the mechanisms used to remove antibiotics from wastewater in CWs ^{[8][9]}. Antibiotics can accumulate in plants by water transport and passive absorption and high quantities of antibiotics in water or soil can be harmful to plant development and metabolic activity ^[10]. Since there are very few informative publications on the decontamination of antibiotics using CWs, this area of research could benefit from combined support from other disciplines, primarily soil science, botany, environmental chemistry, and chemical engineering ^[11].

1.2. Biological Treatment

The microorganisms utilize organic compounds and nutrients to gain energy and build the blocks for their growth in biological treatment methods. Despite the presence of high density and diverse consortium of microorganisms in activated sludge, antibiotics cannot be completely removed in biological treatment methods ^[12]. Some reasons for the incomplete removal of antibiotics in biological methods include relatively low concentration of antibiotics in the wastewater, which leads to a lack of enzymes responsible for antibiotic biodegradation and inhibitory or toxic properties of antibiotics that can stop the microorganism activity responsible for antibiotic biodegradation, antibiotic properties, and operation conditions ^[13]. Different biological treatment methods have been investigated in relation to the removal of antibiotics from wastewater. For instance, using a biological aerated filter system (BAF), 89–91% of nine antibiotics were removed from swine wastewater. Those antibiotics include oxytetracycline, leucomycin, lincomycin, ofloxacin, trimethoprim, norfloxacin, sulfamonomethoxine, sulfamethazine, and sulfachloropyridazine ^[14]. Using anaerobic digestion, 65% tetracyclines and 85% of quinolones were removed from swine wastewater after 16d hydraulic retention time (HRT) ^[15].

Another study indicated that the lab-scale intermittently aerated sequencing batch reactor (IASBR) was applied to treat anaerobically digested swine wastewater. The results from the referred study show that 87.9% tetracyclines were removed, and 96.2% sulfonamides were removed at about 3–5 d HRT ^[16]. The elimination of antibiotics using the sequencing-batch membrane bioreactor (SMBR) was investigated for the treatment of swine wastewater. Nine antibiotics, which were divided into sulfonamides, tetracyclines, and fluoroquinolones, and three categories of frequently used veterinary antibiotics were investigated. The results demonstrated that SMBR effectively removed sulfonamides and tetracyclines (90%), whereas fluoroquinolones were removed less effectively (70%) ^[12]. Many antibiotics have been identified in the literature as being resistant to biodegradation. While some antibiotics can be partially decomposed, the majority of antibiotics including ciprofloxacin, metronidazole, ceftriaxone, ofloxacin, and trimethoprim are not biodegradable ^{[18][19]}. More research is needed to understand the factors affecting the process and possibility of improving the degradation of pharmaceuticals.

1.3. Advanced Oxidation Processes (AOP)

AOPs comprise water and wastewater treatment technologies that use powerful oxidizing agents such as hydroxyl radical (OH•), ozone (O₃), chloride (Cl⁻), and superoxide radical (O₂⁻) ^[20]. The generated species react with the medium's organic molecules ^[21] to start a series of oxidation reactions until all of the components have been mineralized to CO₂ and H₂O ^[22]. AOP methods can be divided according to the source of OH• production with UV–hydrogen peroxide processes, with Fenton and photo-Fenton, ozone-based processes, photocatalysis, and sonolysis being the most common ^[23]. Such methods have proven to be effective at removing a wide range of contaminants in general and antibiotics in particular ^[21]. Electrochemical oxidation was used to study the removal of tetracycline (TC) antibiotics from the livestock wastewater. The electrochemical treatment of the TC in aqueous solutions for 6 h with a Ti/IrO₂ anode and Na₂SO₄ electrolyte resulted in concentrations decreasing from 100 mgL⁻¹ to less than 0.6 mgL⁻¹ ^[24].

With sinusoidal alternating electro-Fenton (SAEF), the removal efficiency and the mechanism of TC degradation were studied. According to the findings, the removal rates of TC were 94.87% in optimal conditions ^[25]. A study was done to examine the efficacy of three AOPs for removing antibiotics from wastewater: ozonation, photo-Fenton process, and heterogeneous photocatalytic process with a TiO₂ semiconductor. The ozonation process was discovered to be effective at removing all types of antibiotics ^[26]. The majority of the literature to date, however, has been devoted to bench- or pilot-scale experiments. The use of AOPs on a large scale is still a work in progress. The high operational cost of AOPs, especially when compared to the conventional methods that are routinely used today, is likely to be the greatest challenge for the development of AOPs on an industrial scale ^[21]. Further research is needed to address the challenges associated with AOPs in attempt to make the processes affordable and useful in the real wastewater treatments.

1.4. Membrane Technology

A membrane is described as a thin layer, film, or sheet that serves as a specific barrier between two phases which may be vapor, gas, or liquid. To put it in another way, a membrane is the boundary between two adjacent phases that function as a selective barrier to control the movement of species between the two compartments. Membrane technology includes the associated engineering and scientific techniques for transporting or excluding the parts, species, or substances from membranes ^[2Z]. Ultrafiltration (UF), electrodialysis (ED), membrane distillation (MD), microfiltration (MF), nanofiltration (NF), particle filtration (PF), pervaporation (PV), reverse osmosis (RO), and membrane bioreactor (MBR) are just a few of the membrane-based technologies that have been developed based on the impurities that need to be removed and the method of application ^{[28][29]}.

Various membrane technologies have been evaluated for pharmaceutical removal at both the pilot and full-scale levels $^{[30]}$. The membrane technology is preferred due to significant reductions in equipment size, energy requirements, and low capital costs. It has the potential to close the economic and sustainability gap with low or no chemical usage, environmental friendliness, and ease of access for many $^{[31]}$. A few studies have investigated the removal of antibiotics from wastewater using membrane technology. For instance, one study on wastewater treatment indicate that the rate of antibiotic removal was 87% when UV/ozone and nanofiltration were used $^{[32]}$. The combination of nanofiltration and reverse osmosis technologies was utilized to treat swine wastewater and efficiently removed various antibiotic resistant genes $^{[33]}$. As a conclusion, additional research on the use of membrane technology to remove antibiotics from wastewater should be done.

2. Methods Studied for Removal of Ceftriaxone from Water and Wastewater

The techniques studied regarding the removal of ceftriaxone from aqueous systems include photochemical degradation, ion ex-change, chemical oxidation, biological treatment, and adsorption $^{[\underline{34}]}$. **Table 1** summarizes some of the studies on the methods for the removal of ceftriaxone from wastewater.

Method	Results	Reference
Chemical oxidation	Degradation occurs through Type I and Type II mechanisms.	[35]
UVC/H ₂ O ₂ and UVC	At a solution pH of 5 and an H_2O_2 concentration of 10 mg/L, the most ceftriaxone degradation was observed. Pseudo-first- and second-order kinetics models with reaction rate constants of 0.0165 and 0.0012 min ⁻¹ , respectively, better represent UVC/H ₂ O ₂ and UVC processes.	[<u>36]</u>
O ₃ /UV/Fe ₃ O ₄ @TiO ₂	Maximum ceftriaxone removal 92.40% Organic carbon reduction 72.5% Optimal conditions, time: 30 min, photocatalyst dosage: 2 g/L, pH: 9, initial ceftriaxone concentration: 10 mg/L, and ozone dosage: 0.2 g/h)	[37]
Immobilized TiO ₂ and ZnO	Results revealed that photodegradation using UV/TiO ₂ process was more effective than photodegradation using the UV/ZnO process. Ceftriaxone photodegradation followed pseudo-first-order kinetics in both systems.	[38]
Electrochemical in aqueous solutions containing sodium halides	Ceftriaxone gradually decomposes, but not fully, in the presence of fluoride ions in about 60 min without yielding a reaction product. The electro (degradation/transformation) of ceftriaxone is practically complete in 10 and 5 min with completion of the electro-transformation reaction, which take 60 and 30 min, respectively. Ceftriaxone and the iodide ions formed instantaneous interactions.	[39]
Heterogeneous catalytic AOP y-Fe ₂ O ₃ encapsulated NaY zeolites solid adsorbent	initial concentration of 20 mg/L, catalyst 1.17 g/L, H_2O_2 30 mM, and UV light, ceftriaxone may be effectively removed within 90 min at pH 4.0. The adsorption mechanism was investigated using the kinetic and isotherm model, and the results demonstrate that the model and data are in good agreement.	[40]

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