Removal of diclofenac and sulfamethoxazole from aqueous solutions and wastewaters using a three-dimensional electrochemical process

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ABSTRACT

The three-dimensional (3D) electrochemical treatment process was studied for the removal of two pharmaceuticals, diclofenac (anti-inflammatory) and sulfamethoxazole (antibiotic), in mono and bi-component systems. Adsorption and conventional two-dimensional electrochemical processes were initially studied and then combined to develop the 3D process. The influence of different operating parameters on the removal efficiency was studied: the distance between the cathode and the anode, the pharmaceutical and electrolyte (NaCl) concentrations, the pH, and the (carbon-based) adsorbent used as particulate electrode (biochar and commercial activated carbon, granulometry, and amount). The energy consumption and the electric energy per order were evaluated. The results demonstrate the efficiency of the 3D process for the removal of diclofenac and sulfamethoxazole from aqueous solutions, both for mono- and bi-component systems, achieving their complete removal respectively in 10 and 30 min, using a Mixed Metal Oxide anode (titanium-coated with RuO_2-IrO_2-TiO_2), a stainless steel cathode, a biochar particulate electrode (1–2 mm), an initial pharmaceutical concentration of 10 mg/L, an inter-electrode distance of 7.5 cm, a pH value of 7 and a current density of 7 mA/cm². The optimised 3D process was also successfully applied to a wastewater treatment plant effluent, but lower removal efficiencies were observed (after 30 min) for bi-component fortified samples; 49% for DCF and 86% for SMX, with energy consumptions of 1224 and 613 Wh/g and an electric energy per order of 19.1 and 8.77 kWh/m³ respectively. On the other hand, the pharmaceuticals were completely removed from the effluent when real concentrations (i.e. without their addition) were used.

1. Introduction

The concentration of emerging pollutants, particularly pharmaceuticals, in the aquatic environment has risen due to the exponential growth of the population, industrialisation and advances in medical care, and consequent increase in life expectancy [1,2]. In addition, pharmaceuticals are inefficiently removed from conventional wastewater treatment plants (WWTPs) because these were not designed for this purpose and there is no obligation to remove them. In the environment, pharmaceuticals can be found in their original form or as metabolites [1]. Although generally present at low concentrations, their presence is recognised as an emerging concern due to the possible threats to aquatic ecosystems and the human population, considering their constant release, bioaccumulation, persistence, biotransformation, and toxic characteristics [1,3].

Diclofenac (DCF) is a highly consumed non-steroidal anti-

inflammatory drug applied in human and veterinarian medical care for inflammation and pain treatment [3,4]. The global annual consumption of DCF has been estimated at around 940 tons [3]. In Portugal, DCF has the highest share of the over-the-counter drugs (without prescription) market; 18.4% in 2018 [5]. Around 65% of the oral dosage of DCF is eliminated through urine [3]. This, together with its incomplete removal by conventional WWTPs (the biological processes used cannot eliminate DCF), has led to its detection, in Portugal, in waters; up to 3200 ng/L in river waters [6,7], up to 241 ng/L in seawater from the Atlantic ocean [8], and up to 6200 ng/L in wastewaters [2,6,9,10].

Sulfamethoxazole (SMX) is a broad-spectrum sulfonamide antibiotic frequently used in human and veterinary medicine to treat respiratory, urinary, skin, and gastrointestinal infections. Besides being commonly used in aquaculture and livestock breeding in some countries, SMX is used as a growth promoter [11]. Once administered, 51–58% of SMX is metabolised, and 15–25% is excreted unchanged in urine [11]. SMX residues, and especially its transformation products, may adversely affect organisms and there is a particular concern about developing antibiotic-resistant bacteria and the spread of resistance genes in the environment [11]. SMX was also detected in Portuguese rivers (up to 43 ng/L) and wastewaters (up to 600 ng/L) [2,6]. Additionally, values as high as 2623 ng/L were reported in a recent review regarding the presence of antibiotics in the European aquatic environment [12].

The removal of SMX by biological treatments is lower (68%) than by tertiary treatments, such as sand filtration (up to 95%). The combination of treatments such as UV radiation with neutral photo-Fenton has been reported to completely remove this compound [13]. For example, in a recent study, from the 15 monitored sulfonamide antibiotics in European WWTPs, only sulfapyridine and SMX were detected in the final effluents [14]. As stated before, the biological processes used in conventional WWTPs cannot eliminate DCF. However, advanced oxidation processes have arisen as a promising treatment option, with ozonation achieving 90% of removal and complete removal was achieved with a biological-sono-photo Fenton treatment [3].

Adsorption technologies are also efficient alternatives, frequently using activated carbon [15]. However, the cost of activated carbon often restricts its economic viability and, since the removal process is non-destructive, the fate of the adsorbent material after removal is another cost to be added to the process. Therefore, the search for natural low-cost adsorbents, such as biochars prepared from wastes from agriculture and agro-industrial processes, can be promising alternatives for wastewater treatment [3]. On the other hand, two-dimensional (2D) electrochemical oxidation is one of the most important advanced oxidation processes for pollutant degradation. Nevertheless, this process also has disadvantages: the short lifetime of the electrodes, mass transfer limitation, temperature increase during the process, and low current efficiency [16]. To overcome these obstacles and enhance the degradation potential, several researchers proposed a three-dimensional (3D) electrochemical process by loading adsorbent particles between the anode and cathode in the electrochemical system [16]. Pourzamani et al. [16] used Ti/RuO_2-TiO_2 electrodes in the presence of multi-walled carbon nanotubes to remove DCF from aqueous solutions achieving an average removal efficiency of 98.5% [16]. In another study, aluminum electrodes in the presence of granular activated carbon derived from walnut were applied to remove DCF from synthetic wastewater, with a 96.99% removal efficiency [17]. Additionally, 3D electrochemical processes were also applied for the removal of ibuprofen [18], tetracycline [19], p-aminophenol [20], Cu-EDTA [21], pollutants from landfill leachate [22], nitrogen from microbial fuel cells [23], and in the treatment of cooking wastewater [24]. In only three of these works' biochar-based particulate electrodes were applied [22–24], but none for the removal of pharmaceuticals.

In this context, the present work aimed to apply a 3D electrochemical process to the removal of DCF and SMX from aqueous solutions and wastewaters. For this purpose, the influence on the removal efficiency of the anode and cathode materials and the type of carbon-based adsorbent (biochar and commercial activated carbon) were studied. Several operating conditions, such as pH, particulate electrode dosage, initial pharmaceutical concentration, the distance between the electrodes, current density, and reaction time were studied. Finally, the optimised process was applied to aqueous solutions and treated wastewater fortified with DCF and SMX.

2. Materials and methods

2.1. Reagents and equipment

DCF and SMX were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Individual stock solutions (1000 mg/L) were prepared in 50% acetonitrile and 50% methanol and stored at − 20 °C. The working solutions were prepared daily by diluting the stock solutions with ultrapure water. Ultrapure water (resistivity: 18.2 MΩ.cm) was obtained from a Milli-Q water purification system (Millipore, Molsheim, France). For the 2D and 3D electrochemical experiments, a Mixed Metal Oxide (MMO) electrode (titanium-coated with RuO_2-IrO_2-TiO_2, 10.50 μm thickness, $100 \times 20 \times 2$ mm, UTronTechnology, Youchuang, China) was used as the anode, and stainless steel (STS) (AISI-304, austenitic grade, $100 \times 20 \times 2$ mm) was used as the cathode. The electrochemical processes were performed using an H.Q. Power D.C. supply, model PS3020 (Velleman®, Gavere, Belgium) with adjustable potential (0–30 V) and current (0–20 A) outputs. The conductivity and pH were measured using a multiparameter analyser (Consort C861, Turnhout, Belgium, with a conductivity electrode (Consort SK10B) and a combined pH electrode (Consort SP10B)). The airflow was controlled using an ELITE 802 air pump with two outputs of 1500 mL/min each (Hagen, Yorkshire, United Kingdom). A multiposition shaking plate, model Multistirrer 15 Velp Scientifica (Usmate, Italy) and a Centrifuge Thermo Scientific Heraeus-Fresco 21, rotor $24 \times 1.5/5$ mL (Waltham, Massachusetts, USA) were used to prepare the samples.

The quantification of DCF and SMX was performed by high-performance liquid chromatography (HPLC) using a Shimadzu HPLC (Shimadzu Corporation, Kyoto, Japan), consisting of an LC-20AB pump, a DGU-20A5 degasser, an SIL-20A automatic injector, a CTO-20AC column oven, and an SPD-M20A diode-array detector. A LUNA C18 column (particle size 5 μm, 150×4.60 mm) connected to a C18 pre-column (particle size 5 μm, 4×2.0 mm), both from Phenomenex (Torrance, California, USA), were used. The HPLC chromatographic program and analytical conditions are presented in supplementary material S1.

The experiments performed with treated wastewater samples with pharmaceuticals present in real concentrations were analysed by ultra-high performance liquid chromatography, using a Shimadzu Nexera UHPLC system (Shimadzu Corporation, Kyoto, Japan) equipped with two solvent delivery modules, a degasser, an autosampler, a column oven, and coupled to a triple–quadrupole mass spectrometer detector LCMS– 8030 with an electrospray ionization source (ESI).

The isotopically labelled compounds, used as internal standards, salicylic acid-d4 was purchased from Sigma-Aldrich (Madrid, Spain) and azithromycin-d3 was acquired from Toronto Research Chemicals Inc. (Ontario, Canada). Individual stock standard and isotopically labelled internal standard solutions were prepared at a concentration of 1000 mg/L on a weight basis in acetonitrile:methanol (50:50, v/v) for diclofenac and methanol for sulfamethoxazole. All stock solutions were stored at − 20ºC. Working standard solutions, containing all pharmaceuticals, were prepared in acetonitrile:ultrapure water (30:70, v/v). A mixture with all isotopically labelled internal standards was also prepared to be used for internal standard calibration.

Acetonitrile LiChrosolv® hypergrade LC-MS was supplied by Supelco (Darmstadt, Germany), methanol LC-MS Ultra CHROMASOLV® grade and hydrochloric acid 37% (HCl) were obtained from Sigma-Aldrich (Spain), formic acid 98% and ethylenediaminetetraacetic acid disodium salt 2-hydrate (Na_2EDTA) were purchased from Panreac

(Barcelona, Spain). All chromatographic solvents were filtered through a 0.22 μm nylon membrane filter (Fioroni Filters, Ingré, France) using a vacuum pump (Dinko D-95, Barcelona, Spain) and degassed for 15 min in an ultrasonic bath (Sonorex Digital 10 P, Bandelin DK 255 P, Germany).

Solid phase extraction (SPE) was performed on Strata-X (200 mg, 3 mL) cartridges from Phenomenex (USA). Nylon syringe filters 0.22 μm were purchased from Specanalitica, Lda. (Carcavelos, Portugal).

The extraction procedure, the LC-MS/MS chromatographic program, mass spectrometry conditions and the validation of the methods are presented in the supplementary material (S2). The procedure used, the chromatographic and mass spectrometry conditions were optimized in previous studies of the authors [25].

2.2. Adsorbents

Vineyard pruning residues from Touriga Nacional (TN), sampled at Quinta dos Carvalhais (Dão region) in 2015, provided by Sogrape Vinhos, S.A. (Porto, Portugal), were used to produce biochar at an industrial scale. The pruning residues were pyrolyzed in an industrial oven by Ibero Massa Florestal (Aveiro, Portugal) as previously described by Fernandes et al. [26]. The characterization of the adsorbents was reported in previous studies by Fernandes et al. [26] and Correia-Sá et al. [27]. The obtained biochar was milled (ZM200, Retsch, Haan, Germany) and sieved (AS 200 Basic Retsch, Haan, Germany) to obtain two fractions with particle sizes of 1–2 mm and < 75 μm, which were used in the experiments.

The polymer-based spherical activated carbon, SARATECH ® reference 102282 [28], was supplied by Blücher (Germany).

2.3. Adsorption experiments

In the kinetic studies, 50.0 mg of the SARATECH® activated carbon and 150 mg of the biochars (corresponding to adsorbent concentrations of 2.00 g/L and 6.00 g/L, respectively) were added to 25.0 mL of aqueous solution in Erlenmeyer flasks and magnetically stirred at 370 rpm (Multistirrer 15, Velp Scientifica, Usmate, Italy) at constant temperature (21 °C). The experimental conditions were set to an initial concentration of 10 mg/L of DCF or SMX, pH 7 and 0.02 M NaCl. In the equilibrium studies the following range of masses of adsorbent was used: from 5.00 to 75.0 mg (0.200–3.00 g/L) for the SARATECH® activated carbon and from 60.0 to 800 mg (2.40–32.0 g/L) for the biochars.

At the end of the assays, an aliquot of the solutions was immediately centrifuged (Heraeus Fresco 21 Microcentrifuge, Thermo Scientific, Waltham, Massachusetts, USA) at 14,500 rpm for 10 min at 4 °C. Then, the supernatant was vacuum filtered through a PTFE membrane filter with a 0.45-μm pore size (Filter-Lab®, Barcelona, Spain) and all solutions were analysed by HPLC (supplementary material S1) to determine the final concentration. In parallel, blank assays were prepared with the same DCF or SMX concentration without adsorbent. The adsorption capacity was calculated according to the equation provided in the supplementary material (S3).

The influence of the pH, NaCl concentration and pharmaceutical concentration were evaluated. The assays were performed in triplicate, and the results were expressed as mean±standard deviation (SD).

The Freundlich [29] and Langmuir [30] models were selected to adjust the adsorption equilibrium. The respective equation models are presented in supplementary material (S4).

2.4. 2D electrochemical process

The 2D electrochemical oxidation experiments were performed in batch mode in an acrylic cell (2 × 15 × 8 cm) with a total volume of 240 mL (produced by Cromotema, Vila Nova de Gaia, Portugal). This cell has the possibility of placing the electrodes at two different distances, 3.50 and 7.50 cm [27]. The electrodes (MMO and STS) had an effective geometric area of 15.0 cm^2. A volume of 150 mL of an aqueous solution of DCF or SMX with different concentrations, with the addition of NaCl, was placed in the cell, and an airflow of 3000 mL/min was used during the process. The current intensity was maintained constant at 0.1 A, corresponding to a current density of 7 mA/cm^2. The 2D electrochemical tests were optimised by varying the distance between the electrodes, the NaCl concentration, the pH and the initial pharmaceutical concentration. The study of the influence of each parameter was performed in ranges that include real operating conditions. Aliquots of the solution contained in the cell were taken at the start and during the experiments (0–10 min). The DCF or SMX removal was assessed by HPLC after vacuum filtration through a PTFE membrane filter with a 0.45-μm pore size (Filter-Lab®, Barcelona, Spain). The experiments were performed at a constant temperature (21 °C). Initial and final temperatures of the solutions were monitored, showing variations less than 0.5 °C. All experiments were performed in triplicate, and the results were expressed as mean±standard deviation (SD).

2.5. 3D electrochemical process

The conditions used in the studies of the 3D process were based on the optimum parameters found in the studies of both the 2D electrochemical and adsorption processes. Besides this, environmental and economic aspects were considered in the definition of the most adequate conditions. The following masses of particulate electrodes were added to the cell containing 150 mL of solution, between the anode and the cathode: 30.0 mg of SARATECH® activated carbon (0.200 g/L) and 30.0 (0.200 g/L), 300 (2.00 g/L) or 600 mg (4.00 g/L) for the biochars. The masses selected for these experiments were based on the equilibrium studies (see 2.3). The adsorbents were tested dry and saturated (i.e., after being kept overnight in a 10.0 mg/L solution of each pharmaceutical, being added without drying). Aliquots of the solution contained in the cell were taken at the start and during the experiments (time 0–10 min) and, after vacuum filtration through a PTFE membrane filter with a 0.45-μm pore size (Filter-Lab®, Barcelona, Spain), were analysed by HPLC. The experiments were performed at a constant temperature (21 °C). Initial and final temperatures were monitored, showing variations less than 0.5 °C. Experiments were performed in triplicate, and the results were expressed as mean±standard deviation (SD).

The 3D experiments were performed both in mono- and bi-component aqueous solutions (AS), in fortified treated wastewater, with approximately 10 mg/L of each pharmaceutical and in real wastewaters (with no addition of pharmaceuticals). The treated wastewater was collected from a WWTP in the Northern region of Portugal and presented a pH value of 6.95, a conductivity of 0.864 mS/cm, total dissolved solids of 30.0 mg/L, a total nitrogen content of 27.0 mg/L, biochemical oxygen (after 5 days) and chemical oxygen demands of 28.0 and 73.5 mg/L O$_2$, respectively. The samples were fortified with 10 mg/L of DCF and/or SMX solutions, and 0.02 M of NaCl was added.

2.6. Application of 2D and 3D electrochemical process to treated wastewater samples (real concentrations)

The efficiency of the 2D and 3D treatments for the removal of diclofenac and sulfamethoxazole from treated wastewater samples (WWTP effluent) was evaluated. The WWTP effluent samples (without and with fortification) before and after the treatments were extracted by SPE and analysed by LC-MS/MS, as described in detail respectively in sections S2.1 and S2.2 of the supplementary material.

2.7. Energy consumption and efficiency of the electrochemical processes

The removal percentage of the pharmaceuticals was used to calculate the energy consumption (ECon) associated with each of the tests (Eq. 1) [27].

$$ECon(Wh/g) = \frac{U \quad I \quad t}{60(C_0 - C_t) \quad V} \tag{1}$$

The energy efficiency of the electrochemical treatment was also estimated (Eq. 2) using the electric energy per order (EE/O) [31], which expresses the electric energy (in kWh/m^3) required to reduce the concentration of DCF and SMX by one order of magnitude in a unit volume of contaminated water.

$$EE/O(kWh/m^3) = \frac{UIt}{60Vlog(\frac{C_0}{C_t})} \tag{2}$$

In both equations: U - potential difference (V); I - current intensity (A); t - processing time (h); V - treated volume (L); C_0 and C_t - initial pharmaceutical concentration and at time t, respectively (g/L).

2.8. Statistical analysis

The data of the equilibrium studies of the adsorption process were fitted by non-linear curve fitting using Origin software (Origin Lab Corporation, USA).

The software program IBMS SPSS for Windows, version 26 (IBM Corp., Armonk, N.Y., USA) was used to perform statistical analyses. The data normality was evaluated by Kolmogorov–Smirnov and Shapiro–Wilk tests. The removal in % was represented as mean ± standard deviation, and comparisons between groups were made using the Mann-Whitney test, at a significance level of $p < 0.05$ for the 3D treatment experiments.

3. Results and discussion

The adsorption and two-dimensional electrochemical processes were studied before the development of the 3D electrochemical process in mono- and bi-component aqueous solutions and treated wastewaters, fortified with DCF and SMX at the same concentrations.

3.1. Adsorption experiments

3.1.1. Kinetic studies and isotherms

The kinetic studies (Table S5) were conducted to investigate the effect of contact time on the adsorption processes of DCF and SMX and to determine the equilibrium time. In Fig. S5.1 can be observed that the adsorption onto the SARATECH® activated carbon increases with the contact time until achieving equilibrium, which happened at 25 min, for both pharmaceuticals. For both particle sizes of the biochar adsorption occurred in a faster way at the beginning of the process when compared with the SARATECH® activated carbon, achieving equilibrium in less than 10 min for DCF, and 20 min for SMX. However, the final DCF adsorption capacity for the biochars (0.64 mg/g for biochar TN < 75 μm and 0.35 mg/g for biochar TN 1–2 mm) was much lower than the one obtained for the SARATECH® activated carbon (5.43 mg/g). The adsorption of SMX on the biochars was even lower than the ones reported for DCF; 0.03 mg/g for biochar TN < 75 μm and no adsorption was observed for the biochar TN 1–2 mm. The SARATECH® activated carbon presented a much higher adsorption capacity (6.2 mg/g).

The equilibrium adsorption isotherm is fundamental to describe the interactive behaviour between solutes and adsorbents and is the basic requirement in the design of adsorption systems [32]. The experimental results of the equilibrium isotherms and the fits to the Freundlich and Langmuir models are presented in Fig. S5.2 and the models' parameters are presented in Table S5. According to the Giles classification, these isotherms show a characteristic L-type behaviour (except for the system SMX/biochar TN < 75 μm), consequently representing a system in which the adsorbate is strongly attracted by the adsorbent [32]. Although the Freundlich model gives a better representation of the

experimental results for all the tested adsorbents, except for the system DCF/biochar TN 1–2 mm, taking into consideration the parameters obtained (R^2 and the reduced χ^2 values), the Langmuir model can also fit the experimental results, except for the adsorption of SMX onto the biochar TN < 75 μm, which has the shape of an initial S-Type or unfavourable isotherm.

The SARATECH® activated carbon achieved the highest maximum adsorption capacities, estimated by the Langmuir model, of 20 ± 2 and 10 ± 2 mg/g, for DCF and SMX, respectively. The biochars presented lower maximum adsorption capacities for DCF, 1.8 ± 0.7 and 0.044 ± 0.006 mg/g, respectively for the biochars TN < 75 μm and 1–2 mm. Although the biochars presented lower maximum adsorption capacities than the SARATECH® activated carbon, that has a much higher specific surface area (1736 m^2/g [28]) than the biochars (< 10 and 62 m^2/g respectively for biochars TN < 75 μm and 1–2 mm [26]), as reported by Viotti et al. [33], they were also tested as particulate electrodes given the sustainability of the material. Moreover, it is known that in 3D processes other phenomena occur that may be more relevant to the overall efficiency of the treatment than adsorption itself.

3.1.2. Influence of pH

In general, the pH of the solution may affect the functional groups of both the pharmaceutical and the adsorbent, altering chemical properties and interaction mechanisms [33]. So, the effect of four different pH values (3, 5, 7, and 9) on the adsorption of DCF and SMX onto the tested adsorbents was investigated (Fig. S6.1).

For DCF the highest adsorption capacity for all the tested adsorbents was obtained at pH 9. With a pKa of 4.2, DCF is neutral at pH values below this value (Fig. S6.1a), therefore, non-electrostatic interactions involving hydrogen bonds are present in the interaction mechanism. On the other hand, for pH values above the pKa, especially above 6, DCF is negatively charged, favouring electrostatic interactions with the positively charged adsorbent surfaces [33].

The maximum adsorption capacity of SMX using the SARATECH® activated carbon was observed at pH 7. The adsorption capacities of the biochar TN < 75 μm for SMX are quite low, although higher at pH 3. The ionic forms of SMX (SMX$^+$ and SMX$^-$) are the dominant species at pH values lower than 1.6 (pKa1) and higher than 5.7 (pKa2) due to the protonation of the amino group and deprotonation of sulfonamide group [34,35], respectively (Fig. S6.1b).

Tagliavini et al. [36] measured the electrokinetic potential of the activated carbon over the pH range 2–12, and the determined zeta potential was 0 mV in the pH range of 4.5–9.5, which indicates that the surface remained uncharged within this pH range. Considering this fact and that below pH 4.5 there are no adsorbent/adsorbate electrostatic attractions it was expected that the adsorption capacities of SARATECH® activated carbon had no significant changes for the different pH values tested. The exception is for DCF at pH 3; at this pH it has a very low water solubility causing the precipitation of DCF [37] and this in turn could affect adsorption, due to the decrease in the initial concentration of this pharmaceutical in solution and therefore a much lower adsorption capacity was observed.

For the biochars, the pH value at the point of zero charge (pH$_{pzc}$) was 9.6 [26], indicating basic properties. The adsorbent surface tends to be negatively charged at pH > pH$_{pzc}$ and attracts cations, while at pH < pH$_{pzc}$ it tends to be positively charged attracting anions from the solution [26]. At all the tested pH values the biochar's surface was therefore positively charged. As DCF is negatively charged above pH 6.2 (pKa+2), the adsorption capacity should be higher in the range of 6.2–9.6 (pH$_{pzc}$). The same behaviour would be expected for SMX, with higher adsorption capacities in the range 7.7 (pKa2 +2) to 9.6 (pH$_{pzc}$). Due to the low adsorption capacities of the biochars (Fig. S5.1), this is not evident; for the biochar 1–2 mm the q_m was always 0 mg/g and at pH 3 was 0.08 mg/g, and for the biochar < 75 μm the q_m was almost equal over the studied pH range (around 0.10 mg/g).

3.1.3. Influence of initial DCF and SMX concentration

Although the range of concentrations evaluated in this study (2.5–20 mg/L) is considerably higher than the ones found in WWTP effluents, these higher values allowed a better follow-up of the analysis by HPLC.

The adsorption capacity increased with increasing DCF and SMX concentration for the SARATECH® activated carbon (Fig. S6.2), which indicates that there are still active adsorption sites available. However, it is expected that further increases in concentration may result in an adsorption capacity plateau and a decline of adsorption efficiency because of saturation of the available adsorption sites. For the biochar TN < 75 μm the same pattern was observed for DCF (Fig. S6.2a), while for SMX the adsorption capacities are too low to show any influence of the initial concentration. For the same reason, for the biochar TN 1–2 mm no significant differences were observed for the different DCF and SMX concentrations (Fig. S6.2). This may be related to its low specific surface area and consequently lower availability of active adsorption sites.

3.1.4. Influence of NaCl concentration

The influence of the ionic strength, using NaCl solutions (0.01, 0.02 and 0.05 M), on the adsorption capacity (Fig. S6.3) was tested. However, no significant changes were observed for all tested adsorbents. This was expected because the ionic exchange contribution was not relevant, and the solution's salinity was low. Several authors have reported the effect of ionic strength on the adsorption of organic compounds on activated carbon. The effect of salt concentration on a given adsorbate/adsorbent system is generally explained based on two distinct phenomena: the salting out and the screening effect. In the first case, the solubility of the compound in the aqueous phase is decreased when ionic strength increases resulting in an increase of the adsorption, when no electrostatic interactions are involved. For an adsorption governed by electrostatic interactions, high salinity conditions disturb the electrical double layer surrounding the charged adsorbent surface, and reduce the interfacial electrokinetic potential, weakening the electrostatic attraction toward the organic adsorbate [38].

3.2. 2D electrochemical experiments

The 2D electrochemical tests were optimised for mono-component solutions of DCF and SMX by varying the distance between electrodes, the NaCl concentration, the pH of the working solutions and the initial pharmaceutical concentration. The other operational conditions were kept constant, such as: MMO as the anode, STS as the cathode, a current density of 7 mA/cm^2, and an airflow of 3000 mL/min (at 21 ± 1 °C). The summary of the experimental conditions for the 2D-electrochemical assays with DCF and SMX, their removal and energetic efficiencies are presented in supplementary material (S8).

3.2.1. Influence of inter-electrode distance

The efficiency of DCF and SMX removal was evaluated for inter-electrode distances of 3.5 and 7.5 cm (Fig. S8.1). For both compounds, the removal increased when a smaller inter-electrode distance was used. For the used current density, 3.5 cm seems to be the most adequate distance between the electrodes for this reactor. The DCF removal is higher than 95% after 4 and 6 min, for 3.5 and 7.5 cm, respectively. For SMX, the removal is higher than 95% after 4 min for both distances.

Considering the energy consumption (Wh/g), when using a shorter distance (3.5 cm) between the electrodes (Tables S8.1 and S8.2) the consumption is lower (38.5 and 20.0 Wh/g for DCF and SMX, respectively) when compared to 7.5 cm (53.9 and 34.9 Wh/g for DCF and SMX, respectively). This fact can be explained by the amount of energy necessary to supply to the system to generate an electric field and induce ion movement. With a shorter distance between the electrodes, the energy required to move the ions is smaller, as the path they must take is shorter [39], reducing mass transfer and electron transport resistances

[40]. The explanation for this phenomenon may be related to the decrease in the effective current density between the electrodes with the increase in the distance between them, for a constant current. However, the spacing between the electrodes must not be too small. A short circuit can occur when the spacing between the electrodes is minimal. Moreover, due to the short inter-electrode distance, a higher current density would reduce the lifetime of the electrodes [41].

Lin et al. (2013) [42] reported a decrease in the SMX oxidation rate with the increasing distance between the anode and cathode using 3–20 mm. They concluded that more electrolysis time was required at a larger electrode distance due to the longer diffusion distance. These authors also concluded that the energy efficiency was higher at smaller distances, corresponding to a lower cost. This can be attributed to the decrease of the electrolysis cell resistance and substrate diffusion distance.

However, when stirring is used, the mass transfer resistance decreases, and a relatively larger electrode distance can be employed, which allows the treatment of a greater volume of wastewater using the same electrode area, improving the space efficiency, and reducing the number of electrodes [42]. Besides this, a larger distance also allows that the particle electrode used in the 3D process remains between the anode and the cathode [27]. For these reasons, 7.5 cm was chosen to perform the 3D experiments.

3.2.2. Influence of pH

The effect of initial pH on DCF and SMX removal was investigated for different pH values (in the range 3–9) (S8.2). It can be observed that the removal rate for DCF was faster for pH values of 3 and 5 when compared with higher pH values. At pH 3 this fastest elimination might be related to the possible precipitation of DCF at this pH [37]. Rosales et al. (2019) [37] found that although DCF degradation was consistently faster at a more acidic pH due to precipitation, they suggest that the most adequate option is to work at a neutral pH.

Regarding SMX, the removal was fastest at pH 3 and slowest at pH 9. The SMX removal efficiency was previously determined at pH values ranging from 3 to 10 using MMO as the anode and Ti as the cathode materials [42]. The authors of this study reported that SMX solutions with a lower initial pH had a slightly higher oxidation rate than those with a higher pH, indicating that the oxidation process was more favourable in acidic solution, implying that the pH may affect the speciation and hydration of the molecules, which has an impact on the diffusivity of SMX. The pKa values of SMX are 1.6 (pKa1) and 5.7 (pKa2), respectively (Fig. S7.1). When pH < pKa1, SMX is positively charged due to protonation, while when pH > pKa2, the -NH sulfonamide group is deprotonated and more prone to radical oxidative activity [43]. The ionic form between pKa1 and pKa2 is essentially neutral. The higher removal of DCF and SMX at acidic pH values might also be related to the action of reactive chlorine species and hydroxyl radicals (supplementary material, S9).

Although at pH 3 both pharmaceuticals present faster removal and lower energy consumption (Tables S8.1 and S8.2) in the 2D studies, the use of pH 7 was considered more adequate for economic reasons because the common pH of domestic wastewaters is around 7. Moreover, the studies of pH influence (Section 3.1.2) on the adsorption and the fast degradation rates observed for both compounds at pH 7, support the selection of this value for the 3D experiments.

3.2.3. Influence of the NaCl concentration

The study of the influence of NaCl concentration on DCF and SMX removal was carried out using different concentrations (0.01, 0.02, 0.05 and 0.10 M), and the results are shown in Fig. S8.3.

It was found that for the lower concentrations the removal of the pharmaceuticals was lower when compared with the higher concentrations. These results agree with those obtained in the study carried out by Mohammadi et al. (2021) [44] in which was concluded that an increase of the NaCl concentration led to an increase in the removal of DCF

since more electrical current is transferred to the solution. Furthermore, an increase in NaCl concentration leads to an increase in the production of oxidants, which reduces the final DCF concentration [44]. The reactive chlorine species formed during the electrochemical oxidation using an MMO anode, particularly hypochlorite, are the most important contribution to the increase of efficiency [45,46]. The reactive species are generated on the electrode surface in aqueous solutions and the subsequent Cl$^-$ oxidation on the anode surface, when HClO predominates in solution ($2.5 < pH < 7.5$) [46], are presented in the supplementary material (S9).

According to previous studies [47,48] of DCF behaviour during water chlorination processes in the presence of reactive chlorine species, at pH 7, a constant degradation rate was verified. Partial removal of DCF can therefore be expected in the presence of reactive chlorine species without further processing. The presence of reactive chlorine species in the samples increases the removal of DCF after their collection, therefore it interferes with the quantification of the analyte as the reaction continues to occur. For this reason, a compound with high reducing power able to reduce HClO and ClO$^-$ formed during the electrochemical process was used. Several authors suggested that sodium thiosulfate ($E°$ $S_4O_6^{2-}/S_2O_3^{2-} = 0.08$ V) does not oxidise pharmaceuticals and can inhibit reactive chlorine species [49,50]. Therefore, sodium thiosulfate was used as quencher to inhibit the oxidation of both pharmaceuticals; 20 μL of 0.005 M $Na_2S_2O_3$ was added to each aliquot after its collection.

Regarding SMX, Hai et al. (2020) [43] studied the impact of the supporting electrolytes on the oxidation capacity of the boron-doped diamond-stainless steel (BDD-STS) system. In this study, 0.1 M NaCl, Na_2SO_4 and $NaNO_3$ were selected as supporting electrolytes using a current density of 30 mA/cm^2 and pH 7. Compared with Na_2SO_4, the oxidation ability of NaCl for SMX degradation was more significant, while $NaNO_3$ inhibited the degradation of SMX. In addition, these authors reported that, during electrolysis, direct oxidation of the chloride ions (Cl$^-$) on the anode surface originated the active chlorine species Cl_2, HClO and ClO$^-$, while indirect oxidation produced mainly Cl_2 enhancing the degradation of SMX [43].

When the NaCl concentration increases, the removal of DCF and SMX increases, and the energy consumption decreases from 1526 (0.01 M) to 53.9 (0.10 M) Wh/g for DCF and from 815 (0.01 M) to 34.9 (0.10 M) Wh/g for SMX (Tables S8.1 and S8.2). However, several problems can arise when using high quantities of NaCl in a WWTP, such as corrosion. In Portugal, current legislation recognises the competence of municipal councils to authorise and set the conditions for the discharge of wastewater into public drainage systems. The conductivity of the solution at the end of the reaction (Tables S8.1 and S8.2) respects the limits established by the legislation [51] regarding wastewater conductivity (3000 μS/cm) and the limit of chloride present in water of 1000 mg/L only when a NaCl concentration of 0.02 M (709 mg Cl$^-$/L) is used. For this reason and considering the future application in a WWTP, a NaCl concentration of 0.02 M was selected.

3.2.4. Influence of the initial concentration of the pharmaceuticals

The effect of the initial DCF and SMX concentrations on their removal is presented in Fig. S8.4. As expected, for lower initial concentrations, the maximum removal is reached more quickly when compared to higher concentrations. For a DCF concentration of 2.5 mg/L removal of 98% was achieved after 4 min. On the other hand, for 20 mg/L only about 40% was removed after 10 min. These observations are in accordance with a previous study, which reported a decrease of the removal efficiency with the increase of the initial pharmaceutical concentration [52], from 98% to 90% when increasing the initial concentration of DCF from 278 to 950 mg/L (electrolyte concentration of 2 g/L of Na_2SO_4, current density of 100 mA/cm^2 and pH 3).

Another study [42] reported that for initial SMX concentrations in the range of 10–100 mg/L the removal was similar, while the rate decreased for concentrations between 100 and 400 mg/L. The authors suggested that the system is diffusion-controlled for a low concentration

of reactants. Considering that the active species generated at the anode had the same concentration in all experiments, when using a higher SMX concentration, the ratio between the active species and SMX lower, indicating a smaller probability of SMX molecules being attacked by the active species, which could explain the rate decrease [42]. At high substrate concentration, the desorption of degradation products from the electrode is also negatively affected, reducing the net reaction rate.

As mentioned in Section 3.1.3, although it's a much higher concentration than the one found in the WWTPs effluents, a pharmaceutical concentration around 10 mg/L was used in the subsequent experiments.

3.3. 3D electrochemical experiments

The 3D experiments were performed applying the conditions previously selected in the 2D electrochemical experiments and using the three adsorbents tested in the adsorption studies (Biochars TN < 75 μm and 1–2 mm, and SARATECH® activated carbon) as particulate electrodes. Moreover, the incorporation of environmental and economic aspects in the definition of the most adequate conditions for the 3D process is essential.

The electrochemical operational conditions for all 3D experiments (selected from Section 3.2) were: current density of 7 mA/cm^2, inter-electrode distance of 7.50 cm, a pH value of 7, NaCl concentration of 0.02 M, initial DCF or SMX concentration around 10 mg/L, an air flow of 3000 mL/min, and a temperature of 21.0 ± 1.0 °C. The summary of the experimental conditions used in the 3D assays with DCF and SMX, their removal and energetic efficiencies are presented in Tables S10.1 and S10.2, in the supplementary material.

### 3.3.1. Application of the 3D electrochemical process to mono-component aqueous solutions

Experiments were carried out with different adsorbent masses (30.0, 300 and 600 mg of biochars TN 1–2 mm and < 75 μm, and 30.0 mg of SARATECH ® activated carbon, corresponding to adsorbent concentrations of 0.200, 2.00 and 4.00 g/L, respectively), which were selected according to the equilibrium adsorption studies (Section 3.1.1). Due to the high adsorption capacity of the activated carbon, for comparison with the biochars, only 30.0 mg was tested. The results obtained for mono-component aqueous solutions of DCF and SMX are presented in Fig. 1. The 2D process was also performed for comparison.

Regarding DCF (Fig. 1a), both biochars were found to have higher removal for 30.0 mg (0.200 g/L), than for 300 (2.00 g/L) and 600 mg (4.00 g/L). There are significant differences ($p < 0.05$) in the removal between 30.0, 300 and 600 mg of biochar TN 1–2 mm when compared to the 2D process. For SARATECH® activated carbon, only 30.0 mg was used and a maximum removal of 95% was observed. For biochar TN < 75 μm, removal percentages of 78.3%, 59.5% and 55.4% were obtained for 30.0, 300 and 600 mg, respectively. When using biochar TN 1–2 mm, removal percentages of 78.5%, 75.8% and 66.4% for 30.0, 300 and 600 mg, respectively, were observed.

Concerning SMX, the obtained results (Fig. 1b) show significant differences between all adsorbents and the 2D process after 7 and 10 min. Both biochars were found to have higher removal when using 30.0 mg (0.200 g/L) than for 300 (2.00 g/L) and 600 mg (4.00 g/L), as observed for DCF. There are no significant differences between them when using 30.0 mg.

Regarding SMX, no studies were found using a 3D electrochemical process for its removal. For DCF, Pourzamani et al. (2018) [16] demonstrated that the 3D process, using a Ti/RuO$_2$–TiO$_2$ electrode in the presence of multi-walled carbon nanotubes, had a higher removal percentage when compared to the 2D process, achieving a removal of 99.6% (initial pH 3.8, initial concentration 4 mg/L, current intensity 20 mA/cm^2 and adsorbent concentration 70 mg/L) after 85 min

In another study [44], a 3D electrochemical process with aluminium electrodes in the presence of granular activated carbon derived from walnut shells was used to remove DCF from water. The authors
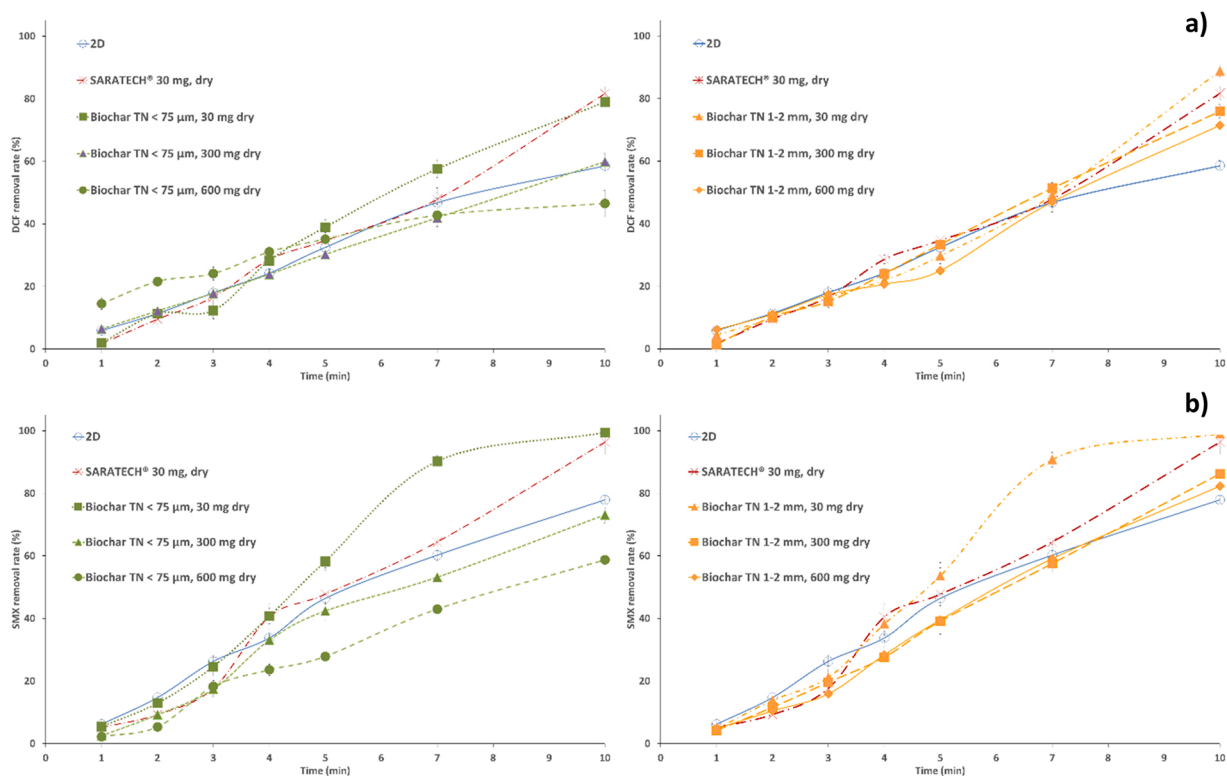
Fig. 1. Effect of the adsorbent quantity on a) DCF and b) SMX removal. Operational conditions: initial pH 7, NaCl 0.02 M, $C_0 = 10$ mg/L, inter-electrode distance $= 7.5$ cm.

concluded that the presence of activated carbon and the NaCl concentration were the factors with the highest influence on the removal efficiency, and that the NaCl concentration was the most significant factor affecting electrical energy consumption. The optimal conditions, concerning maximum removal efficiency and minimum electrical energy, were 4.36 g of granular activated carbon, 40 min contact time, and 0.075 M of NaCl, using a current density of 31.25 mA/cm². In the electrochemical cell, direct and indirect oxidative processes occurred, producing reactive species, such as hydroxyl radicals, besides the active chlorine species from NaCl, and also adsorption/electrosorption. The formation of these species and their reactions are the reasons for the high removal efficiency [44]. According to these authors, in the 3D processes the pharmaceutical compounds are mainly removed by direct oxidation and eventually are mineralised to CO_2 and H_2O by indirect oxidation [44].

The main disadvantages of the 2D process are the higher energy consumption and operational cost when compared with the 3D process. As shown in Fig. 1, the carbon-based adsorbents effectively increase the DCF and SMX removal percentage. The carbon particles are possibly charged due to the current applied in the electrochemical process, leading to electro-sorption/desorption of contaminants, resulting in the electrolytic degradation of the adsorbed pollutants. Furthermore, these particles can also act as catalysts to convert reactive oxygen species [44]. Also, a small amount of activated carbon can be used in the 3D process as a possible option to minimise the toxic and persistent inorganic by-products that may be formed during oxidation.

For both pharmaceuticals, an increase in the amount of biochar showed a decrease in the removal efficiency. This may be because an excess of adsorbent can eliminate reactive species available to oxidise DCF and SMX [16], and at the same time increase the electrosorption under the induced electric field which resulted in a short-circuiting current in the presence of additional adsorbent [53]. The removal and energy consumption presented in Tables S10.1 and S10.2 show that the best results were obtained for 30.0 mg of biochar TN < 75 μm and

biochar TN 1–2 mm, for both pharmaceuticals, also presenting lower energy consumption (for DCF, 309, 299 and 288 Wh/g, and for SMX, 204, 175 and 168 Wh/g, respectively for SARATECH® and biochars TN < 75 μm and 1–2 mm used dry). The energy consumption and the EE/O are presented in Figs. 2a) and 2b) for DCF and SMX respectively. Considering that the adsorption capacities of the biochars for DCF and SMX were very low (Section 3.1.1), the high increase in the removal efficiency observed in the 3D process may be attributed to the electrochemical oxidation of DCF and SMX enhanced by the microelectrode function of the adsorbent particles, rather than adsorption [54].

As can be seen in Fig. 2, the energy consumption in the 2D process was around 40% higher than that of the 3D process, with 30.0 mg of biochar TN 1–2 mm for DCF and 30% for SMX. This may be due to the increased electroactive surface area and high electro-activity of biochar particles [53] used in the 3D process. With the addition of 300 and 600 mg of biochar, the energy consumption increased from 288 Wh/g (30.0 mg) to 313 and 293 Wh/g, respectively for DCF, and from 168 Wh/g (corresponding to 30.0 mg) to 215 and 220 Wh/g, respectively for SMX. A similar trend was observed for the energy efficiency as EE/O increased from 2.26 kWh/m³ (for 30.0 mg) to 3.22 and 3.57 kWh/m³, respectively for DCF, and from 1.02 kWh/m³ (for 30.0 mg) to 2.32 and 2.60 kWh/m³, respectively for SMX. Therefore, 30.0 mg of biochar TN 1–2 mm was considered more adequate for the subsequent studies.

To assess the possible effect of adsorbent saturation, as a consequence of a continuous and long-term process, the adsorbents were saturated with a 10 mg/L mono-component solution overnight [55]. The masses used were 30.0 mg of each adsorbent (0.200 g/L), considering that this condition showed the best results for the 3D process. The results obtained are shown in Fig. 3.

Significant differences were observed between dry and saturated material (Fig. 3) ($p < 0.05$). Comparing dry and saturated SARATECH® activated carbon with the 2D process, there are only significant differences at the beginning of the process and after 10 min for DCF, while for
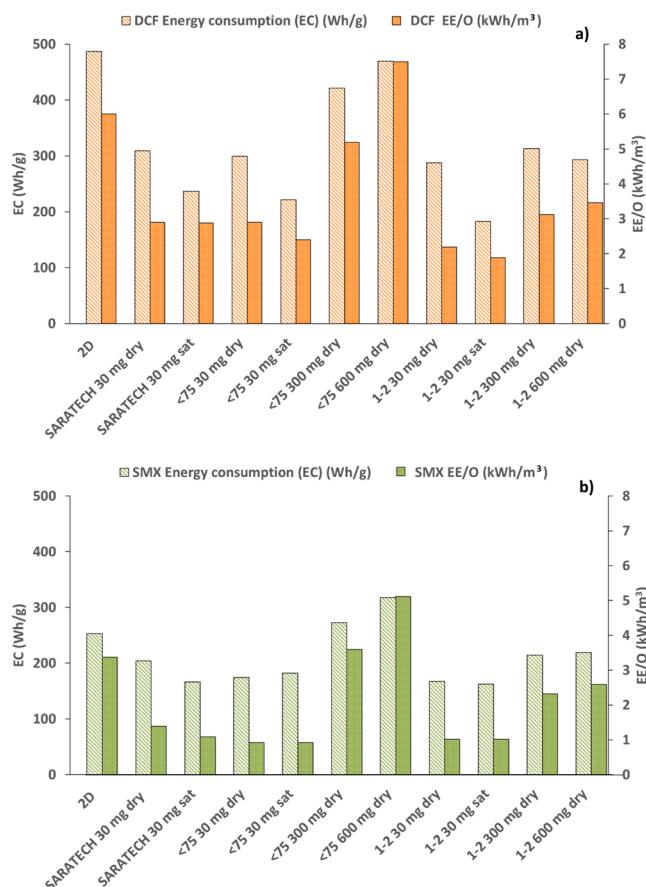
Fig. 2. Effect of the adsorbent quantity and saturation on the energy consumption and EE/O for a) DCF and b) SMX removal. Operational conditions: initial pH 7, NaCl 0.02 M, $C_0 = 10$ mg/L, inter-electrode distance = 7.5 cm.

SMX the results are always significantly different. Regarding the biochar TN 1–2 mm (Fig. 3), the differences are significant during the entire process for SMX and DCF, except for the 10th minute. However, there are always significant differences when compared to the 2D process. Therefore, the use of saturated adsorbent does not reduce the removal of DCF and SMX.

The superior removal percentage of SMX and DCF in the 3D system compared to the 2D system reflects the high electrochemical functionality of the tested adsorbents, particularly when saturated [56]. Considering the low biochar adsorption capacity of SMX and DCF (see Table S5.1), it suggests that the biochar participates in the electrochemical reaction rather than in the adsorption process. The wettability of the carbon material is of considerable importance, it improves the solid liquid contact and therefore allows a more accessible admittance of the species into the narrowest pores improving the global electrochemical performance [57,58].

This behaviour was also verified by Zhan et al. (2019) [55] using activated carbon to remove pharmaceuticals in an aqueous solution through a 3D electrochemical process. Because the adsorbents had been pre-saturated in the pharmaceutical solution before it was used in the 3D process, these authors suggested that adsorption has a minor role in pharmaceutical removal. Instead, the increase in pharmaceutical removal is more likely caused by the enhanced radical production from the adsorbent-catalyzed oxidative reactions.

3.3.2. Application of the 3D electrochemical process to bi-component aqueous solutions

In Fig. 4 is presented the simultaneous removal of DCF and SMX from an aqueous solution using the optimized conditions for the 3D process

discussed previously.

The removal of DCF and SMX from an aqueous solution with both pharmaceuticals when the optimized conditions were used shows that, after 10 min, 98% of SMX and 83% of DCF were removed.

3.3.3. Application of the 3D-electrochemical process to a bi-component treated wastewater sample (fortified concentrations)

The simultaneous removal of DCF and SMX from fortified treated wastewater with a mixture of 10 mg/L of each pharmaceutical and using biochar TN 1–2 mm (30.0 mg) as the particle electrode is presented in Fig. 5. A brief characterisation of the wastewater was performed (Section 2.5) before the addition of NaCl. For a contact time of 10 min, it was observed that without the addition of NaCl less than 5% of the compounds were removed from the solution (Table S10.3), while with 0.02 M NaCl, 28.9% and 20.7% of SMX and DCF were removed from the wastewater (Fig. 5), respectively. Also, the energy consumption decreased from 799 to 544 Wh/g for SMX and from 5930 to 971 Wh/g for DCF with and without NaCl, respectively. The experimental conditions, removal and energy consumption to remove a mixture of DCF and SMX from aqueous solution and fortified wastewater are presented in Table S10.3.

The analysis of Fig. 5 shows that the use of biochar TN 1–2 mm as the particulate electrode allows higher removal percentages for DCF and SMX when compared with SARATECH® activated carbon. There are significant differences between the biochar and the activated carbon, and between the 3D process using the biochar and the 2D process, after 20 min for both pharmaceuticals ($p < 0.05$).

The analysis of Figs. 4 and 5 shows that removing DCF and SMX from the aqueous bi-component mixture is much faster than removing them from treated wastewater. After 30 min, around 50% of DCF was removed from the wastewater while in the ultrapure water 97% was removed after this time. For SMX, after 30 min, 77% was removed. Therefore, the energy consumption for removing the pharmaceuticals from the wastewater is higher with lower energy efficiency than for the aqueous solution using the conditions described in Table S10.3 as can be seen in Fig. 6.

The observed variations in DCF and SMX removal between the different water matrices are most likely caused by competing inorganic and organic compounds, present in the complex treated wastewater matrix, for the oxidant species formed during the 3D oxidation process [59]. In the case of deionised water, there is no competition between target molecules and other inorganic and organic components, leading to maximum efficiency removal. Heim et al. (2020) [59] reported the efficiency of using BDD electrodes in an electrochemical advanced oxidation process to remove DCF from different water matrices, including wastewater effluents. These authors concluded that the additional presence of organic compounds in the wastewater effluent prolonged the electrochemical oxidation process until the complete removal of DCF [59].

Regarding SMX, Hai et al. (2020) [43] prepared simulated wastewater by adding different amounts of humic acid (0, 10, 20, 40 mg/L), and analysed its effects on SMX degradation in a BDD-STS system. It was observed that the addition of humic acids inhibited the electrochemical degradation of SMX. Without humic acids, SMX was completely removed after 3 h, while in the presence of these acids, 30% SMX was still in the solution. Thus, the matrix effect has a clear impact on removal rates. Furthermore, it is also important to evaluate the interaction between the contaminants, as wastewaters are complex matrixes with several pharmaceuticals present in mixture. Brice et al. (2022) [60] studied both effects in the photo-oxidation of three pharmaceuticals in wastewaters, confirming the effect of both matrix and cocktail effect and highlighting the prevalence of matrix impact.
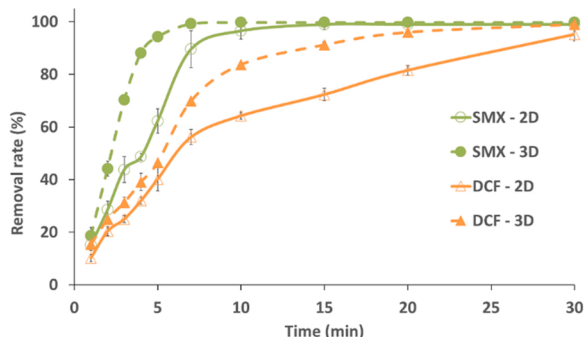
3.3.4. Application of 2D and 3D electrochemical process to a treated wastewater sample (real concentrations)

The analysis of the WWTP effluent sample (without fortification)
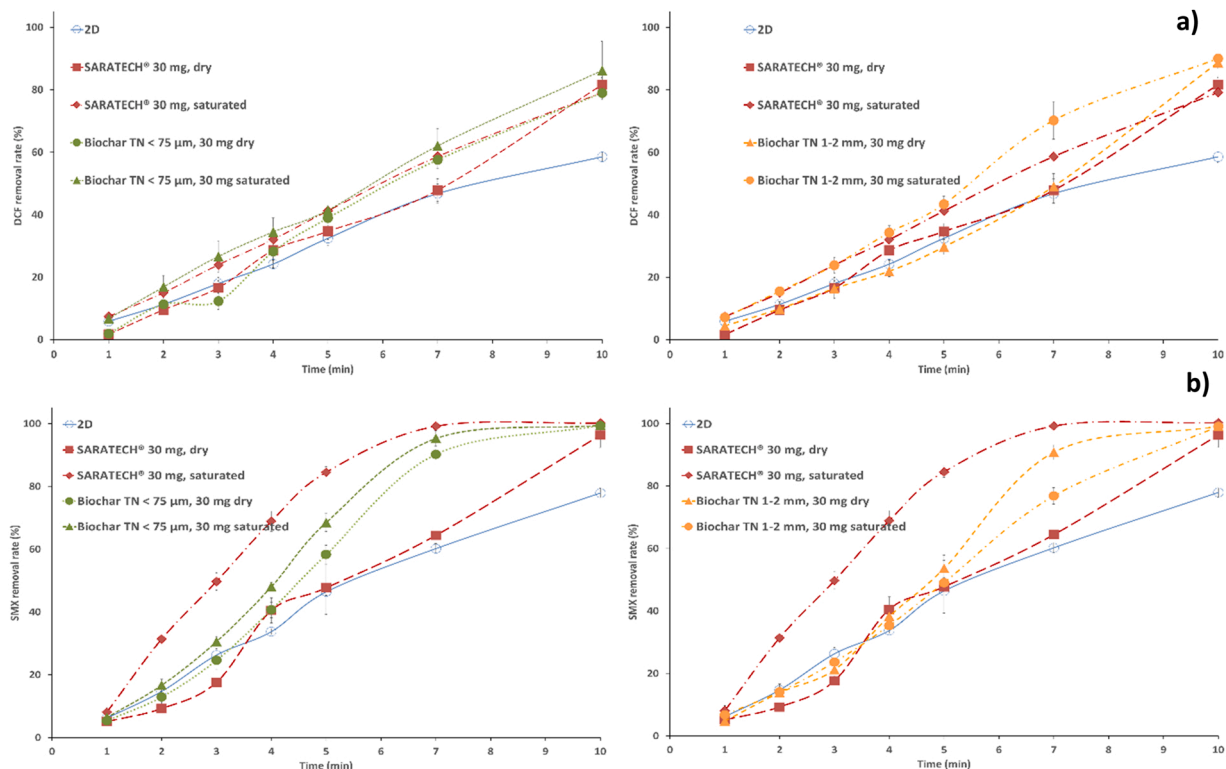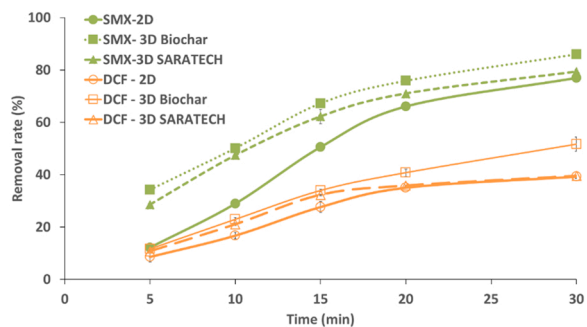
Fig. 3. Effect of the pre-saturation of adsorbents for a) DCF and b) SMX. Operational conditions: initial pH = 7, NaCl = 0.02 M, C_0 = 10 mg/L, inter-electrode distance = 7.5 cm, adsorbent concentration 0.200 g/L.

Fig. 4. Comparison of the simultaneous removal of DCF and SMX from aqueous solution (AS). Operational conditions: initial pH = 7, NaCl = 0.02 M, C_0 = 10 mg/L, interelectrode distance = 7.5 cm, saturated adsorbent 0.200 g/L, current density 7 mA/cm².

Fig. 5. Comparison of the simultaneous removal of DCF and SMX from fortified wastewater. Operational conditions: initial pH = 7, NaCl = 0.02 M, C_0 = 10 mg/L, inter-electrode distance = 7.5 cm, saturated adsorbent 0.200 g/L, current density 7 mA/cm².

revealed a diclofenac concentration of 1084 ng/L, but sulfamethoxazole was not detected (below 12.0 ng/L). For the same experimental conditions of the previous experiments (30 min contact time), after the application of both the 2D and 3D electrochemical processes the diclofenac was not detected (below 2.5 and 0.94 ng/L, respectively) (see S2.3). As was expected, because this concentration was much lower than the used in the fortified samples (Section 3.3.3).

4. Conclusions

The results of the studies of adsorption and 2D electrochemical processes were used to develop a 3D electrochemical process for DCF and SMX removal from wastewaters. The main findings indicate that adsorption is not the most relevant contribution to the 3D electrochemcial process' removal efficiency. This allows the use of materials with lower specific surface areas than activated carbon, such as a

biochar from vineyard pruning wastes from Touriga Nacional, which may be considered a more economic and sustainable alternative. From the study of the 2D process was concluded that it is necessary to use an electrolyte, such as NaCl, to improve the removal and energy efficiencies.

In the 3D process, the use of a Mixed Metal Oxide anode (titanium-coated with RuO_2-IrO_2-TiO_2), a stainless steel cathode, and a biochar particulate electrode (TN 1–2 mm), removed 90% of both pharmaceuticals, after 10 min, from mono-component aqueous solutions (initial pharmaceutical concentrations of 10 mg/L, 30.0 mg of Biochar TN 1–2 mm, an inter-electrode distance of 7.5 cm, a pH value of 7, and a current density of 7 mA/cm²). Under the same conditions, the complete removal of both pharmaceuticals from an aqueous bi-component solution was achieved after 30 min. Lower removal efficiencies were observed (after 30 min) when both pharmaceuticals were added at the same concentrations to a wastewater treatment plant effluent; 49% for
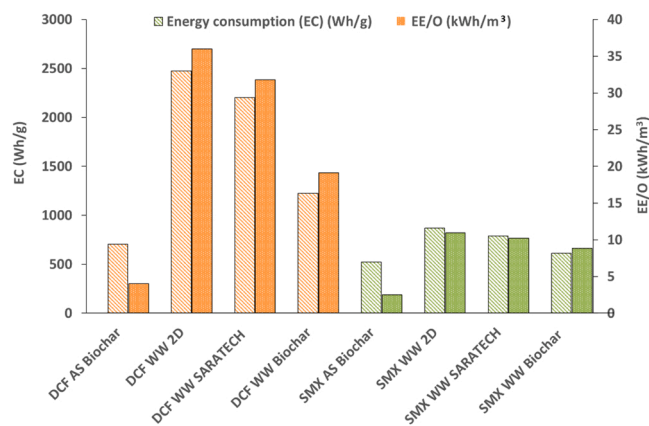
Fig. 6. Effect of the adsorbent quantity and saturation on the energy consumption and EE/O for DCF and SMX removal in wastewater. Operational conditions: initial pH 7, NaCl 0.02 M, $C_0 = 10$ mg/L, inter-electrode distance = 7.5 cm.

DCF and 86% for SMX, with energy consumptions of 1224 and 613 Wh/g and an electric energy per order of 19.1 and 8.77 kWh/m^3, respectively. When real effluent concentrations were used, without the addition of pharmaceuticals, they were completely removed.

This work could be a valuable contribution to the application of the 3D process as tertiary treatment in urban wastewater treatment plants and also demonstrates the viability of using a biochar as particulate electrode, being a potential alternative of biomass waste valorisation.

CRediT authorship contribution statement

Conceptualization, **Sónia Figueiredo, Olga Freitas, Hendrikus Nouws and Cristina Delerue-Matos**; Formal analysis, **Cristina Soares, Luísa Correia-Sá; Paula Paíga; Carlos Barbosa, Paula Remor and Manuela Moreira**; Funding acquisition, **António J. Rodrigues, Carlos M. Oliveira and Cristina Delerue-Matos**; Investigation, **Cristina Soares, Luísa Correia-Sá, Olga Matos Freitas and Sónia Figueiredo**; Methodology, **Olga M. Freitas, Henri P. A. Nouws, Sónia A. Figueiredo, Cristina Delerue-Matos**; Project administration, **António J. Rodrigues, Carlos M. Oliveira, Cristina Delerue-Matos**; Resources, **António J. Rodrigues, Carlos M. Oliveira, Cristina Delerue-Matos**; Supervision, **Olga M. Freitas, Henri P. A. Nouws, Sónia A. Figueiredo, Cristina Delerue-Matos**; Validation, **Olga M. Freitas, Manuela M. Moreira, Henri P. A. Nouws, Manuela Correia, Amir Ghanbari, António J. Rodrigues, Carlos M. Oliveira, Sónia A. Figueiredo, Cristina Delerue-Matos**; Writing – original draft, **Cristina Soares, Luísa Correia-Sá; Paula Paíga**; Writing – review & editing, **Olga M. Freitas, Manuela M. Moreira, Henri P. A. Nouws, Manuela Correia, Amir Ghanbari, António J. Rodrigues, Carlos M. Oliveira, Sónia A. Figueiredo, Cristina Delerue-Matos**.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.108419.

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