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Removal of Diclofenac in Wastewater Using Biosorption and Advanced Oxidation Techniques: Comparative Results

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Abstract: Wastewater treatment is a topic of primary interest with regard to the environment. Diclofenac is a common analgesic drug often detected in wastewater and surface water. In this paper, three commonly available agrifood waste types (artichoke agrowaste, olive-mill residues, and citrus waste) were reused as sorbents of diclofenac present in aqueous effluents. Citrus-waste biomass for a dose of $2 \text{ g} \cdot \text{L}^{-1}$ allowed for removing 99.7% of diclofenac present in the initial sample, with a sorption capacity of 9 mg of adsorbed diclofenac for each gram of used biomass. The respective values obtained for olive-mill residues and artichoke agrowaste were around $4.15 \text{ mg} \cdot \text{g}^{-1}$. Advanced oxidation processes with $\text{UV}/\text{H}_2\text{O}_2$ and UV/HOCl were shown to be effective treatments for the elimination of diclofenac. A significant reduction in chemical oxygen demand (COD; 40–48%) was also achieved with these oxidation treatments. Despite the lesser effectiveness of the sorption process, it should be considered that the reuse and valorization of these lignocellulosic agrifood residues would facilitate the fostering of a circular economy.

Keywords: agrowaste biomass; biosorption; diclofenac removal; advanced oxidation treatments; low-cost sorbents

1. Introduction

Water is a renewable but limited natural resource, which forces us to manage it, especially in arid and semiarid areas where water resources are limited. The presence of some pollutants can jeopardize water recovery, and the reuse of urban and industrial effluents [1]. In addition to pollution from municipal discharges, water bodies are also contaminated by industry, mining, and pollution from agrochemicals used on irrigated land, which in many cases are discharged directly into lakes and rivers without prior treatment [2].

The reuse of urban and industrial wastewater with some pollutants can contribute to soil contamination, as well as its passage into the tissue of cultivated plants. This can produce adverse effects on the ecosystem [3–6].

While the international scientific community continues to make considerable efforts to minimize or alleviate the problem of what we may call traditional pollutants (heavy metals, organic matter, inorganic nutrients, etc.), other environmental pollutants, called emerging pollutants (ECs), are of growing concern [7] and are leading us to adapt our strategies to respond to their threats [8,9].

Aqueous effluents that arrive at urban wastewater-treatment plants show a complex composition associated with current human and industrial development. Therefore, the presence of certain pollutants can, in many cases, interfere with the proper functioning of biological wastewater-treatment systems. Emerging contaminants are considered among these pollutants [9]. Emerging contaminants

are compounds of different origin and chemical nature of which the presence in the environment has gone largely unnoticed [10].

The lack of international monitoring programs for ECs makes it impossible to fully know their effects, problems, and behavior from an ecotoxicological point of view [2]. They can be a danger to the environment and human health [11,12]. Another particularity of this type of pollutant is that, due to its high production and consumption, and the constant and continuous introduction of these pollutants into the environment, they do not need to be persistent to cause negative effects.

Emerging contaminants can be classified as pharmaceutical and personal-care products, plasticizers, food additives, wood preservatives, contrast media, detergents, surfactants, fire retardants, biocides, hormones, and some disinfection byproducts. Advances in analytical technologies have helped to identify this group of contaminants [13,14].

These compounds have high transformation/disposal rates that can compensate for their continued introduction into the environment. For this reason, it is necessary to raise awareness of their origin and transformation, and the effects that this new generation of pollutants can have in order to propose modifications or improvements in water-treatment mechanisms. Some authors suggested the use of toxicity tests with chemical analysis to evaluate the efficiency of treatment methods [15–18].

The ongoing processing of aqueous effluents in conventional wastewater-treatment systems does not provide an adequate approach for the removal of emerging contaminants. These can arrive in their original form and/or be metabolized, making it difficult to operate biological wastewater treatment, sludge treatment, and the subsequent reuse of wastewater; there is also a lack of knowledge about the possible impact of these pollutants on the environment [19]. In many cases, products resulting from the transformation of the original emerging contaminants produce compounds that turn out to be more toxic than the original ones are [20].

Diclofenac (2-(2,6-dichloroanilino) phenylacetic acid) is one of the best-selling nonsteroidal anti-inflammatory drugs [21]. The high consumption level of this compound means that it is one of the most detected pharmaceuticals in aqueous effluents, and according to reported data, the measured values of diclofenac in municipal wastewater can be up to $7.1 \mu\text{g}\cdot\text{L}^{-1}$ [22,23]. A distinctive feature of diclofenac is that it undergoes low biodegradability and high persistence in wastewater-treatment plants, leading to its bioaccumulation in surface waters, sediments, and sludges [24,25]. Therefore, it is necessary to implement specific treatments to reduce or eliminate its presence in effluents.

Different sorption studies of diclofenac are reported in the literature. The highest bioremoval efficiencies were obtained with carbon nanotubes [26], clays [27], and biochars [28] as sorbents. Raw lignocellulosic biomass was also used as a low-cost biosorbent, but the achieved efficiency was not as high as that with previous sorbents [29,30]. Despite this, biosorption has lately been presented as a very interesting technology, in line with the concept of the circular economy [31,32]. Efficient biowaste management is among the most important challenges in agrifood industries. Suggested uses for these lignocellulosic residues include their utilization as sorbents of pollutants in aqueous effluents [33–35] since they present very interesting physicochemical properties, such as their high surface area and the presence of a variety of functional groups that facilitate the sorption process [36–38]. Bioadsorptive techniques are the best ecofriendly solutions for removing contaminants because they are economical, efficient, highly selective on pollutants, and easily operable.

The most commonly used treatments for the removal of emerging contaminants, such as diclofenac, are advanced oxidation processes [39–43], which utilize free radical reactions to directly degrade chemical contaminants as an alternative to traditional treatments. For these oxidative treatments, it is necessary to carry out research studies that examine what the most appropriate combination of oxidizing reagents is to degrade a specific pollutant.

The main objective of this work was to carry out a comparative study of diclofenac elimination in aqueous effluents through biosorption with agrifood residues and through different advanced oxidation techniques (ultraviolet radiation (UV), sodium hypochlorite, and combinations of ultraviolet radiation with hypochlorite and with hydrogen peroxide).

2. Materials and Methods

2.1. Preparation and Characterization of Agrowaste Biomass

In preliminary studies, different agricultural wastes residues were processed and examined for their ability to remove diclofenac from a test solution. Of these, the three most interesting agrifood waste types that are abundant in the Murcia region (Spain) were chosen to be investigated in this study: artichoke agrowaste, olive-mill residues, and citrus waste from agrifood industries. Biomass samples were washed with distilled water and dried at 70 °C for 24 h before being ground and passed through a sieve with a number 18 mesh (1 mm). The different surface morphologies of each biomass were explored, and a qualitative determination of each was made using a field-emission scanning electron microscope and an energy-dispersive X-ray analyzer (SEM) (Hitachi S-3500N). FTIR measurements of the sorbents were performed in the range of 4000 to 400 cm⁻¹ in a Thermo Nicolet 5700 (Karlsruhe, Germany). Moreover, the pH point of zero charge (pH_{ZPC}) was determined by the mass-titration method [44].

2.2. Preparation of Diclofenac Solutions

A diclofenac stock solution (1 g·L⁻¹) was prepared using diclofenac sodium (C₁₄H₁₀Cl₂NNaO₂, ≥99%; Sigma-Aldrich, Madrid, Spain) in deionized water. The working solution (20 L) was achieved by diluting the stock solution in treated and filtered wastewater from a wastewater-treatment plant. The pH value was adjusted to 6.6 with a 0.1 mol·L⁻¹ HCl or 0.1 mol·L⁻¹ NaOH solution using a Metrohm 654 pH meter with a pH combination electrode. All chemicals were of analytical grade. The analytical characterization of the working solution was performed by American Public Health Association (APHA) methods [45].

2.3. Batch-Biomass Tests

Batch-biosorption experiments were performed at 25 °C under stirring in a reciprocal contact agitator with 100 mL of the diclofenac working solution at a fixed concentration ($C_0 = 37.6 \text{ mg} \cdot \text{L}^{-1}$) and a known amount of sorbent for 24 h in a conical flask at a constant stirring speed (150 rpm). Lastly, the solutions were filtered and quantified obtaining the final concentration (C_e). The initial (C_0) and final (C_e) concentrations were quantified by high-performance liquid chromatography (HPLC).

The amounts of diclofenac adsorbed at equilibrium (q_e), also called diclofenac removal efficiency and expressed as mg diclofenac/g dry biomass, were determined by mass-balance equation (Equation (1)) on the basis of values of diclofenac concentration in the solution at the beginning (C_0) and end (C_e) of the test:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m}, \quad (1)$$

where V is the solution volume (L) and m the sorbent dry weight (g).

The percentage of diclofenac elimination in each case was calculated by Equation (2):

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100, \quad (2)$$

where C_0 is the initial concentration (mg·L⁻¹) and C_e is the equilibrium concentration (mg·L⁻¹) of diclofenac.

2.4. Diclofenac Determination

Diclofenac concentration in the water samples was determined by high-performance liquid chromatography (HPLC). A Waters modular liquid chromatography system (Waters, Milford, MA, USA) equipped with two M510 pumps, a 717 plus autosampler, and an M996 photodiode array detector (PDA) was used. HPLC was run by the data system of the Millennium 2010 Chromatography Manager.

An Atlantis C18 5 μm , 25 cm \times 4.6 mm i.d. (Waters) column was used. Elution was performed using a gradient between 175 mM phosphoric acid in water and 175 mM acetic acid in acetonitrile as the mobile phase. Flow rate was 0.6 mL/min. Samples, before being analyzed, were filtered using a 0.45 μm pore size cellulose acetate membrane, and the filtrate was analyzed for HPLC. Diclofenac was monitored at 270 nm. The retention time of diclofenac was about 6.4 min.

2.5. Advanced Oxidation Treatments

2.5.1. Sodium Hypochlorite

Treatment with sodium hypochlorite was performed with 1000 mL of filtered diclofenac solution. Four different amounts of available chlorine, namely, 1.0, 2.0, 3.0, and 4.0 mL of a 5% (*w/v*) sodium hypochlorite solution (Panreac, Barcelona, Spain) were added to each sample. Experiments were carried out in sealed glass bottles. They were incubated for 2 h until the moment of their quantification in a dark isothermal chamber at 20 $^{\circ}\text{C}$, with slow agitation. Lastly, samples were filtered and analyzed by HPLC.

2.5.2. UV Light Treatments

UV radiation was applied using an 8 watt low-pressure UV lamp (UV-C 8 watt Strahler–Messner, Kalletal, Germany), with a flow range of 0.5 to 1.1 L \cdot h $^{-1}$ and a wavelength of 254 nm. The facility was designed to be used with 500 mL of a sample, irradiated for short periods of time of 2, 5, 10, and 15 min. According to these irradiation durations, the provided doses were 15, 37, 73, and 110 mJ \cdot cm $^{-2}$, respectively. Before each treatment, the lamp was cleaned with deionized water. After irradiation, samples were filtered with a 0.45 μm filter and analyzed by HPLC.

2.5.3. UV Radiation Combined with Sodium Hypochlorite (UV/HOCl) and Hydrogen Peroxide (UV/H₂O₂)

UV/HOCl and UV/H₂O₂ assays were conducted as batch experiments using a concentration of 5 mg \cdot L $^{-1}$ sodium hypochlorite and 5 mg \cdot L $^{-1}$ of hydrogen peroxide, respectively, which were added into the initial sample and subjected to different UV exposure times (2, 5, 10, and 15 min) before filtration and analysis of diclofenac concentration was performed by HPLC.

2.6. Chemical Oxygen Demand

Chemical oxygen demand (COD) was determined using the methods described in APHA [45]. For COD measurements, a Spectroquant Nova 30 spectrophotometer (Merck, Darmstadt, Germany) was used.

3. Results and Discussion

3.1. Characterization of Biomass Samples

The surface characteristics of the different biomass samples used in diclofenac bioadsorption studies were investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), as shown in Figures 1–3. SEM is considered to be one of the most widely used tools in the scientific field for studying the surface characteristics of biomass used as biosorbent [46]. In the different micrographs that were made in the SEM, important differences in the surface characteristics of the different studied agrifood waste types were observed, presenting a majority composition of carbon and oxygen in all cases.

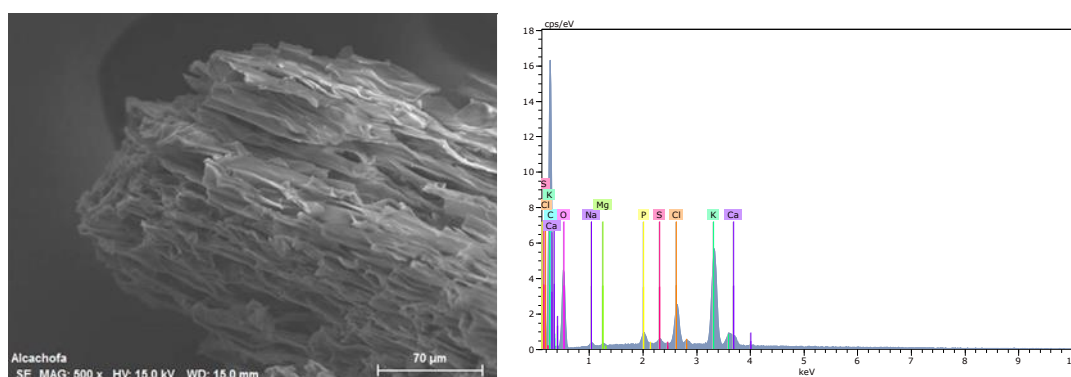


Figure 1. SEM image and EDS analysis of artichoke-agrowaste biomass.

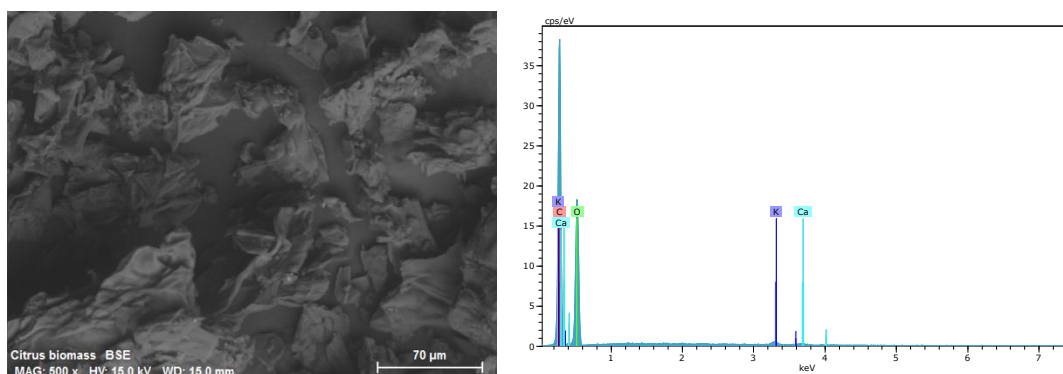


Figure 2. SEM image and EDS analysis of citrus-waste biomass.

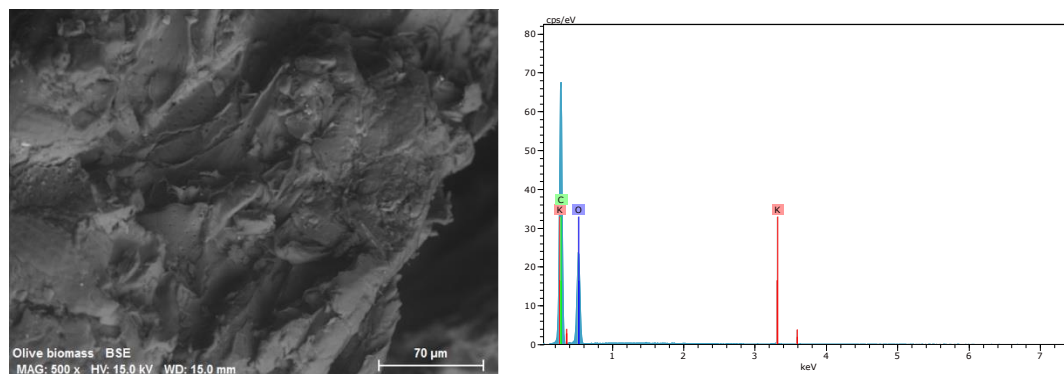


Figure 3. SEM image and EDS analysis of olive-mill residue biomass.

Figure 1 shows that artichoke biomass had filamentous structures made up of fiber cells that were longitudinally aligned. This fibrous structure provides consistency, resistance, and a large surface area [47] that, together with the small channels, allows for the rapid movement of fluids through the fibers, increasing the possibility of retaining diclofenac molecules. SEM analysis also showed that it was a rough surface, with the presence of holes of irregular shape and size [47] that could improve the retention of diclofenac.

Citrus-waste biomass (Figure 2) presented an irregular surface, but with a much more compact appearance and with fewer cavities than in the previous case, although with cracks that provided a large surface for the retention of diclofenac. Olive-mill residues (Figure 3) also presented an irregular surface with a fairly compact appearance, but with few cavities. In all cases, the presence of cavities of irregular shape and dimensions would enhance the fixation of contaminants to be retained.

FTIR analysis allowed for inferring the structure of the sorbents on the basis of the locations and shapes of the bands in the spectra (Figure 4). The three sorbents showed a broad band at $3600\text{--}3100\text{ cm}^{-1}$

that was assigned to $-OH$ stretching vibrations of hydroxyl and carboxyl groups. A $-CH$ aliphatic stretching vibration band was also observed at $2900\text{--}2850\text{ cm}^{-1}$ in all sorbents. Around 1630 cm^{-1} , a band attributed to $C=O$ stretching vibrations and typical skeletal vibrations of aromatic rings was presented. In the region of $1030\text{--}1000\text{ cm}^{-1}$, a broad band, an indication of $C-O$ and $C=C$ vibrational stretching, was revealed. These are, in fact, typical FTIR spectra, corresponding to nonmodified plant biomass samples, where the lignocellulosic constituents are particularly outstanding [32,47–49].

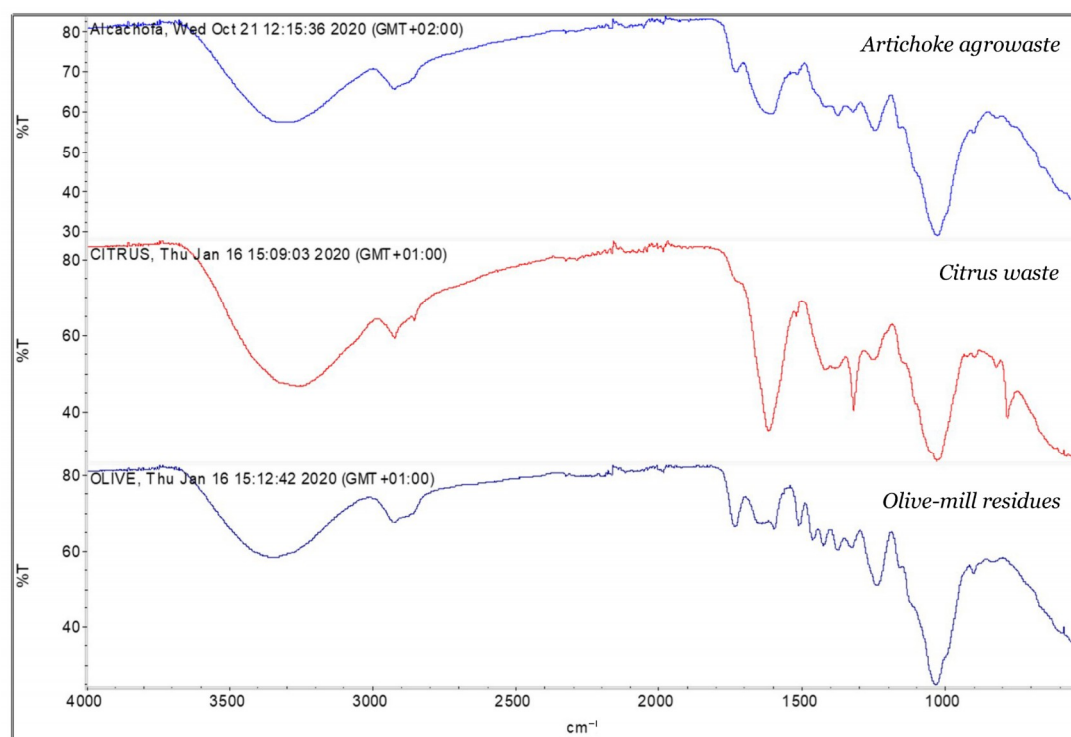


Figure 4. FTIR spectra between 4000 and 400 cm^{-1} for sorbent samples.

3.2. Diclofenac Biosorption

Table 1 shows the characterization of the working water prepared from diclofenac stock solution and filtered effluent from a treatment plant. The initial concentration (C_0) of diclofenac for the different experiments was $37.6\text{ mg}\cdot\text{L}^{-1}$ and an initial COD value of $282\text{ mg O}_2\cdot\text{L}^{-1}$.

Table 1. Initial composition of working solution. COD, chemical oxygen demand.

Parameter	Value
pH	6.6 ± 0.2 *
Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	12.5 ± 2.5
TSS (mg/L)	98.2 ± 8.6
Turbidity (NTU)	4.7 ± 0.3
NO_3^- ($\text{mg}\cdot\text{L}^{-1}$)	16.8 ± 2.7
PO_4^{3-} ($\text{mg}\cdot\text{L}^{-1}$)	5.6 ± 1.1
BOD ($\text{mg O}_2\cdot\text{L}^{-1}$)	113.3 ± 10.2
COD ($\text{mg O}_2\cdot\text{L}^{-1}$)	282.0 ± 15.0
Diclofenac initial ($\text{mg}\cdot\text{L}^{-1}$)	37.6

* mean \pm SD of 3 determinations.

The sorption capacities and percentages of diclofenac removal in the experiments carried out for the different used sorbents and doses (Table 2) revealed that citrus-waste biomass was the most effective. Citrus residues, with a zero point of charge of 4.2, reduced the pH of the solution during the

sorption process to 5.7 by the end of the experiment. These pH reductions were less pronounced in the olive-mill-residue ($\text{pH}_{\text{ZPC}} = 5.4$) and in the artichoke-agrowaste ($\text{pH}_{\text{ZPC}} = 4.8$) sorption tests, of which the final pH values were 6.4 and 6.1, respectively. In all cases, the modifications in pH were very slight, hardly affecting the solubility of the adsorbate and sorption-capacity values. The biomass of artichoke agrowaste showed the least capacity to retain diclofenac. In the case of citrus waste, for a dose of 2 g/L, all the diclofenac is retained, obtaining a sorption capacity (q_e) of 9 $\text{mg}\cdot\text{g}^{-1}$. Olive-mill residues had intermediate and very similar retention values regardless of the dose used in the experiments.

Table 2. Elimination of diclofenac for different biomass samples.

Biomass	Sorbent Dosage ($\text{g}\cdot\text{L}^{-1}$)	Removal %	q_e ($\text{mg}\cdot\text{g}^{-1}$)
Artichoke agrowaste	1	18.7 ± 2.4 *	3.9 ± 0.5
	2	19.9 ± 3.1	4.2 ± 0.4
Olive-mill residues	1	46.4 ± 4.4	4.2 ± 0.6
	2	46.3 ± 5.8	4.2 ± 0.8
Citrus-waste	1	87.1 ± 5.7	7.8 ± 1.1
	2	99.7 ± 0.5	9.0 ± 0.3

* mean \pm SD of 3 determinations.

The results of this study revealed that the reuse of raw lignocellulosic biomass from agrifood waste for the sorption of diclofenac may be an efficient and common method of wastewater treatment. The sorption capacities of diclofenac obtained in this study were lower than those reported for microalgae biomass (20–28 $\text{mg}\cdot\text{g}^{-1}$) [29] and grape bagasse (24 $\text{mg}\cdot\text{g}^{-1}$) [49], but comparable for that shown with activated carbon from olive stones (11 $\text{mg}\cdot\text{g}^{-1}$) [50]. In the present investigation, the agrifood waste used as sorbent was not previously modified or subjected to any thermal treatment. The obtained results in the present investigation reveal that this is a new line of research that is worth further exploring, and it may be of interest to test some cost-effective activation mechanism that enhances the bioadsorptive capacity of waste to specific contaminants. In this context, future studies will be made in application in real systems, where fixed-bed citrus-waste adsorbers can be implemented for the treatment of wastewater with diclofenac.

3.3. Advanced Oxidation Treatments

As summarized in Table 3, when the working solution ($C_0 = 37.6 \text{ mg}\cdot\text{L}^{-1}$) was exposed to different exposure times of UV radiation ranging from 2 to 15 min, significant reductions in the initial diclofenac concentration were achieved, ranging from 9.78% removal for 2 min of exposure and 88.49% removal for 15 min of exposure, without being able to achieve total removal. A significant reduction in COD values was also achieved, in a similar way to that in other reported investigations [51].

Table 3. Treatment with ultraviolet (UV) radiation.

Contact Time (min)	Diclofenac ($\text{mg}\cdot\text{L}^{-1}$)	Removed Diclofenac %	COD Reduction %
2	33.9 ± 2.8 *	9.8 ± 2.4	44.3 ± 3.6
5	16.6 ± 2.1	55.9 ± 3.9	62.1 ± 3.5
10	6.1 ± 1.1	83.8 ± 4.6	62.4 ± 4.1
15	4.3 ± 0.9	88.5 ± 3.8	66.3 ± 3.9

* mean \pm SD of 3 determinations.

In the treatment with sodium hypochlorite and a contact time of 2 h (Table 4), for a dose of $4 \text{ mg}\cdot\text{L}^{-1}$, all diclofenac present in the starting sample was eliminated. As the dose of hypochlorite was increased, greater elimination was achieved. The reduction in COD was also quite significant.

Table 4. Treatment with sodium hypochlorite (contact time 2 h).

Hypochlorite Concentration ($\text{mg}\cdot\text{L}^{-1}$)	Diclofenac ($\text{mg}\cdot\text{L}^{-1}$)	Removed Diclofenac %	COD Reduction %
1	14.4 ± 3.3 *	61.7 ± 4.7	24.1 ± 2.3
2	4.4 ± 1.2	88.4 ± 5.1	38.3 ± 2.8
3	3.3 ± 0.9	91.3 ± 4.4	44.0 ± 2.6
4	n.d. †	100	44.7 ± 1.8

* mean \pm SD of 3 determinations; † not detected.

In the treatment that combined UV radiation with the addition of sodium hypochlorite (Table 5), practically all the diclofenac (93.59%) was eliminated for a radiation time of 10 min. When exposure time was increased (15 min), it was possible to eliminate it completely. In addition, the unreacted chlorine in this process provided residual protection for water reuse purposes [52]. Comparable reductions in COD were achieved as those with previous treatments. For the treatment in which UV radiation was combined with hydrogen peroxide (Table 6), the initial diclofenac was eliminated for all treatments. For an exposure time of 2 min of UV radiation, 99.20% of the initial diclofenac was degraded. The achieved elimination of COD was quite comparable in all performed treatments.

Table 5. Ultraviolet radiation treatment combined with sodium hypochlorite ($5 \text{ mg}\cdot\text{L}^{-1}$).

Contact Time (min)	Diclofenac ($\text{mg}\cdot\text{L}^{-1}$)	Removed Diclofenac %	COD Reduction %
2	29.1 ± 2.2 *	22.6 ± 2.8	14.2 ± 1.9
5	13.5 ± 1.8	64.2 ± 3.1	22.0 ± 2.4
10	2.4 ± 0.5	93.6 ± 4.8	45.0 ± 3.8
15	n.d. †	100	47.9 ± 3.4

* mean \pm SD of 3 determinations; † not detected.

Table 6. UV radiation treatment combined with H_2O_2 ($5 \text{ mg}\cdot\text{L}^{-1}$).

Contact Time (min)	Diclofenac ($\text{mg}\cdot\text{L}^{-1}$)	Removed Diclofenac %	COD Reduction %
2	0.3 ± 0.1 *	99.2 ± 4.4	23.4 ± 1.7
5	n.d. †	100	25.9 ± 2.3
10	n.d.	100	36.5 ± 2.0
15	n.d.	100	40.1 ± 3.1

* mean \pm SD of 3 determinations; † not detected.

It is scientifically accepted that advanced oxidation processes are highly effective novel methods that accelerate the oxidation and the degradation of a wide range of organic and inorganic pollutants that are resistant to conventional treatment methods [53]. In our experiments, diclofenac was 88% by UV-C degraded irradiation; when the wastewater was treated for a time as short as 15 min, this result verified that this compound absorbs UV irradiation well at 254 nm and can be easily photolyzed [54]. When UV-C irradiation treatment was combined with $5 \text{ mg}\cdot\text{L}^{-1}$ of sodium hypochlorite, the degradation of diclofenac was increased to 100%. Nevertheless, UV/ H_2O_2 was the most efficient oxidation process, combining the immediate UV effect and the action of the $\text{HO}\cdot$ radicals produced from the homolytic disruption of H_2O_2 . The levels of diclofenac degradation under the adopted experimental conditions were higher than the values reported in the literature for oxidation processes, such as ozonation (32%) and UV/ H_2O_2 (39%), after 39 min treatment [55]. The use of hypochlorite to degrade diclofenac in

aqueous effluents was also reported with successful results [56]. Recent research in a Fenton-like system with $\text{FeCeOx-H}_2\text{O}_2$ achieved 84% degradation of diclofenac within 40 min [57]. All these results are in accordance with those obtained in our experimental design and confirm the feasibility of the tested methods. A significant reduction in chemical oxygen demand (COD) (40–48%) was also achieved with these oxidation treatments, although there was no direct relationship between the percentage of diclofenac degradation and the decrease in COD.

4. Conclusions

This paper offers a comparative study between the application of biosorption and advanced oxidation techniques to remove diclofenac from wastewater at high concentrations.

Artichoke agrowaste, olive-mill residues, and citrus waste were used as low-cost biosorbents to remove diclofenac from aqueous effluents. Citrus-waste biomass, at a sorbent dosage of $2 \text{ g}\cdot\text{L}^{-1}$, showed the highest sorption capacity ($9 \text{ mg}\cdot\text{g}^{-1}$). This value was achieved with raw biomass without being subjected to any chemical or thermal activation process. The obtained results highlight the sustainable reutilization of agrifood waste for producing cost-effective sorbents, providing additional income for the agroindustrial sector. Waste valorization can efficiently help in reducing environmental stress by decreasing unwarranted pollution and promoting economy circularization.

UV-driven advanced oxidation treatments were effective in the degradation of diclofenac in wastewater. The $\text{UV/H}_2\text{O}_2$ ($5 \text{ mg}\cdot\text{L}^{-1}$) oxidation process was faster than UV/HOCl ($5 \text{ mg}\cdot\text{L}^{-1}$) to reach the same degradation rate. Chemical oxygen demand (COD) was considerably reduced (40–48%) with these oxidation treatments.

The obtained results in this study confirm biosorption as a low-cost and environmentally sustainable technique, and the high efficiency demonstrated by advanced oxidation techniques, may lead to applying specifically designed techniques that combine biosorption and advanced oxidation to eliminate specific emerging contaminants in aqueous effluents.

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