Removal of Pharmaceuticals from Water

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It is important to consider and characterize the efficiency of pharmaceutical removal during wastewater and drinking-water treatment processes. Various treatment options have been investigated for the removal/reduction of drugs (e.g., antibiotics, NSAIDs, analgesics) using conventional or biological treatments, such as activated sludge processes or bio-filtration, respectively. The efficiency of these processes ranges from 20–90%.

pharmaceutical products | wastewater | advanced oxidation technologies | adsorption

1. Introduction

In the past three decades, pharmaceutical residues have been discovered in almost all environmental matrices on every continent [1]. Approximately 3000 pharmaceutical substances are used in the European Union. Pharmaceuticals have been detected in groundwater, urban wastewater, surface water, and drinking water in a range of ng to µg per litre [2][3][4][5][6]. Because of their low biodegradability and high hydrophilicity, pharmaceuticals are difficult to eliminate from water systems using conventional wastewater treatment techniques [7]. Therefore, their disposal in wastewater treatment plants is a major concern [6][8]. Indeed, pharmaceuticals are considered the most significant groups of environmental pollutants of special concern. The most consumed type of pharmaceutical products may differ from one country to another. For example, in Spain, antihistamines, analgesics, and antidepressants are the most consumed based on the National Health System [9]. However, in Italy, antibiotics, sulphamethoxazole, ofloxacin and ciprofloxacin, β-blocker atenolol, antihistaminic ranitidine, diuretics furosemide, hydrochlorothiazide, and steroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen are the most detected pharmaceuticals in sewage treatment plants [10]. Klein et al. [11] reported that Tunisia was considered the second-highest consumer of antibiotics in 76 countries analyzed between the years 2000–2015, and consumption was estimated at around 47 defined daily doses per 1.000 inhabitants per day.

Many studies have shown that wastewater treatment plants (WWTPs) do not totally remove pharmaceutical compounds [9]. More than 100 different drugs have been found in the aquatic environment [3][12]. Antibiotics and NSAIDs were reported in surface water samples from various countries at concentrations ranging from 5 to 150 µg/L [9][13][14]. Castiglioni et al. [10] noted that there is a difference in concentrations in pharmaceutical compounds in WWTPs between winter and summer. This is mainly due to greater attenuation and lower use of pharmaceuticals in summer. Thus, pharmaceuticals and their metabolites are detected regularly in aquatic and terrestrial environments [15][16]. Hence, tertiary treatment is needed to eliminate these emerging pollutants. Today, countries are facing high COVID-19 pandemic incidence rates and struggling to manage the dramatic increase in medical waste production by healthcare facilities, in particular with respect to pharmaceutical products. For instance, Wuhan inhabitants in China (~11 M) produced ten times more daily medical waste than the previous average (200 tons on a single day, 24 February 2020). A drastic increase in medical waste was also reported in other parts of the world, such as in Catalonia, Spain, and in China, with increments of 350% and 370%, respectively [17]. Recent studies indicated that the COVID-19 pandemic has led to an increase in waste generation by an average of 102.2 % in both private and public hospitals [18]. In addition, the hazardous waste volume in the hospitals' investigations has increased by an average of 9% in the amount of medical waste and by 121% compared to the first wave and before the epidemic COVID-19 [19][20].

The hydrophobic/hydropholic nature of pharmaceutical compounds facilitates their interaction with microplastics, frequently present in surface water and playing the role of a vector of pharmaceuticals within aqueous environments through π–π interactions [21]. The literature cites about 160 pharmaceutical compounds that have been recently found in the water surface and wastewater [21]. There are already approaches and strategies for minimizing this issue that proved their efficiencies and estimates to be implemented and prioritized in the near future. Currently, the accuracy of techniques for pharmaceutical removal from wastewater differs from drugs to other (80–100%). With this purpose, the development of new technology such as combined techniques based on an in situ census is still needed.

2. Removal of Pharmaceuticals during Wastewater Treatment

2.1. Conventional Treatments

Conventional wastewater treatment consists of a combination of physical, chemical, and biological processes and operations to remove solids, organic matter, and, sometimes, nutrients from wastewater. General terms are used to describe different degrees of treatment in order of increasing treatment level; preliminary, primary, secondary, and tertiary and/or advanced wastewater treatment. In some countries, disinfection to remove pathogens sometimes follows the last treatment step [22]. It has been shown that pharmaceuticals can be removed only partially, as these wastewater treatment plants are not designed for full removal [1]. Depending on the composition of wastewaters, preliminary treatments with activated sludge systems or classic membrane bioreactors may be needed [23]. However, membrane fouling comprises a significant obstacle to their broad application [24]. Pharmaceutical compounds are characterized by their limits of elimination by volatilization because of their low vapor pressure and pKa values between 3 and 10. Some drugs, such as ibuprofen, diclofenac, and carbamazepine, include extremities vulnerable to biodegradation and sorption. According to the review of Petrie et al. [25], diclofenac is removed by ≤50%, and any carbamazepine removal is low. From the study carried out by Tauxe-Wuersch et al. [26], in Switzerland, they noted the difficulties faced in the removal of different drugs such as ibuprofen, mefenamic acid, and diclofenac with biological and physico-chemical treatments. Additionally, this work reported that there was a difference in the elimination rates within wet and dry seasons. The removal of ibuprofen and ketoprofen was inhibited during winter in comparison to that during the dry period. This can be explained by the difference in the residence time of treated water in treatment plants depending on the rainfall.

2.2. Biological Removal of the Pharmaceuticals

Bacteria occupy a dominant place in the biosphere; through their various metabolic capabilities, they support the metabolic cycles that are fundamental to all life on Earth [27]. Researchers are investigating the potential of different bacteria to degrade pharmaceuticals and personal care products (PPCPs) into eco-friendly monomers, which could be an alternative emerging way to eliminate pharmaceutical residues from the ecosystem [28]. Mainly related to the bacterial populations concerned, technologies that use sludge (aerobic, activated, or granular) have been highly efficient in the treatment of municipal wastewater [29]. A study evaluating the efficiency removal of pharmaceutical products such as atorvastatin, caffeine, paracetamol, xylazine, trimethoprim, sulfamethoxazole, naproxen, fluoxetine, diclofenac, ibuprofen, clarithromycin, carbamazepine, atenolol, azithromycin, erythromycin, ketoprofen, metoprolol, erythromycin, ciprofloxacin, valsartan, simvastan, and losartan, using activated sludge in the laboratory, at concentrations ranging from 13.2 ng/L to 51.8 μg/L in Latvia in municipal wastewater highlighted that biostimulation through the addition of nutrients to the sludge showed biodegradation of these pharmaceutical contaminants by Nitrospirae, Actinobacteria, Verrucomicrobia, Firmicutes, Acidobacteria, Proteobacteria, Chloroflexi, and Bacteroidetes. As well, some genera and species involved in removal processes of pharmaceutical compounds such as metoprolol, venlafaxine, fluoxetine, alprenolol, propranolol, bisoprolol, salbutamol, norfluoxetine, gemfibrozil, and 17β-estradiol have demonstrated a 90% or higher removal efficiency [30]. Another study improved the efficiency of using a Gram-positive bacterium, designated as strain B1 (2015b) for the degradation of ibuprofen and naproxen, after six days for 20 mg/L of concentration and 35 days for 6 mg/L, respectively [31].

2.3. Electrocoagulation Process

Electrocoagulation is a treatment process in which cations are formed by metal electrodes in an electrical field [32][33]. It produces coagulants using metal electrodes that are more likely to encounter pharmaceutical products with several advantages, including sludge minimization, automatic treatment, and efficient and low operating costs [33][34]. The removal efficiency of the three most consumed pharmaceutical products such as carbamezapine (70%), diclofenac (90%), and amoxicillin (77%) was investigated by Ensano et al. [35] for a density of 0.5 mA/cm^2, an initial concentration of 10 mg/L, and a hydraulic retention time HRT of 38 h. Oxytetracycline, an antibiotic drug, was analyzed by Nariyan et al. [36]. The optimum current density was 20 mA/cm^2 for both anodes: iron and aluminum had a removal efficiency of 93.2% and 87.75%, respectively. The initial concentration on removal efficiency was also studied: increasing the initial concentration of oxytetracycline hydrochloride up to 200 mg/L did not have a significant impact on its removal. The pH, Eh, and dissolved oxygen of all samples were measured during the experiments: with both anode–cathode combinations, pH was seen to increase considerably, while Eh and dissolved oxygen decreased substantially. Furthermore, the total removal of ciprofloxacin using electrocoagulation process was achieved at a density of 15 mA.cm^{-2}, pH 7.5, initial CIP concentration of 60 mg.L^{-1}, electrolyte dose of 0.07 M NaCl, and inter-electrode distance 1.58 cm within the equilibrium time of 20 min [35][37].

2.4. Sorption Process for the Removal of Pharmaceutical Products

The adsorption process by solid adsorbents shows potential as one of the most efficient for the treatment of a wide range of waters and wastewaters [1] that contain pharmaceutical products. In fact, there are excellent studies of carbon materials used to remove pharmaceutical pollutants, which is a financially attractive alternative for wastewater treatment.

Different types of adsorbents are classified into natural and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many cases, are relatively low-cost and abundantly available and have significant potential to modify and ultimately improve their adsorption capacities. Synthetic adsorbents are adsorbents prepared from agricultural products and waste, household waste, industrial waste, sewage sludge, and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and the nature of its adsorbent surfaces. Many wastes used include fruit waste, coconuts, date nuts, used tires, bark and other tannin-rich materials, sawdust, rice husk, petroleum waste, fertilizer waste, fly ash, sugar industry waste, blast furnace slag, chitosan and seafood processing waste, and algae, peat, clays, red mud, zeolites, sediment and soil, ores, etc. [38].

The current application of advanced materials for the removal of PPCPs from wastewater can be viewed from three main perspectives: activated carbon (AC), clays. and biochar. Other more recent materials have also been reported, such as molecular imprinted polymers (MIPs), thermo-responsive gel, and magnetic nanoparticles, though comparatively, they still lack development and supporting case studies.

3. Various Methods for the Removal of Pharmaceuticals from Waters

The removal of pharmaceuticals depends on different water treatment processes that result in different efficiencies. Wastewater treatment plants are not designed to completely remove pharmaceuticals [1]. Adsorption has advantages over other methods because of its simple design that can involve low investment in terms of both initial cost and space required [39]. Adsorption processing for water remediation includes low capital investment, applicability at low adsorbate concentrations, suitability for batch or continuous processing, and the ability to reuse and regenerate adsorbents. Adsorption is a low consuming energy process that can be very efficient and lead to a removal of up to 90%, but it has a mild operation condition. With the Fenton process, it is possible to treat large volumes of wastewaters (need of large electrodes or cell stacks). The greatest advantage of photocatalysis lies in the use of the semiconductor TiO 2, which is non-hazardous, eco-friendly, inexpensive, and stable [40]. Indeed, in a quick and very high percentage of organic matter, degradation can be reached and can be more remarkable under sunlight irradiation and using in situ cathodic production of H 2O 2. However, this process presents many disadvantages such as the need for acidic conditions with a pH value near to 3.0. Thus, a neutralization is requested after the treatment, leading to the production of a large amount of sludge. Special attention should be paid to the formation of halogenated byproducts. According to Patel et al. [1], an advanced oxidation process can lead to a high degradation of pharmaceuticals, but it is difficult to apply on a wide scale of WWTPs due to the oxidative byproducts and high operation cost. A common problem to all AOPs is their high cost, mainly because of the high demand for electrical energy .

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