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Comparison of different removal techniques for selected pharmaceuticals

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ABSTRACT

Recently, there is an emergence of endocrine-disrupting compounds, pharmaceuticals, and personal care products (EDC/PPCPs) as important pollutants to remove from drinking water and reclaimed wastewater. In this work, the efficiency of removing pharmaceuticals (PCs) from model aqueous solutions and raw wastewater with ultrafiltration (UF), nanofiltration (NF), activated carbon adsorption (AC), biological methods (SBR) and oxidation with ClO_2 was investigated. Some treatments have also been used as combined processes: UF + NF, UF + AC, SBR + ClO_2. Ibuprofen, Acetaminophen, Diclofenac, Sulfamethoxazole, Clonazepam, and Diazepam were selected as model compounds. In order to evaluate their removal, PC solutions were also considered at several operating conditions (pH, conductivity, concentration, and temperature), and optimal conditions were obtained. Experiments were performed at usual PC concentrations in wastewaters: 1000 ng/L for Ibuprofen and Acetaminophen, 300 ng/L for Diclofenac, Sulfamethoxazole, Clonazepam, and Diazepam. Separation was evaluated by liquid chromatography–mass spectroscopy. Results indicated that the removal efficiency depends on their Log K_{OW}, which is intrinsically related to their hydrophobicity and then, to their adsorption onto the surface (UF, NF, and AC). Also, NF, AC, and combined processes (UF + NF, UF + AC) were the most suitable separation techniques to obtain high removal efficiencies for most of the PCs used, except for Acetaminophen (which showed great removal efficacy using SBR). UF presented low removal yields for all PCs tested. ClO_2 treatment was more effective at high concentration (50 mg ClO_2/L). Furthermore, results also showed that there are significant differences on the performance of the processes applied and which treatment is the most effective for each PC analyzed.

1. Introduction

The presence of pharmaceuticals and personal care products (PPCPs) in the environment is recognized as emerging issue due to their negative environmental and human health effects [1]. Pharmaceuticals (PCs) are introduced into the environment from discharges of wastewater treatment plants (WWTPs), which are not designed to treat all these substances and thus, they cannot be completely removed [2]. In this way, these effluents from WWTPs are relevant pollutant sources for the environment. Although PCs are present at very low concentrations (μg/L to ng/L range), they may cause environmental and health hazards [3]. Antimicrobial agents are the most widely used. As a major consequence, this usage could generate antibiotic-resistant bacteria, especially in quinolones and sulphonamides [4].

Furthermore, the application of sewage sludge to soils may be a potential route for these PCs to reach the terrestrial environment and then, the human food chain. In that way, it is not surprising that these antibiotics were detected even at subinhibitory concentrations in surface and groundwaters, treated wastewater, biosolids, soils, and sediments [5]. Removal efficiency for PCs at WWTPs depends on biological treatments [6], of which activated sludge process is the most frequently used. Although some promising technologies have been implemented, more studies are required to develop really effective treatments, especially for the most persistent chemicals.

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A combination between membrane filtration processes and biological treatment replaces advantageously a secondary clarification and tertiary steps. Ultrafiltration (UF) is used in wastewater treatment and drinking water production to remove natural organic matter (NOM) and micropollutants, such as pesticides and PCs [7,8]. In addition, these previous studies investigated different separation mechanisms (size/steric exclusion, hydrophobic adsorption, and electrostatic repulsion, among others). Recently, other membrane processes have been evaluated to remove PCs from wastewater. Nanofiltration (NF) has been used to successfully remove low-molecular-weight organic compounds such as pesticides, endocrine disruptors, and various PCs during water treatment [8–10]. This removal can occur through multiple mechanisms. At the beginning of the filtration process, removal can be governed by the adsorption phenomenon of different contaminants with hydrophobic nature or strong hydrogen-bonding characteristics [11–14]. Examples of this kind of contaminants are 2-naphthol, estrone, and non-phenolic pesticides. In many cases, removal can also occur through steady-state rejection. This may be due to steric effects for uncharged solutes or the combination of steric and electrostatic effects for charged solutes. These rejection mechanisms can affect different water-quality parameters including pH, ionic strength, and organic content [15].

The removal of PCs by adsorption is one of the most promising techniques. Adsorption process using activated carbon (AC) is frequently applied for removing natural or synthetic organic compounds (OCs) in drinking water treatment [16]. This process has numerous advantages: applicability at very low concentrations of pollutants, ease of operation, suitable for batch and continuous processes, possibility of regeneration and reuse, and low capital cost [17]. AC is a useful adsorbent to remove PCs due to its high surface area, high degree of microporosity, and well-developed surface chemistry properties. AC surface is predominantly hydrophobic but may also contain functional groups formed during the activation process. These groups mainly contain oxygen and hydrogen, but they may also contain chlorine, nitrogen, and sulphur. The nature of these functional groups depends on activation conditions, which contribute to the acidic/basic character of the adsorbent surface and thus, it has influence on specific interactions with adsorbed compounds [18]. It has been demonstrated that the presence of oxygen-containing functional groups on the surface and their concentration levels play an important role in adsorption capability and removal mechanism [19–21]. Other important AC properties are: pore size distribution [20,22], ash content [23], and pH of point of zero charge (pHPZC), as an indicator of AC surface chemistry [24]. AC can be produced from several carbonaceous materials, including wood, coal, lignin, and coconut shells [25]. Recent studies have reported excellent performance of low cost ACs for the removal of pharmaceutical compounds, which is an attractive and economic alternative for water treatment along with waste disposal and recycling [24]. AC can be commonly found in two different forms: powdered activated carbon (PAC) and granular activated carbon (GAC). Several authors demonstrated the efficiency of both ACs (PAC and GAC) in the removal of organic micropollutants from water [26,27]. Since PAC is dynamically added to the plant, it can be used seasonally to treat wastewater in which the risk of OCs traces could be great (e.g., low-flow events). The capability of PAC to remove OCs depends on the PAC dose and the contact time, as well as the target contaminant properties (e.g. water solubility, hydrophobicity, charge, polarizability, size, aromaticity and the presence of specific functional groups) [20,28]. GAC used in packed bed filters was also highly effective. However, more hydrophilic contaminants can break the GAC filter much more rapidly than strongly bound hydrophobic contaminants. Therefore, in both powdered and granular forms, AC demonstrates a great potential for removal OCs traces, although PAC dose and GAC regeneration/replacement are two critical parameters to be considered for obtaining a successful removal [28]. Generally, loaded GAC is regenerated ex situ by heating [29] or steaming [30]. After several regenerations, GAC is managed as a waste and is incinerated [31].

Other interesting technique to remove PCs is using a Sequencing Batch Reactor (SBR), which is based on the principles of the activated sludge process. In a SBR, oxygen is bubbled through the wastewater to reduce biochemical oxygen demand (BOD) and chemical oxygen demand (COD). After that, the effluent is suitable to be discharged to surface waters or to be used in agriculture. The operation cycle is divided into five phases: filling, aeration-reaction, settling, decantation, and idle. SBR has been successfully employed in the treatment of both municipal and industrial wastewater [32]. Moreover, it has been demonstrated that SBR is valid as a system to remediate polycyclic aromatic hydrocarbons (PAH) contaminated sediments, while offering a high flexibility to adapt the process to the characteristics of the compounds to be treated. For instance, if the value of the volumetric exchange ratio could be properly controlled, it would be possible to limit the pollutant load of the biomass in the SBR. So, it could be avoided the inhibition phenomena [33].

Additional chemical oxidation step can be used in WWTPs if the pollutants are not completely removal by biological treatment [34,35]. Among the chemical oxidants used in wastewater treatment, chlorine dioxide (ClO_2) is an interesting compound due to its potential to remove PCs in wastewater. The application of ClO_2 to remove PCs from drinking water, surface water, and wastewater effluents has shown promising results. The non-steroidal anti-inflammatory drug Diclofenac, reported as one of the most frequently detected compounds in water at concentrations up to the mg/L level [36], is completely degraded during water treatment with low ClO_2 doses [37]. In wastewater effluents, steroid estrogens and industrial estrogenic chemicals were removed by using ClO_2 doses between 1.25 and 3.75 mg/L. At the same time, the reduction of estrogenic potency was observed [38]. The capability of ClO_2 as an oxidant has also demonstrated in the removal of several antibiotics found in water effluents [39,40]. When ClO_2 was used in biologically treated wastewater for selective oxidation of organic micropollutants, it was found that smaller doses were rapidly consumed through reactions with soluble components in water. This fast consumption in wastewater was observed in previous studies by other authors [34,38,41]. Based on ClO_2 reactivity in wastewater effluents, it has been suggested that ClO_2 could be used as an alternative to ozone for the removal of micropollutants [42,43].

Taking into account all the information above mentioned, the aim of this work consists of evaluating the removal efficiency of some common PCs (Ibuprofen, Acetaminophen, Diclofenac, Diazepam, Clonazepam, and Sulfamethoxazole) from both model aqueous solutions and raw wastewaters. As a novelty, the performance of the most often used techniques for removal PCs (UF, NF, AC, SBR, and ClO_2) were compared to the efficiency achieved by combining these techniques (AC + UF, UF + NF, SBR + ClO_2). In addition, best techniques to remove each PC in terms of removal efficiency were suggested.

2. Materials and methods

2.1. Pharmaceutical compounds

The choice of pharmaceutical compounds and their respective concentrations were performed according to their occurrence in the environment as explained above. The active principles and the main characteristics of the target PCs extracted from literature [8,28,44–46] can be observed in Table 1.