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Effective adsorption of non-biodegradable pharmaceuticals from hospital wastewater with different carbon materials

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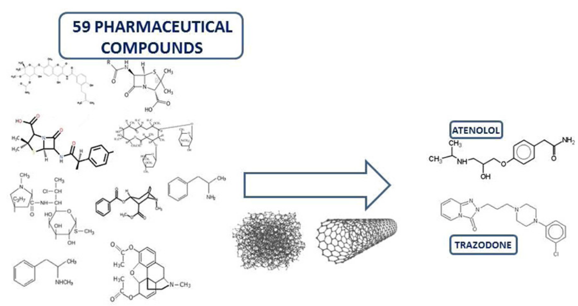
HIGHLIGHTS

- Different carbon adsorbents were tested for the removal of pharmaceuticals.
- Adsorption tests for the removal of carbamazepine and ciprofloxacin were developed.
- The mixture of carbamazepine-ciprofloxacin in water was treated by adsorption.
- TOC, TN, carbonates and aromaticity was removed from a hospital effluent by carbon adsorbents.
- Pharmaceuticals in the real effluent, at ng L^{-1}, was efficiently treated by adsorption onto carbon materials.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption on carbon materials (AC-F400, AC-PS, AC-RH, CNF and MWNT) has revealed as an effective treatment for the removal of two representative pharmaceutical compounds (carbamazepine, CBZ, and ciprofloxacin, CPX) in ultrapure water, as isolated compounds and as a mixture of both of them. Accordingly, a real pharmaceutical effluent containing these substances was efficiently treated by adsorption with the tested carbon adsorbents. A relatively high adsorption rate (equilibrium time of 4 h) and large carbamazepine and ciprofloxacin adsorption capacities ($q_{CBZ} = 242$ mg g^{-1}, $q_{CPX} = 264$ mg g^{-1}) were found, using adsorbent doses ranging from 2 to 3 g L^{-1}, natural pH, temperature of 30 °C and stirring rate of 250 rpm. Thus, the decreasing in the adsorption removal was observed for both contaminants when the mixture CBZ-CPX was treated, reaching up to 80.5% of decreasing in CBZ adsorption (in presence of CPX) onto F-400 activated carbon. The bi-component adsorption systems were reasonably well-fitted by the extended Freundlich model equation. Meanwhile, the reduction of macroscopic parameters (Total Organic Concentration, TOC, Total Nitrogen, TN, carbonates (CO_3^{2-}) and aromaticity) in the real hospital wastewater was achieved in high percentages (from 64 to 98.8%). Moreover, the carbon adsorbents were proven as efficient materials in the removal of the pharmaceutical compounds from the hospital effluent matrix; after the treatment, only trace-level concentrations of atenolol and trazodone were detected.

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1. Introduction

Pharmaceuticals are a class of emerging environmental contaminants that are extensively and increasingly being used in human and veterinary medicine. These chemicals are a large and diverse group of compounds designed to prevent and treat diseases.

The worldwide consumption of pharmaceutical compounds has increased in both hospitals and households, which represents a major concern in terms of their possible harmful effects on the environment and human health [1,2]. The usage and consumption are increasing consistently due to the expanding and inverting age structure in the worldwide population. After intake, significant fractions of the parent compound are excreted in un-metabolized forms or metabolites into raw sewage and wastewater treatment systems, where they are partially removed before being discharged into surface water [3].

Otherwise, many pharmaceuticals are still unregulated; according to the European Community Directive, 2015/495, diclofenac, an anti-inflammatory compound, and the hormones 17β-estradiol and 17α-ethinylestradiol, among others, have been included as priority contaminants. Whereas, according to the US EPA, erythromycin, nitroglycerin, and nine hormones would need to be considered as priority compounds, based on their health effects and occurrence in environmental waters [4].

Hospital wastewater treatment has become the object of several investigations in the last few years [5–7], but under our point of view, few studies have been focused on the tertiary treatment of real hospital wastewater effluents. Due to their specific nature, it is expected that hospital effluents are loaded with a complex mixture of compounds, including a huge number of pharmaceuticals and their metabolites, heavy metals, radioactive markers and iodinated contrast media, disinfectants and detergents at relatively high concentrations [8]. Furthermore, hospital effluents play a relevant role in the introduction of pathogens into public waters, especially concerning to multi-resistant bacteria, contributing to the spread of antibiotic resistance into the environment [9]. Nowadays, the scientific community has been warned about the acceptability of the general practice of co-treating hospital effluents with urban wastewater [10,11].

In addition, the removal efficiency of pharmaceuticals in WWTPs is not complete, ranging from 7 to 8% for carbamazepine, while the highest found removal efficiencies averaged about 60% [12].

Analgesics/anti-inflammatories, antibiotics and X-ray contrast agents are amongst the therapeutic groups most widely detected in hospital effluents, as it has been reported by Verlicchi et al. [8]. Thus, antibiotics are one of the pharmaceutical categories with major presence in hospital wastewater. Among them, fluoroquinolone antibiotics class is widely used in human medicine and animal breeding for preventing and curing diseases and promoting animal growth [13]. Ciprofloxacin is a wide-spectrum fluoroquinolone antibiotic extensively used in the world, that can generate contributions to public sewers as high as 272% [11].

Accordingly, psychoactive drugs are of ubiquitous nature and persistence in the aqueous environment due to their general low removal in wastewater treatment plants. Carbamazepine is one of the most widely prescribed medicine for the treatment of epilepsy, trigeminal neuralgia, and some other psychiatric diseases (e.g., bipolar affective disorders). This pharmaceutical, showing important endocrine disrupting effects, it is frequently detected in high concentrations in both WWTP effluents and river water. Carbamazepine is completely transformed by metabolism, with less than 5% of a dose excreted unchanged. Some of the metabolites showed concentrations higher than the parent compound in WWTPs influents and effluents, reaching few μg L^{-1} [14,15].

In this scenario, it is imperative to find new treatment alternatives in order to increase the removal efficiency of non-biodegradable compounds. Tertiary and advanced treatments, e.g., membrane bioreactors, ozonation, chlorination, disinfection, ultraviolet light, photocatalysis, reverse osmosis, membrane and nano-filtration, catalytic wet air oxidation and adsorption on activated carbon have been revealed as promising treatments. Adsorption process is an efficient technology for wastewater tertiary treatment and reclamation. Thus, adsorption onto carbon materials resulted in an efficient removal of a broad spectrum of micropollutants, in particular uncharged and non-polar compounds (log $K_{ow} > 2$). This is attributed to its porous structure, providing a large surface area for adsorption. In addition, surface chemistry and pore size distribution are critical factors governing the extent of the pharmaceuticals removal [16].

The aim of the present work is to evaluate both kinetic and equilibrium adsorption of carbamazepine and ciprofloxacin as isolated and mixture ultrapure water solutions by using commercial carbon materials (AC-F400 activated carbon, multi-walled carbon nanotubes, MWNT, and carbon nanofibers, CNF) and lab-synthesized activated carbons from peach stones (AC-PS) and rice husk (AC-RH) as precursors. Accordingly, carbon adsorbents have been used to treat a real hospital wastewater containing both CBZ and CPX, evaluating the removal efficiency of quality macroscopic parameters (TOC, TN, carbonates, CO_3^{2-}, and aromaticity) and each of the pharmaceuticals contained in the wastewater.

2. Experimental

2.1. Reagents and target compounds

Acetonitrile (HPLC Plus gradient grade) was supplied by Carlo Erba (Barcelona, Spain) and ortho-phosphoric acid (H_3PO_4, 85% wt) was obtained from Panreac (Barcelona, Spain).

Carbamazepine (CBZ, 99.8% wt) and ciprofloxacin (CPX, 99.8% wt) were purchased from Sigma-Aldrich (Steinheim, Germany). The pharmaceuticals solutions were prepared daily by dilution of the stock solution to the appropriate concentrations. The physico-chemical properties of the compounds are shown in Table 1.

2.2. Adsorbents

The tested commercial adsorbents were granular activated carbon F-400 (AC-F400), supplied by Calgon (France); multi-walled carbon nanotubes (MWNT) supplied by Sun Nanotech Co. Ltd. (Beijing) and carbon nanofibers (CNF) obtained from Grupo Antolín Ingeniería S.A. (Spain). Carbon nanofibers were obtained by the floating catalyst method, namely as VGCF, where the catalyst (Fe, Co or Ni) is introduced continuously in the reaction chamber at 1050–1100 °C. During the process, hydrocarbons decompose over its surface and the carbon nanofibers grow following a helix spiral stacked cup structure. All the commercial materials were used without any additional modification.

Accordingly, two activated carbons were prepared in the laboratory by chemical activation with H_3PO_4 as activating agent, using peach stones (AC-PS) and rice husk (AC-RH) as precursors, respectively. The synthesis procedure has been described in a previous work [22].

The adsorbents were thoroughly washed several times with ultrapure water in order to remove surface impurities and then they were dried at 105 °C for 24 h. Later, granular activated carbons were sieved, selecting a size fraction of 0.250–0.355 mm for the adsorption tests.