Removal of Drugs in Polluted Waters with Char Obtained by Pyrolysis of Hair Waste from the Tannery Process

Francisco Rodríguez, Carolina Montoya-Ruiz, Idoia Estiati, and Juan F. Saldarriaga*

ABSTRACT: The presence and final destination of pharmaceutical compounds in waters constitute one of the emerging events in current environmental chemistry. Two widely consumed compounds have been evaluated in this study, amoxicillin (AMOX) and diclofenac (DFC), at a concentration of 200 mg L\(^{-1}\). The presence of both in wastewater has been verified, generating problems in ecosystems and human health. Pyrolysis of hair waste from a tannery process was performed in a fixed-bed reactor. Char was obtained at different operating temperatures (300, 350, 400, and 450 °C), which underwent a characterization of heavy metals and elemental composition. An activation process was applied to the char obtained at 450 °C by means of physicochemical processes and with two chemical agents (KOH and K\(_2\)CO\(_3\)). For the removal of drugs, two separate tests were performed, one for 28 days and the other one for 4 h, to assess the efficiency and the percentage of removal. It was found that the char obtained at 450 °C is the one that removes most of both compounds: more than 90% of AMOX and more than 80% of DFC.

1. INTRODUCTION
The presence and final destination of active pharmaceutical compounds in water constitute one of the emerging events in current environmental chemistry. The most significant effects that have been reported are a variation in the chemical composition of discharges, their identification as possible organic pollutants, and the effect on some biological treatment processes due to their presence in high concentrations. The pharmaceutical pollutants that generate the greatest concern are antibiotics since their consumption reaches approximately 100 tons per year, surpassing any other types of medications. In recent decades, great concern has been generated due to the excessive use of antibiotics, both in humans and in livestock production, generating the spread of bacterial resistance phenomena and becoming a great threat to public health. Along these lines, it is affirmed that the overuse of antibiotics has led to their accumulation in the environment. Among the antibiotics with the highest report in water bodies are amoxicillin, sulfamethoxazole, some aminoglycoside compounds, macrolides, and other β-lactams. Their effects against pathogenic bacteria for animals and humans and their wide use in food preservation have generated an increase in their production and consumption, generating large discharges on water bodies and exceeding the permissible limits on the water resource. According to some authors, contamination by this type of compound when it occurs in an order of magnitude of parts per billion (ppb) or even in parts per trillion (ppt) can have a potential risk to human and animal health, mainly due to the generation of microbial resistance phenomena.

Amoxicillin (C\(_{16}\)H\(_{19}\)N\(_3\)O\(_5\)S, AMOX) is an antibiotic used in both veterinary and human medicine. Its presence in waters is associated with toxic effects in algae such as *Synechocystis sp.*, inhibiting its mechanisms of photosynthesis. Also, its constant consumption by animals and humans can generate phenomena of bacterial resistance. This effect could lead to their inability to treat conventional diseases. Several studies have been carried out and have found concentrations from 50 ng L\(^{-1}\) to 50 mg L\(^{-1}\); Zuccato et al. have found a concentration of 382 mg d\(^{-1}\) in the influent and a concentration of 37 mg d\(^{-1}\) in the effluent. On the other hand, diclofenac (C\(_{14}\)H\(_{11}\)Cl\(_2\)NO\(_2\), DFC), a nonsteroidal anti-inflammatory drug, is also considered as a relevant contaminant of the water cycle by The Global Water Research Coalition. When humans ingest DFC, approximately 15% is excreted in the urine. Currently, wastewater treatment plants (WWTPs) are not able to eliminate DFC, and small concentrations are still being detected in its effluents, as

Received: June 11, 2020
Accepted: September 8, 2020
Published: September 17, 2020
well as in the surface and groundwater. The concentrations in the influent have been reported to be between 370 and 560 ng L⁻¹, while the concentrations in the effluent have been reported to be between 0.99 μg L⁻¹ and 365 ng L⁻¹. The increased consumption of DFC in water sources can cause adverse human health effects such as gastritis and kidney failure, which has become a major concern worldwide.

These compounds are only partially removed in WWTPs; therefore, there is a possibility that waste is released through the effluents into the aquatic environment. Thus, considering the origin of contamination by these types of compounds in the surface and groundwater discharges from the point and nonpoint sources of municipal and agricultural wastewater.

Today, many processes have been studied for the removal of these types of compounds from wastewater, including adsorption and membrane filtration (RO-UF). However, the membrane filtration methods must remove adsorbed contaminants, or they will be ineffective in wastewater treatment. Adsorption is considered the most effective method for removing pollutants found in wastewater, as it is simple and cost-effective. Among the reported adsorbents are chitosan balls, activated carbon and bentonite, magnetite nanoparticles, and zero-valence iron nanoparticles. According to the research performed by Zhao et al., the adsorption of more than 30 types of antibiotics involves several adsorbents, including activated carbon, bentonite, magnetite nanoparticles of titanium dioxide, steel shavings, sawdust biochar, wheat straw biochar, and sludge biochar. Not all adsorption techniques are effective, and their use depends on the properties of the sorbent, such as particle size, surface area, functional groups, and porosity, among others. The disadvantage of mineral adsorbents compared to organic ones is that the former is characterized by the porosity and poor surface area, which makes them nonsuitable for the adsorption of organic compounds. Likewise, there are environmental factors that affect their efficiency, such as pH, ionic strength, and the presence of natural organic matter. Carbonaceous materials are widely used because they have high stability, a large surface area and pore volume, and broad pore size distribution, making them a promising solution in the removal of contaminants. Biochar, as a by-product of thermal decomposition, has great potential in remediating pollutants in both water and soil.

Biochar is currently used in various environmental fields, such as air quality control, toxicology studies, public health risk analysis, and wastewater treatment because high efficiencies of cation and anion removal have been obtained in aqueous or gaseous matrices. In the pyrolysis process, temperature is an important parameter for obtaining biochar with suitable conditions to be used as an adsorbent. It has been found that as the temperature increases, the biochar yield decreases from 72% at 300 °C to 52% at 700 °C. Therefore, the performance of the biochar at temperatures above 500 °C is very low.

The physicochemical properties of the biochar prepared at different pyrolysis temperatures often affect the adsorption and fixation of the contaminants because they are affected by the presence of functional groups that contain oxygen (carboxyl, hydroxyl, etc.), as well as by the aromatization structure, specific surface area, porosity, and degree of graphitization.

The adsorption of pharmaceutical compounds has mainly focused on biochar obtained from lignocellulosic materials, although some authors have tried biochar obtained from other types of waste such as bovine manure. An example of this is cow hair, which has been used for the removal of short-chain carboxylic acids in wastewater.

Hair is found within the waste from livestock and tannery activities, which in the process is discarded and mixed with other waste and compounds such as hydroxides and chromium, making its later use complex due to the lack of specialized technology to decrease its dangerousness. During the pyrolysis process of hair, when the proteins, which are part of keratin, reach ~250 °C, they are melted, then at 300 °C, the formation of aromatic compounds occurs, at 350 °C, the formation of cyclic amines occurs, and finally between 350 and 600 °C the degradation of cyclic and aromatic frameworks occurs. However, the use of adsorbents from waste hair valorization is interesting because of its composition, such as the presence of keratin. This is a useful material to use in adsorption or filtration systems in the elimination of toxic compounds, due to the number of functional groups present in the main and secondary chains of proteins. Biochar can be activated to improve its physical and chemical properties. Currently, there are two types of biochar activation processes: physical and chemical. Physical activation in which the development of porosity is sought by gasification with an oxidizing agent at relatively high temperatures. Common activating agents are CO₂, steam, or their combination. Chemical activation uses a chemical agent. The most common

---

### Table 1. Heavy Metal Analysis for the Carbon Samples Obtained

| Parameter | Char (300 °C) (C1) (mg kg⁻¹ db) | Char (350 °C) (C2) (mg kg⁻¹ db) | Char (400 °C) (C3) (mg kg⁻¹ db) | Char (450 °C) (C4) (mg kg⁻¹ db) |
|-----------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Cadmium   | <                              | <                              | <                              | <                              |
| Calcium   | 13.40                          | 10.10                          | 6.60                           | 1.84                           |
| Zinc      | 5.30                           | 1.82                           | <                              | <                              |
| Copper    | <                              | <                              | <                              | <                              |
| Chromium  | <                              | <                              | <                              | <                              |
| Iron      | <                              | <                              | <                              | <                              |
| Magnesium | 10.30                          | 5.20                           | 3.10                           | 0.06                           |
| Manganese | <                              | <                              | <                              | <                              |
| Nickel    | <                              | <                              | <                              | <                              |
| Potassium | 15.70                          | 1.67                           | 1.78                           | <                              |
| Lead      | <                              | <                              | <                              | <                              |

**<**: Value below the detection limit.
activating agents are potassium hydroxide, phosphoric acid, and zinc chloride.62–65

There are limited studies focused on the pyrolysis of cow hair waste from the tannery process to obtain char, which can be used as an adsorbent in the removal of pharmaceutical compounds such as AMOX and DFC. Also, there is a real difficulty in detecting amoxicillin in natural waters due to its instability toward the extraction treatment of environmental samples and the low sensitivity of analytical methods.66,67 In this work, the main objective is to evaluate the pyrolysis of hair from tannery at different working temperatures in a fixed-bed reactor, to obtain an adsorbent with the appropriate physicochemical properties to remove AMOX and DFC.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Chars before Applying the Adsorption Test. In the preliminary tests of heavy metals (Table S) carried out on tannery hair, a high concentration of calcium was observed. This is because of the conventional process of treating the skin with sodium sulfide (Na2S), and lime (CaO), causing the sulfide to dissolve keratin, and the hydrated lime converts the aqueous buffer to an alkaline pH.68 Some authors have found that the most important structural components of hair are lipids, fats, and proteins like keratin, biotin, etc., which are mostly composed of minerals such as calcium, zinc, potassium, iron, and magnesium.69 Similarly, the chars from the pyrolysis process have undergone an analysis of heavy metals to determine if after the pyrolysis process these metals are deposited in the char or, conversely, transformed into the gas or liquid state. Table 1 shows the analysis of heavy metals carried out on the chars.

In Table 1, it is observed that in all of the analyzed samples, as the pyrolysis temperature increases, the concentration of metals decreases; also, at a temperature of 450 °C, the potassium is no longer in the detection limits of the equipment, evidencing that it is no longer present in the sample.

From Table 1, it can be concluded that the increase in the temperature decreases the concentration of metals by 80–95% compared to the analysis of the initial tannery hair. In the literature, to our knowledge, there are very few or no studies on the pyrolysis of residues from tannery processes and especially of hair generated in this activity. This study shows how the pyrolysis process applied to the treatment of hair, which is currently disposed in landfills, helps improve conditions and obtain a product that could be applied in other processes such as adsorption of contaminants. Similarly, it is observed that in the four applied temperatures, there is an important presence of potassium, which can contribute to chemical activation since, on many occasions, the impregnation of the reagent includes this element.70 Table 1 also shows that the C3 and C4 char has low metal concentrations according to the initial characterization of the raw material, so it can be ruled out that these products are dangerous for other uses. These results are similar to those found in other studies in which, as the pyrolysis temperature increases, the metals found in the residues are distributed in the three pyrolysis by-products and, in regard to the char, the concentration of these decreases significantly. The rest of the metals can be expected to be in the gas or liquid state.71

As shown in Table 2, while the carbon content increases, likewise, the sulfur content decreases notably in C4 compared to C1–C2 and at temperatures higher than 450 °C, according to other research studies.72–74 The high carbon content in the samples may indicate that it can be a good adsorbent when it is used to remove contaminants, as is the case with antibiotics, either inactivated or activated. The latter occurs because some authors have found that when the char samples have a considerable presence of carbon, the surface area could be increased, creating porous, allowing the optimization of the adsorption process, being removed at a shorter time.69

On the other hand, the presence of heteroatoms, such as nitrogen, sulfur, hydrogen, and molecular oxygen, allows the formation of surface groups that could favor activation and allows the pore volume to take on a uniform structure and a considerable size that increases the necessary forces for the adsorption process.50

Brunauer–Emmett–Teller (BET) measurements were performed by N2 adsorption, and the values found were 0. Therefore, CO2 adsorption was carried out. It is observed that as the temperature increases, the surface area increases. This suggests that the small surface area produced at low temperatures is attributable to the little formation of the carbonaceous matrix. On the other hand, it can be associated with the fact that at temperatures of 400 and 450 °C, significant structural changes have occurred, the porosity of which increases as the pyrolysis temperature increases.

2.2. Adsorption Tests for the Removal of AMOX and DFC. 2.2.1. Adsorption Capacity of the Chars Untreated for Amoxicillin. Initially, adsorption tests were carried out with the C1, C2, C3, and C4 chars for AMOX to verify that the chars were suitable adsorbents and to evaluate their effectiveness in removing these types of antibiotics. Using only three char samples in the application of these adsorption tests, the elimination of trace elements could affect the readings in the spectrophotometer.

In Figure 1, it is shown that for all of the evaluated weights of chars on the third day, the high removal of AMOX is present, being the greatest removal of AMOX for the weight of 20 g. As the residence time increases, the removal percentages increase between days 0 and 3 and the highest percentages are present for all treatments, then it increases a little more until day 7, and the removal becomes constant until day 28. Additionally, the percentages of removal on the last day of testing for the weight of 20 g are 63.29, 65.31, 68.04, and 75.39% for C1, C2, C3, and C4, respectively. These results are similar to those found with other types of adsorbents.75–77 Furthermore, C4 presented better adsorption percentages with 7% more removal than C3, which makes it possible to obtain a material with better conditions to be used as an adsorbent at this temperature. In this study, it was found that the washing process was effective in removing impurities that appeared after the pyrolysis process, because in the preliminary tests, the hair, due to its original composition (fats, tannins, among others), showed that in the experiments the water changed...
color because of this interference with the reading on the spectrophotometer. This treatment allowed the retention of the drug to increase in a shorter time, possibly due to a rapid interaction through the bonds generated, which in turn allowed the surface layers to attract the adsorbate.

In all treatments, between days 7 and 14, the desorption phenomenon occurred, which consists of the detachment of the solid particles present in the liquid solution, after having contact with the adsorbent.78 The desorption phenomenon is graphically reflected in the downward tipped peaks present in most of the presented removal curves and coincides with other studies.79 According to other authors, this may be because perfect mixing is needed while the contact is made and, on many cases, the solid phase (adsorbent) is deposited and only the particles resting on the top have optimal contact with the sample.78,80 Regarding the kinetics, it is also observed in all of the applied tests that the velocity reaction is faster toward the first days since the slopes are very steep compared to the last days, which is attributed to the same case of the adsorption of the others samples, where in the first instance the active sites and the surface area are fully available to adsorb the contaminant.79 Taking these results into consideration, the char obtained at 450 °C was activated and the tests were carried out on the two drugs (AMOX and DFC). In order to evaluate whether this char is a good adsorbent of other types of pharmaceutical compounds with more complex molecular formulas and also to evaluate if activating this char, the removal efficiencies increase in both drugs.

2.2.2. DFC Adsorption Test with Char Obtained at 450 °C (C4). According to the results for AMOX, removal tests for diclofenac with C4 were performed (Figure 2). This was the char with the highest percentage of carbon and the least metallic compounds that could interfere in the adsorption process of drugs, with the char showing the best results for AMOX. 

Figure 2 shows that in DFC there was a 58% removal percentage with C4, i.e., lower than that obtained for AMOX (Figure 1d). This may be due to several factors; the first is the chemical structure of both drugs, considering that AMOX has a greater amount of C, O, and H than for the relationship between the adsorbent and the adsorbate, allowing a better attraction and creation of links in the adsorption process.81 The other factor is the configuration of the structure since AMOX has a greater number of functional groups such as carboxylic acids, amides, amines, alcohols, and aromatics, whereas DFC has no amides or alcohols. Nevertheless, it presents individual radicals such as chlorine, which is additionally not an element with a high affinity in the attraction between the adsorbent and the adsorbate.82

2.2.3. Adsorption Removal Tests with Activated Char. To evaluate the removal of these two drugs, two adsorptions were performed, one for 28 days (similar to those previously evaluated) and another one for 4 h. These tests assess whether with the activated char, the removal percentage increases, determining if time is an important factor in the process and if the final values at 28 days are similar to the ones at 4 h.

Figure 5 shows that the AMOX adsorption process was optimal for the two activated chars. However, in the case of activated char with K2CO3, the same final percentages are presented as that obtained with nonactivated char (Figure 3b). It is also notable that in the transition from day 0 to day 3, adsorption with activated char (KOH) achieved the removal of up to 60%, while the removal with activated char (K2CO3) reached a value of 45%. Likewise, at the end of the test, the activated char with KOH achieved the removal of up to 91% (Figure 5a) vs 70% obtained using K2CO3 (Figure 3b). This difference is approximately 20%; therefore, the adsorption with
KOH has a higher efficiency compared to the samples previously analyzed (without activating and K2CO3).

In the case of DFC, it is shown in Figure 3 that the removal percentage of up to 81.33% is achieved for activated char with KOH (Figure 3c) and 67% with K2CO3 (Figure 3d). In this case, a different behavior was present compared with that of the treatment with AMOX; between days 0 and 3, the greatest antibiotic removal occurred with the activated char with K2CO3 instead of KOH (52 and 43%, respectively). However, despite this initial behavior, on day 28, the activated char that presented the best removal percentages was the one activated with KOH (81.33%). Like AMOX, the activated char in both samples was effective in removing DFC. In addition, by obtaining greater removal through the chemical activation method, the structural behavior explained for AMOX was confirmed, where KOH as an activating chemical agent is able to show that the char retains a greater amount of adsorbate particles for the reason that it has a greater surface area and active sites.

On the other hand, DFC removal was better with activated chars than with nonactivated carbon, with the activated char with KOH being the best treatment, performing similarly to the results with AMOX. This can be explained by the fact that KOH is a good precursor for activation when the char sample has a low content of volatiles and a high content of carbon (greater than 50%). In addition, the carbon–hydrogen bond of the chemical agent leads to a greater proportion of surface active sites, thus achieving a better adsorbent–adsorbate interaction.

Furthermore, it has been found in different studies that this activating agent is suitable when it is impregnated with a carbonaceous material, which had a heat treatment between 200 and 500 °C, proving to be effective in the adsorption of pharmaceutical compounds and contaminating acids in water.83–87

2.3. Kinetic Model for Adsorption Drugs. When the highest amount was used, 20 g, for which the adsorbent mass/solution volume is 200 mg L\(^{-1}\), efficiency increased fast, attaining values of 80% for AMOX and 60% for DFC in less than 5 min, and a maximum value close to 95% for AMOX and 80% for DFC in only 30 min. These results are similar to those found in other studies, in which the used concentrations of AMOX vary from 10 to 1000 mg L\(^{-1}\),\textsuperscript{4,35,77,88} The adsorption isotherms were calculated according to Tran et al.,\textsuperscript{89} who argued that kinetic equations based on the adsorption capacity of solids fit a pseudo-first-order (PFO) equation. According to some authors, the PFO can be expressed in a nonlinear and linear way. In this study, the nonlinear form has been taken (eq 1).

\[
q_t = q_e \left(1 - e^{-kt}\right)
\]

Where \(q_e\) and \(q_t\) are the amounts of adsorbate uptake per mass of adsorbent at equilibrium and at any time \(t\) (min), respectively, and \(k_1\) (1 min\(^{-1}\)) is the rate constant of the PFO equation.

Adsorption isotherms have been determined using the most popular adsorption models by Langmuir, eq 2, and Freundlich, eq 3

\[
q_e = \frac{k_l q_m c_e}{1 + k_l c_e}
\]

\[
q_e = k_f c_e^{1/n}
\]

where \(q_e\) (mg g\(^{-1}\)) is the mass of drug adsorbed per volume unit of adsorbent at equilibrium, \(c_e\) (mg L\(^{-1}\)) is the concentration of the drug in the solution at equilibrium, \(k_l\) (L mg\(^{-1}\)) is the Langmuir constant, which is related to the free energy of adsorption, \(q_m\) (mg g\(^{-1}\)) is the theoretical maximum adsorption capacity, \(k_f\) is the Freundlich constant, which is related to the relative adsorption capacity, and \(n\) is the heterogeneity factor so that 1/\(n\) indicates the intensity of Freundlich adsorption. Likewise, the adsorption kinetics were evaluated according to a mass balance of the adsorbate in between the liquid phases (eq 4) and the solid (eq 5).

\[
\frac{dc}{dt} = \frac{-K_{ds}(c - c_0)}{L}
\]
where \( K \) (L m\(^{-2}\) min\(^{-1}\)) is the mass transfer coefficient, \( a \) is the external surface area of the adsorbent, \( L \) is the fminsearch subroutine to find the objective function, following the Nelder–Mead algorithm. Figure 4 shows the adjustments of both models to the experimental data. It is evident that the curves adequately fit Freundlich isotherms in all cases, while for Langmuir, no fit was observed in any of the experiments carried out. This is because it assumes the formation of a single layer of adsorbate on the surface of the material, and in the results of Section 2.2, it is shown how as time passes, the adsorbate is accumulated, and its behavior is very similar to the behavior of the Freundlich model. The equilibrium parameters for Langmuir and Freundlich, as well as the mass transfer coefficient \( K_a \), were determined by means of an objective function \( OF \), defined as the sum of the squared differences of adsorbate concentrations in the liquid phase measured experimentally and later calculated by the model. The algorithm was written in MatLab, which uses an ode subroutine to solve the mass balances and the fminsearch subroutine, which calculates the minimal objective function without restrictions, based on the Nelder–Mead algorithm. 

Figure 4 shows the parity graph corresponding to the adjustments made for both compounds for the Freundlich model. The fit of all experimental data is observed, with \( R^2 \) greater than 0.9 in all cases evaluated. 

Table 3 shows the values obtained from the fitting of the experimental data for both models and compounds. It is observed that the values of \( q_m \) corresponding to the Langmuir isotherm are very similar to those found in the literature. The values are very similar to those found by Alnajrani and Alsager et al.\(^9\), who obtained a value of 213 mg g\(^{-1}\) using polymers of intrinsic microporosity as an adsorbent. Moussavi et al.\(^7\) obtained a \( q_m \) of 438.6 mg g\(^{-1}\) with NH\(_4\)Cl-induced activated carbon, and Benjedim et al.\(^\) obtained 1270 mg g\(^{-1}\) using the \( E. \ coli \) biofilm supported on activated carbon. Also, the KOH results are similar to those found by Ren et al.\(^2\), 16.1 and 7.42 mg g\(^{-1}\). With these results, it is shown that this type of adsorbent is suitable for the removal of this type of compound and that it is less sophisticated than other adsorbents such as commercially activated carbons. Regarding the heterogeneity factor, \( n \), values between 0.22 and 0.56 have been reported, which can be observed to be very similar to those of this study.\(^9\)

Figure 6 shows the evolution of drug concentration in the liquid phase. The points correspond to the experimental data, and the lines have been calculated with the model. It is observed that the fit of the experimental data to that of the model is quite good. A better behavior of the char is evidenced...
in the AMOX than in the DFC. This behavior may be due to the chemical composition of DFC, which is much more complex with chlorine atoms that make its adsorption process more difficult. With this, it is verified that the adsorption process of both drugs occurs by a physisorption mechanism, which involves the formation of several layers of adsorbate on the surface of the adsorbent. These results are not decisive to conclude that the deposition of the AMOX and DFC on the surface of biochar could correspond to a physical (physisorption) or chemical (chemisorption) mechanism, but they contribute to a better understanding of the process. Many authors argue that this mechanism cannot be assigned based only on adequate kinetic models, but that different analytical techniques such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and Raman spectroscopy, among others, must be performed.

### 2.4. Char Characterization after Adsorption Tests.

The BET surface of the carbon obtained at 450 °C was 430.61 m² g⁻¹, but after being subjected to activation with KOH, this increased to 1316.39 m² g⁻¹, while for K₂CO₃ to 1182.78 m² g⁻¹. The activated biochar showed an increase in the BET surface area of 885.78 and 752.17 m² g⁻¹, respectively. These results coincide with the adsorption results, which were observed that the carbon activated with KOH presents better removal percentages. This implies that the route of impregnation of the char led to activated carbons with high surface areas.

The nonactivated char and activated char by both methods were characterized by means of a selective Boehm titration. This test was applied to the coals before the tests and after the removal tests (Table 4).

### Figure 5.

Parity charts of the adsorption models tested for the Freundlich model: (a) AMOX C₄-K₂CO₃, (b) AMOX C₄-KOH, (c) AMOX C₄, (d) DFC C₄-K₂CO₃, (e) DFC C₄-KOH, and (f) DFC C₄.

### Table 3. Equilibrium Parameters and Mass Transfer Coefficients Calculated for Both Models

| drug | treatment | Freundlich | Langmuir |
|------|-----------|------------|----------|
| AMOX |           | k_f       | q_m     |
| K₂CO₃ | 2.73 × 10⁻⁷ | 2.04 × 10⁻¹ | 1.50 × 10⁻² |
| KOH  | 5.06 × 10⁻⁵ | 1.28 × 10⁻⁸ | 1.05 × 10⁻² |
| nonactivated | 4.02 × 10⁻⁸ | 2.01 × 10⁻¹ | 1.86 × 10⁻³ |
| DFC  |           | k_f       | q_m     |
| K₂CO₃ | 2.90 × 10⁻⁶ | 2.92 × 10⁻¹ | 5.08 × 10⁻⁵ |
| KOH  | 3.34 × 10⁻⁷ | 2.42 × 10⁻¹ | 7.63 × 10⁻² |
| nonactivated | 1.09 × 10⁻⁸ | 2.11 × 10⁻¹ | 6.23 × 10⁻² |
It can be seen in Table 4 that there is a presence of carboxylic, lactonic, and phenolic groups in all of the samples. It is evident that, for example, in the activated char after the test, there is less presence of carboxylic groups compared to the activated char with KOH. Additionally, in both cases, according to the obtained pH value, it is possible to establish that the chars have a basic/alkaline behavior against oxidized compounds, which are consistent with the nature of the agents used in impregnation and activation. The latter can promote adsorption both on the surface and on the internal structure of the adsorbent material.97

It is remarkable that the highest concentration of functional groups occurs in the carboxylic group in both cases and the lowest in the phenolic group. However, these differences are very insignificant since the concentrations are in the same order of magnitude. The existence of lactonic and carboxylic groups tends to lower the pH of the adsorbent due to the presence of carboxylic and oxygenated radicals. This in turn allows the atoms of these radicals to favor the adsorption process given the interactions of the unpaired electrons with those that remain in the structure of the adsorbate.98

Table 4. Concentration of Functional Groups in the Activated Carbon Samples

| activated char        | carboxylic group (mol H⁺ g⁻¹ CA) | lactonic group (mol H⁺ g⁻¹ CA) | phenolic group (mol H⁺ g⁻¹ CA) | pH  |
|-----------------------|----------------------------------|--------------------------------|--------------------------------|-----|
| K₂CO₃ before the test | 3.54 × 10⁻³                      | 3.66 × 10⁻³                    | 1.67 × 10⁻³                    | 8.76|
| K₂CO₃ after the test  | 3.09 × 10⁻³                      | 2.69 × 10⁻³                    | 1.55 × 10⁻³                    | 7.77|
| KOH before the test  | 7.95 × 10⁻³                      | 6.54 × 10⁻³                    | 4.32 × 10⁻³                    | 10.14|
| KOH after the test   | 4.81 × 10⁻³                      | 4.77 × 10⁻³                    | 3.55 × 10⁻³                    | 10.03|
| not activated before | 0.95 × 10⁻³                      | 1.14 × 10⁻⁴                    | 0.14 × 10⁻³                    | 6.45|
| not activated after  | 0.01 × 10⁻³                      | 0.22 × 10⁻⁴                    | 0.02 × 10⁻³                    | 6.97|

Figure 6. Evolution of the AMOX and DFC concentrations with time in the solid phase calculated with the Freundlich model, (a) AMOX C₄-K₂CO₃, (b) AMOX C₄-KOH, (c) AMOX C₄, (d) DFC C₄-K₂CO₃, (e) DFC C₄-KOH, and (f) DFC C₄.
By having positive concentration values of the three functional groups, it is possible to affirm that the activated char samples have structures suitable for the adsorption of organic compounds, given their elemental composition and the presence of basic ions in the solution.99

In the FTIR analysis, for the tests with AMOX, the same behaviors obtained in the adsorption tests can be observed. Figure 7 shows the results for the adsorption of AMOX on the chars evaluated before and after the removal tests. Peaks at 3190 and 2919 cm\(^{-1}\) corresponding to O–H and C–H, respectively, assigned to the vibrations of the hydroxyl groups are evident.100–104 Bands are in 1661 and 1442 cm\(^{-1}\), corresponding to C\(=\)O and N–N due to the adsorption of AMOX.105–107 Another band intensity is in 1060 cm\(^{-1}\) that is mainly associated with O–C stretching in carbohydrates and HO-C\(=\)O bending vibration.104,106,108

3. CONCLUSIONS

Four chars have been obtained from different temperatures, finding that C4 is the one with the best properties. According to the elemental analysis and the Boehm titration, it has suitable carbon functional groups to be a good adsorbent. After carrying out a preliminary test, it was also found that C4 was the one with the best AMOX removal results. After being activated through various physical and chemical processes, it was found that activation with KOH achieved the removal of 88.28% of DFC and 95.53% with AMOX.

With these results, it can be concluded that the pyrolysis of cow hair from tanneries in a fixed-bed reactor and a temperature of 450 °C produces a material with interesting physical and chemical conditions to be used as an adsorbent both activated and nonactivated in API removal. This material could be used in filtration columns to be evaluated in the removal of this type of compound, either in rural areas where the indiscriminate use of these compounds in the livestock industry increases the risk in the drinking waters of downstream populations. Additionally, this char (as a by-product of pyrolysis) allows the removal of emerging contaminating compounds such as antibiotics that in developing countries are being problematic. This is due to the lack of regulations and the free sale of many of them for both human and livestock activities. This study could be the beginning of the use of hair residues in pyrolysis to obtain a char with properties for the removal of compounds that are problematic for the environment.

4. MATERIALS AND METHODS

4.1. Raw Material Characterization. The collection of hair waste was carried out in the Cañon tannery located in the San Benito neighborhood of Bogotá, Colombia. This material was collected in the stage called pelt, where the hair is removed from the leather and falls down the sides of the rotating drum. At that point in the process, the hair has been in contact with reagents based on sulfur and calcium; therefore, it could be considered a hazardous waste.

The sample was dried for 24 h in an oven at 105 °C, according to ASTM D1509.109 This was later crushed in a grinding mill (Corona Brand, Medellín, Colombia) operated with a single-phase motor. The chars were characterized based on the BET surface area determined by CO2 adsorption–desorption (SA-9600 Series, Horiba Scientific, Kyoto, Japan), according to the methodology proposed by Kim et al.110 Then, it was sieved on a 200 nm light sieve to obtain a particle diameter of less than 1 mm. The hair was initially characterized using a heavy metal test on an ICP-OES 6500 duo spectrometer (Thermo Fisher Scientific, Waltham).69 This test was carried out with the objective to rule out the dangerousness of the samples and evaluate the presence of

| Parameter | Equipment detection limit (mg kg\(^{-1}\) bs) | Tannery hair (mg kg\(^{-1}\) bs) | Decree 4741 of 2005 (mg kg\(^{-1}\) bs) | Directive 86/278/EEC (mg kg\(^{-1}\)) | Maximum concentration in sludge (mg kg\(^{-1}\)) US EPA, 1993 |
|-----------|---------------------------------|---------------------------------|---------------------------------|-----------------|-----------------|
| cadmium   | 2.76 < 5.00                     | 5.00                            | 2.00                            | 85              |
| calcium   | 73.50                           | 72.00                           |                                 |                 |
| zinc      | 1.72 35.10                      | 800                             | 7500                            |                 |
| copper    | 9.25 < 10.00                    | 600                             |                                 |                 |
| chrome    | 19.80                           | 5.00                            | 100                             | 3000            |
| iron      | 59.51                           | 70.00                           |                                 |                 |
| magnesium | 14.33                           | 61.70                           |                                 |                 |
| manganese | 1.31 < 10.00                    | 50                              | 75                              |
| nickel    | 2.07 < 5.00                     |                                 | 420                             |
| potassium | 28.36                           | 33.50                           |                                 |                 |
| lead      | 18.10                           |                                 |                                 |                 |

*"<": Value below the detection limit.*

ACS Omega
Inorganic compounds in the sample due to the treatments that are given so that it is removed from the skin in the tannery (Table 5).

In accordance with both Colombian and international regulations, it is observed that the hair sample does not represent danger (Table 5) due to the fact that there were no concentrations above the permitted limit in any of the metals. Additionally, it was found that for the other parameters (such as calcium, zinc, magnesium, nickel, and potassium), the concentration found in the samples is much lower than the maximum allowable, as is the case of the Colombian regulations that require less than 200 mg kg$^{-1}$. Thus, it is confirmed that no analyzed parameter exceeds these values and in turn rules out that there is danger in the material.

4.2. Experimental Equipment. The pyrolysis plant used is shown in Figure 8. It consists of the following elements: (1) gas feed system, (2) flow meter, (3) temperature controller, (4) pyrolysis reactor, (5) cyclone, (6) gas cooling system, and (7) liquid collection device. The feeding system was batch.

Nitrogen has been used as a fluidizing agent, and its flow rate was controlled by means of a flow meter that allows a feed of 20 L min$^{-1}$. Before the gas enters the reactor, it is heated in a preheater. The plant is a fixed-bed reactor with dimensions of 40 cm wide, 20 cm high, and 63 cm long. To study the composition of char and its effect on adsorption processes, runs at 300, 350, 400, and 450 $^\circ$C were carried out. Each experiment was performed on batch and a feeding of 50 g h$^{-1}$ in turn rules out that there is danger in the material.

4.3. Char Treatment. The char samples from the pyrolysis process were prewashed to remove any impurity that may color the water to be treated. A water–carbon ratio of 10:1 was used, removing the liquid supernatant by means of centrifugation and leaving it to stand for 30 min, then it was vacuum filtered. This procedure was repeated several times until the carbon–water mixture was transparent. All char samples after washing were characterized. Elemental analysis was performed using a vario Macro Elemental 2000 equipment (Elementar, Frankfurt, Germany), and a heavy metal analysis was carried out on the spectrometer ICP-OES 6500 duo (Thermo Fisher Scientific, Waltham).

4.3.1. Char Activation Process. Two physicochemical methods ($K_2CO_3$ and KOH activation) were used for the char activation process, both having a high capacity to increase the surface area and porous volume of the particles. With both methods, it has been verified that a decrease in removal time makes the adsorption more effective.

4.3.1.1. Activation with Potassium Carbonate ($K_2CO_3$). The carbon obtained at 450 $^\circ$C was mixed with $K_2CO_3$ (EMSURE, London, England) in a 1:1 ratio by weight, and afterward, it was kneaded. A carbonization process was carried out so that the sample was totally impregnated by the reagent, placing it at 800 $^\circ$C for 1 h in a fixed-bed reactor. Finally, to cool the activated carbon and remove impurities, it was washed with distilled water and dried in an oven at 110 $^\circ$C.

4.3.1.2. Activation with Potassium Hydroxide (KOH). Charcoal (150 g) was taken and KOH (EMSURE, London, England) was added considering a proportion of 2 mL of 40% w/w solution. It was stirred for 1 h and left to stand for 72 h. Subsequently, each sample was dried at 74 $^\circ$C for 48 h. Finally, using a nitrogen (N$_2$) flow of 30 mL min$^{-1}$, carbonization was carried out in the reactor with a temperature ramp of 10 $^\circ$C min$^{-1}$ until reaching 200 $^\circ$C. Finally, it was cooled down until the product was at room temperature.

4.3.2. Characterization of Activated Carbon. The activated char was characterized by Boehm titration, which quantifies and determines the functional oxygen groups of the carbon based on the acidity with which each activation is carried out. Charcoal (0.5 g) was taken, a 50 mL solution of 0.1 N NaOH, 0.1 N $Na_2CO_3$, and 0.1 N NaHCO$_3$ was added and left to stir constantly in a SIF 3000 model shaker (MAX QTM, Chandler) for 24 h. Then, 10 mL aliquots were taken, 8 mL of 0.1 N HCl and three drops of phenolphthalein were added for the titration with NaOH until a purple coloration was obtained. Functional groups were determined using the following equations:

$$\text{carboxylic group} = V_{Na_2CO_3} - V_{NaHCO_3}$$

$$\text{phenolic group} = (V_{NaOH} - V_{NaHCO_3}) - (V_{nNa_2CO_3} - V_{NaHCO_3})$$

$$\text{lactonic group} = (V_{Na_2CO_3} - V_{NaHCO_3}) - (V_{nNaHCO_3} - V_{NaHCO_3})$$

Where $V_B$ corresponds to the volume of the blank (mL) and $V_n$ corresponds to the volume of the resulting sample after the titration (mL). A pH measurement was performed using a basic benchtop pH meter (HANNA, Bilbao, Spain) to correlate the presence of functional groups with this variable.
The infrared spectra of the carbon samples before and after the adsorption process were obtained by Fourier transform infrared (FTIR) spectroscopy, and the spectra were monitored via the Spectrum Two FTIR Spectrometer (PerkinElmer), ranging from 400 to 4000 cm\(^{-1}\).

4.4. Procedure Drug Adsorption Capacity. Two pharmaceutical compounds (AMOX and DFC) were chosen for the adsorption process due to their wide use and sale without prescription. Likewise, it has been reported that the concentrations of these in effluents exceed the permissible limits because, in the case of both compounds, concentrations in effluents in the range of ng L\(^{-1}\) to mg L\(^{-1}\) have been reported.\(^{10,76}\) For this study, the water to be treated was contaminated and brought to a maximum concentration of 200 mg L\(^{-1}\) for each of the drugs in the solution.\(^{77}\) Initially, tests were carried out with AMOX since its chemical structure allows its removal in water to be more efficient and effective. For this purpose, carbon samples obtained at temperatures of 300, 350, 400, and 450 °C were taken to observe the removal percentages. Finally, with the char obtained at 450 °C, DFC removal tests were performed and underwent activation to carry out removal tests on both drugs.

For the adsorption tests, five groups of carbon samples were prepared, each with 10 different weights in the range of 0–20 g, for a total of 50 samples deposited in an amber bottle. The vials were filled with 50 mL of the test solution, and each group was labeled with the specific day of reading (3, 7, 14, 21, and 28). The flasks were then placed in the Model SIF 3000 Shaker (MAX QTM, Chandler) at room temperature and 120 rpm.

For the removal reading, 5 mL were taken from each bottle in test tubes and they were subjected to a rapid centrifugation process (1200 rpm) for 1 min. After this, the content of each tube was filtered through the qualitative paper to separate the liquid phase from any remaining solid carbon particles.\(^7\) The absorbance was measured in the spectrophotometer, and with each value obtained, the concentration removal was calculated.

The calibration of the tests was performed according to ASTM D3860-98.\(^{77}\) A Genesys UV Thermo spectrophotometer (Thermo Fisher Scientific, Waltham) was used to measure different wavelengths to the test solutions (AMOX and DFC) at a concentration of 200 mg L\(^{-1}\). Figure 9 shows an optimal wavelength value obtained for each drug, which is considered as the ideal value for stopping the drug at any time of the test.

In the case of AMOX, the wavelength is 240 nm and for DFC it is 305 nm.

For calibration, 10 drug solutions were prepared with water at concentrations of 5–400 mg L\(^{-1}\) of AMOX and DFC, measuring the value of absorbance and keeping the calculated wavelength value constant. A curve was made where each of the concentrations and their absorbance were related. For AMOX, a slope of 0.0119, an intercept of 0.0193, and an \(R^2\) of 0.9785 were obtained. In the case of DFC, a slope of 0.0134, an intercept of 0.0142, and an \(R^2\) of 0.9943 were obtained.

■ AUTHOR INFORMATION

Corresponding Author
Juan F. Saldarriaga — Department of Civil and Environmental Engineering, Universidad de los Andes, Bogotá 111711, Colombia; orcid.org/0000-0002-2902-2305; Phone: 57 (1) 3394949 ext.1649; Email: jfsaldarriaga@uniandes.edu.co, juanfelorza@gmail.com

Authors
Francisco Rodríguez — Department of Civil and Environmental Engineering, Universidad de los Andes, Bogotá 111711, Colombia
Carolina Montoya-Ruiz — Facultad de Ciencias, Universidad Nacional de Colombia, 050034, Colombia
Idoia Estiati — Department of Chemical Engineering, University of the Basque Country, E48080 Bilbao, Spain

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02768

Author Contributions
This manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was carried out with the support of the Department of Civil and Environmental Engineering of Universidad de los Andes and the funds to the Universidad de los Andes the Early-Stage Research Found-FAPA: (P3.2017.3830). F.R. thanks the Department of Civil and Environmental Engineering of Universidad de los Andes for his grant. I.E. thanks the Department of Civil and Environmental Engineering of Universidad de los Andes: Metabolitos de Farmacos. Una Revisión. Rev. Fac. Cienc. Básicas 2014, 10, 80–101.

■ REFERENCES

1. Alvarez, S.; Ovejero Escudero, G.; García, J. Panorama. Eliminación de Contaminantes Emergentes de Las Aguas Residuales. Investig. Sci. 2017, 485, 10–16.
2. Tejada, C.; Quiñónez, E.; Peña, M. Contaminantes Emergentes en Aguas: Metabolitos de Fármacos. Una Revisión. Rev. Fac. Cienc. Básicas 2014, 10, 80–101.
3. Almakki, A.; Jumas-Bilak, E.; Marchandin, H.; Licznar-Fajardo, P. Antibiotic Resistance in Urban Runoff. Sci. Total Environ. 2019, 667, 64–76.
4. Andreozzi, R.; Canterino, M.; Marotta, R.; Paxeus, N. Antibiotic Removal from Wastewaters: The Oxidation of Amoxicillin. J. Hazard. Mater. 2008, 122, 243–250.
5. Cha, J. M.; Yang, S.; Carlson, K. H. Trace Determination of \(\beta\)-Lactam Antibiotics in Surface Water and Urban Wastewater Using Liquid Chromatography Combined with Electrospray Tandem Mass Spectrometry. J. Chromatogr. A 2006, 1115, 46–57.
(6) Shakil, S.; Khan, R.; Zarrilli, R.; Khan, A. U. Aminoglycosides versus Bacteria – a Description of the Action, Resistance Mechanism, and Nosocomial Battleground. *J. Biomed. Sci.* 2008, 15, 5–14.

(7) Roberts, M. C.; Sutcliffe, J.; Courvalin, P.; Jensen, L. B.; Rood, J.; Seppala, H. Nomenclature for Macrolide and Macrolide-Lincosamide-Streptogramin B Resistance Determinants. *Antimicrob. Agents Chemother.* 1999, 43, 2823–2830.

(8) Jiménez, C. Contaminantes orgánicos emergentes en el ambiente: productos farmacéuticos. *Rev. Lasallista Investig.* 2011, 8, 143–153.

(9) Jones, O. A. H.; Voulvoulis, N.; Lester, J. N. Potential Ecological and Human Health Risks Associated With the Presence of Pharmacologically Active Compounds in the Aquatic Environment. *Crit. Rev. Toxicol.* 2004, 34, 335–350.

(10) Çalışkan Salih, E.; Mahramanlıoğlu, M. Equilibrium and Kinetic Adsorption of Drugs on Bentonite: Presence of Surface Active Agents Effect. *Appl. Clay Sci.* 2014, 101, 381–389.

(11) Putra, E. K.; Pranowo, R.; Sunarso, J.; Indraswati, N.; Ismadji, S. Performance of Activated Carbon and Bentonite for Adsorption of Aminocillin from Wastewater: Mechanisms, Isotherms and Kinetics. *Water Res.* 2009, 43, 2419–2430.

(12) Pan, X.; Deng, C.; Zhang, D.; Wang, J.; Mu, G.; Chen, Y. Toxic Effects of Aminocillin on the Photosystem II of Synechocystis Sp. Characterized by a Variety of In Vivo Chlorophyll Fluorescence Tests. *Aquat. Toxicol.* 2008, 89, 207–213.

(13) Aksu, Z.; Tung, Ö. Application of Biosorption for Penicillin G Removal: Comparison with Activated Carbon. *Process Biochem.* 2005, 40, 831–847.

(14) Andreozzi, R.; Caprio, V.; Cingiglia, C.; de Champdoré, M.; Lo Giudice, R.; Marotta, R.; Zuccato, E. Antibiotics in the Environment: Occurrence in Italian STPs, Fate, and Preliminary Assessment on Algal Toxicity of Aminocillin. *Environ. Sci. Technol.* 2004, 38, 6832–6838.

(15) Zuccato, E.; Castiglioni, S.; Bagnati, R.; Melis, M.; Fanelli, R. Source, Occurrence and Fate of Antibiotics in the Italian Aquatic Environment. *J. Hazard. Mater.* 2010, 179, 1042–1048.

(16) GWRC. *Pharmaceuticals and Personal Care Products in the Water Cycle. An International Review; GlobalWater Research Coalition*: London, 2004.

(17) Landsdorp, D.; Vree, T. B.; Janssen, T. J.; Guelen, P. J. Pharmacokinetics of Rectal Diclofenac and Its Hydroxy Metabolites in Man. *Int. J. Clin. Pharmacol.* 1990, 28, 298–302.

(18) Ardila, L. K.; da Silva, B. F.; Spadoto, M.; Clarice Maria Rispoli, B.; Azevedo, E. B. Which Route to Take for Diclofenac Removal from Wastewater? *Crit. Rev. Toxicol.* 2016, 1061–1068.

(19) Meffe, R.; de Bustamante, I. Emerging Organic Contaminants and Current Issues. *Chemosphere* 2014, 107, 2830.

(20) Richardson, S. D.; Ternes, T. A. Water Analysis: Emerging Contaminants and Current Issues. *Anal. Chem.* 2005, 77, 3807–3838.

(21) Halling-Sørensen, B.; Nors Nielsen, S.; Landzey, P. F.; Ingerslev, F.; Holten Lützhoff, H. C.; Jørgensen, S. E. Occurrence, Fate and Effects of Pharmaceutical Substances in the Environment: A Review. *Chemosphere* 1998, 36, 357–393.

(22) Zhou, Y.; Liu, X.; Tang, L.; Zhang, F.; Zeng, G.; Peng, X.; Luo, L.; Deng, Y.; Pang, Y.; Zhang, J. Insight into Highly Efficient Co-Removal of p-Nitrophenol and Lead by Nitrogen-Functionalized Magnetic Ordered Mesoporous Carbon: Performance and Modelling. *J. Hazard. Mater.* 2017, 333, 80–87.

(23) Wang, H.; Yuan, X.; Wu, Y.; Zeng, G.; Dong, H.; Chen, X.; Leng, L.; Wu, Z.; Peng, L. In Situ Synthesis of In2S3@MIL-125(Ti) Core−Shell Microparticle for the Removal of Tetracycline from Wastewater by Integrated Adsorption and Visible-Light-Driven Photocatalysis. *Appl. Catal., B* 2016, 186, 19–29.

(24) Tixier, C.; Singer, H. P.; Oellers, S.; Müller, M. D. Occurrence and Fate of Norfloxacin in Aqueous Bi2WO6 Dispersions Containing Nonionic Surfactant under Visible Light Irradiation. *J. Hazard. Mater.* 2016, 306, 295–304.

(25) Pan, X.; Deng, C.; Zhang, D.; Wang, J.; Mu, G.; Chen, Y. Toxic Effects of Amoxicillin on the Photosystem II of Synechocystis Sp. Characterized by a Variety of In Vivo Chlorophyll Fluorescence Tests. *Aquat. Toxicol.* 2008, 89, 207–213.

(26) Coleman, A.; Alves, L. R. B. Aminocillin Adsorption on Chitosan Beads: Kinetics, Equilibrium and Validation of Finite Bath Models. *Process Biochem.* 2018, 64, 344–352.

(27) Lang, S.; Lin, H.; Yan, X.; Huang, Q. Electro-Oxidation of Tetracycline by a Magneli Phase Ti4O7 Porous Anode: Kinetics, Products, and Toxicity. *Chem. Eng. J.* 2018, 322, 628–636.

(28) Wang, H.; Yuan, X.; Wu, Y.; Zeng, G.; Dong, H.; Chen, X.; Leng, L.; Wu, Z.; Peng, L. In Situ Synthesis of In2S3@MIL-125(Ti) Core−Shell Microparticle for the Removal of Tetracycline from Wastewater by Integrated Adsorption and Visible-Light-Driven Photocatalysis. *Appl. Catal., B* 2016, 186, 19–29.

(29) Ternes, T. A.; Stüber, J.; Herrmann, N.; McDowell, D.; Ried, A.; Kampmann, M.; Teiser, B. Oxonation: A Tool for Removal of Pharmaceuticals, Contrast Media and Musk Fragrances from Wastewater? *Water Res.* 2003, 37, 1976–1982.

(30) Zhang, L.; Wang, J.; Zeng, G.; Liu, Y.; Deng, Y.; Zhou, Y.; Tang, J.; He, B.; Guo, Z. Enhanced Photocatalytic Degradation of Norfloxacin in Aqueous Bi2WO6 Dispersions Containing Nonionic Surfactant under Visible Light Irradiation. *J. Hazard. Mater.* 2016, 306, 295–304.

(31) Leng, L.; Wei, L.; Xiong, Q.; Xu, S.; Li, W.; Lv, S.; Lu, Q.; Wan, L.; Wen, Z.; Zhou, W. Use of Microalgae Based Technology for the Removal of Antibiotics from Wastewater: A Review. *Chemosphere* 2020, 238, No. 124680.

(32) Li, S.; Li, X.; Wang, D. Membrane (RO-UF) Filtration for Antibiotic Wastewater Treatment and Recovery of Antibiotics. *Sep. Purif. Technol.* 2004, 34, 109–114.

(33) Weng, X.; Cai, W.; Lin, S.; Chen, Z. Degradation Mechanism of Amoxicillin Using Clay Supported Nanoscale Zero-Valent Iron. *Appl. Clay Sci.* 2017, 147, 137–142.

(34) Adriano, W. S.; Veredas, V.; Santana, C. C.; Gonçalves, L. R. B. Adsorption of Aminocillin on Chitosan Beads: Kinetics, Equilibrium and Validation of Finite Bath Models. *Biochem. Eng. J.* 2005, 27, 132–137.

(35) Zhao, Z.; Nie, T.; Zhou, W. Enhanced Biochar Stabilities and Adsorption Properties for Tetracycline by Synthesizing Silica-Coated Biochar. *Environ. Pollut.* 2019, 243, 348–3488.

(36) O’Carroll, D.; Sleep, B.; Krol, M.; Boparai, H.; Kocur, C. Nanoscale Zero Valent Iron and Bimetallic Particles for Contaminated Site Remediation. *Adv. Water Resour.* 2013, 51, 104–122.

(37) Zhang, D.; Niu, H.; Zhang, X.; Meng, Z.; Cai, Y. Strong Adsorption of Chlorotetracycline on Magnetite Nanoparticles. *J. Hazard. Mater.* 2011, 192, 1088–1093.

(38) Zhang, X.; Lin, S.; Chen, Z.; Megharaj, M.; Naidu, R. Kaolinite-Supported Nanoscale Zero-Valent Iron for Removal of Pb2+ from Aqueous Solution: Reactivity, Characterization and Mechanism. *Water Res.* 2011, 45, 3481–3488.

(39) Koutsouba, V.; Heberer, T.; Fuhrmann, B.; Schmidt-Baumler, K.; Tsipi, D.; Hiskia, A. Determination of Polar Pharmaceuticals in Sewage Water of Greece by Gas Chromatography–Mass Spectrometry. *Chemosphere* 2003, 51, 69–75.
Superparamagnetic Iron Oxide Nanoparticles for the Adsorption of Fast Kinetics and High Adsorption Capacity of Green Extract Capped Materials.

Water by Adsorption/Bioadsorption on Activated Carbons and Pesados En Aguas Residuales Usando Materiales de Origen Biológico. Mater. 2003, 39, 1011–1018.

Copper from Aqueous Solution: Adsorption Mechanism and Wei, J.; Luo, L.; Lei, M.; Tang, L. Modification of Biochar Derived from Sawdust and Its Application in Removal of Tetracycline and Copper from Aqueous Solution: Adsorption Mechanism and Modelling. Bioresour. Technol. 2017, 245, 266–273.

Li, Y.; Liu, X.; Zhang, P.; Wang, X.; Cao, Y.; Han, L. Qualitative and Quantitative Correlation of Physicochemical Characteristics and Lead Sorption Behaviors of Crop Residue-Derived Char. Bioresour. Technol. 2018, 270, 545–553.

Rivera-Utrilla, J.; Gómez-Pacheco, C. V.; Sánchez-Polo, M.; López-Peña, J. J.; Ocampo-Pérez, R. Tetracycline Removal from Water by Adsorption/Bioadsorption on Activated Carbons and Sludge-Derived Adsorbents. J. Environ. Manage. 2013, 131, 16–24.

Nithya, K.; Sathish, A.; Sethurimal, P.; Ramachandran, T. Fast Kinetics and High Adsorption Capacity of Green Extract Capped Superparamagnetic Iron Oxide Nanoparticles for the Adsorption of Ni(II) Ions. J. Ind. Eng. Chem. 2018, 59, 230–241.

Jain, A. K.; Gupta, V. K.; Bhattachar, A.; Suhas. Utilization of Industrial Waste Products as Adsorbents for the Removal of Dyes. J. Hazard. Mater. 2003, 101, 31–42.

Chandra, V.; Park, J.; Chun, Y.; Lee, J. W.; Hwang, L.-C.; Kim, K. S. Water-Dispersible Magnetite-Reduced Graphene Oxide Composites for Arsenic Removal. ACS Nano 2010, 4, 3979–3986.

Tejada, C.; Villabona, A.; Garcia, L. Adsorption of Metal N. Residues En Aguas Residuales Usando Materiales de Origen Biológico Adsorption of Heavy Metals in Waste Water Using Biological Materials. Tecnoligías 2015, 18, 723–7999.

Demirbas, A. Effects of Temperature and Particle Size on Bio-Char Yield from Pyrolysis of Agricultural Residues. J. Anal. Appl. Pyrolysis 2004, 72, 243–248.

Hossain, M. K.; Strezov, V.; Chan, K. Y.; Ziółkowski, A.; Nelson, P. F. Influence of Pyrolysis Temperature on Production and Nutrient Properties of Wastewater Sludge Biochar. J. Environ. Manage. 2011, 92, 223–228.

Rodríguez, F.; Cruz, Y.; Estiati, I.; Saldarriaga, J. F. Kinetic Study of Corn and Sugarcane Waste Oxidative Pyrolysis. Energies 2019, 12, No. 4594.

Ahmad, M.; Rajapaksha, A. U.; Lim, J. E.; Zhang, M.; Bolan, N.; Mohan, D.; Vithanage, M.; Lee, S. S.; Lee, S. S. Biochar as a Sorbent for Contaminant Management in Soil and Water: A Review. Chemosphere 2014, 99, 19–33.

Cao, Y.; Xiao, W.; Shen, G.; Ji, G.; Zhang, Y.; Gao, C.; Han, L. Carbonization and Ball Milling on the Enhancement of Pb(II) Adsorption by Wheat Straw: Competitive Effects of Ion Exchange and Precipitation. Bioresour. Technol. 2019, 273, 70–76.

Pouretedal, H. R.; Sadegh, N. Effective Removal of Aminocillin, Cephalexin, Tetracycline and Penicillin G from Aqueous Solutions Using Activated Carbon Nanoparticles Prepared from Vine Wood. J. Water Process Eng. 2014, 1, 64–73.

Zhang, P.; Li, Y.; Cao, Y.; Han, L. Characteristics of Tetracycline Adsorption by Cow Manure Biochar Prepared at Different Pyrolysis Temperatures. Bioresour. Technol. 2019, 285, No. 121348.

Sulyman, M.; Namiesnik, J.; Gierak, A. Low-Cost Adsorbents Derived from Agricultural By-Products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review. Pol. J. Environ. Stud. 2017, 26, 479–510.

Tamiressi, S.; Bouhidel, K.-E. Treatment of Tannery Unhaired Wastewater Using Carbon Dioxide and Zinc Cations for Greenhouse Gas Capture, Pollution Removal and Water Recycling. J. Water Process Eng. 2020, 34, No. 101210.

Senoz, E.; Wool, R. P.; McChalicher, C. W. J.; Hong, C. K. Physical and Chemical Changes in Feather Keratin during Pyrolysis. Polym. Degrad. Stab. 2012, 97, 297–307.

Palomino Amorín, C. C.; Vargas Parker, R.; Visitación Figueroa, L. Aprovechamiento de Pelos de Vacuno Del Proceso de Pelambre Enzimático de Las Curtiembres En La Remoción de Plomo. Rev. Soc. Quim. Perú 2016, 82, 183–195.

Azizogohar, R.; Dalai, A. K. Steam and KOH Activation of Biochar: Experimental and Modeling Studies. Microporous Mesoporous Mater. 2008, 110, 413–421.

Byrne, J. F.; Marsh, H. Porosity in Carbons: Characterization in Applications; HodderArnold: London, 1994.

Lozano-Castello, D.; Lillo-Rodenas, M. A.; Cazorla-Amaro, D.; Linarez-Solano, A. Preparation of Activated Carbons from Spanish Anthracite: I. Activation by KOH. Carbon 2001, 39, 741–749.

Rodríguez-Reinoso, F.; Molina-Sabio, M. Textural and Chemical Characterization of Microporous Carbons. Adv. Colloid Interface Sci. 1998, 76–77, 271–294.

Calamari, D.; Zuccato, E.; Castiglioni, S.; Bagnati, R.; Fanelli, R. Strategic Survey of Therapeutic Drugs in the Rivers Po and Lambro in Northern Italy. Environ. Sci. Technol. 2003, 37, 1241–1248.

Hirsch, R.; Ternes, T.; Haberer, K.; Kratz, K.-L. Occurrence of Antibiotics in the Aquatic Environment. Sci. Total Environ. 1999, 225, 109–118.

Hashem, Md. A.; Nur-A-Tomal, Md. S.; Bushra, S. A. Oxidation-Coagulation-Filtration Processes for the Reduction of Sulphide from the Hair Burning Liming Wastewater in Tannery. J. Clean Prod. 2016, 127, 339–342.

Liu, H.; Ning, W.; Cheng, P.; Zhang, J.; Wang, Y.; Zhang, C. Evaluation of Animal Hairs-Based Activated Carbon for Sorption of Norfloxacin and Acetaminophen by Comparing with Cattail Fiber-Based Activated Carbon. J. Anal. Appl. Pyrolysis 2013, 101, 156–165.

Prados, G. Tratamiento de Aguas Para La Eliminación de Antibioticos -Nitromidasizales- Mediante Adsorción Sobre Carbón Activado y Tecnologías Avanzadas de Oxidación, 2010.

Chen, T.; Zhang, Y.; Wang, H.; Lu, W.; Zhou, Z.; Zhang, Y.; Ren, L. Influence of Pyrolysis Temperature on Characteristics and Heavy Metal Adsorptive Performance of Biochar Derived from Municipal Sewage Sludge. Bioresour. Technol. 2014, 164, 47–54.

Tórres Filho, A.; Lange, L. C.; de Melo, G. C. B.; Praes, G. E. Pyrolysis of Chromium Rich Tanning Industrial Wastes and Utilization of Carbonized Wastes in Metallurgical Process. Waste Manage. 2016, 48, 448–456.

Yilmaz, O.; Cem Kantarli, I.; Yuksel, M.; Saglam, M.; Yanik, J. Conversion of Leather Wastes to Useful Products. Resour., Conserv. Recycl. 2007, 49, 436–448.

Li, Y.; Chang, F.; Huang, B.; Song, Y.; Zhao, H.; Wang, K. Activated Carbon Preparation from Pyrolysis Char of Sewage Sludge and Its Adsorption Performance for Organic Compounds in Sewage. Fuel 2020, 266, No. 117053.

Bellachemi, M.; Djelaila, S. Removal of Aminocillin Antibiotic from Aqueous Solutions by Date Pits Activated Carbons. Environ. Process. 2017, 4, 549–561.

Li, H.; Hu, J.; Wang, X.; An, L. Development of a Bio-Inspired Photo-Recyclable Feather Carbon Adsorbent towards Removal of Aminocillin Residue in Aqueous Solutions. Chem. Eng. J. 2019, 373, 1380–1388.

Mounsi, G.; Alahabadi, A.; Yaghmaeian, K.; Eskandari, M. Preparation, Characterization and Adsorption Potential of the NH4Cl-Induced Activated Carbon for the Removal of Aminocillin Antibiotic from Water. Chem. Eng. J. 2013, 217, 119–128.

García, E. V. Desarrollo de materiales para adsorción. Doctoral Thesis, 2014.

Sulyman, M.; Namiesnik, J.; Gierak, A. Low-Cost Adsorbents Derived from Agricultural by-Products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review. Pol. J. Environ. Stud. 2017, 26, 479–510.

Hall, K. E.; Spokas, K. A.; Gami, B.; Cox, L.; Papiernik, S. K.; Koskinen, W. C. Glyphosate Sorption/Desorption on Biochars - Interactions of Physical and Chemical Processes. Pest Manage. Sci. 2018, 74, 1206–1212.
Bioavailability of Amoxicillin. Int. J. Antimicrob. Agents Pest Manage. Sci. 2006, 27, 428–433.

(82) Mansouri, H.; Carmona, R. J.; Gomis-Berenguer, A.; Souissi-Najar, S.; Ouederni, A.; Ania, C. O. Competitive Adsorption of Ibufrofen and Amoxicillin Mixtures from Aqueous Solution on Activated Carbons. J. Colloid Interface Sci. 2015, 449, 252–260.

(83) Hui, T. S.; Zaini, M. A. A. Potassium Hydroxide Activation of Activated Carbon: A Commentary. Carbon Lett. 2015, 16, 275–280.

(84) Sellaou, L.; Lima, E. C.; Dotto, G. L.; Lamine, A. B. Adsorption of Amoxicillin and Paracetamol on Modified Activated Carbons: Equilibrium and Positional Entropy Studies. J. Mol. Liq. 2017, 234, 375–381.

(85) Moreno Piraján, J. Adsorción de Compuestos Fenólicos Sobre Carbones Activados Modificados Químicamente: Efecto Del Sustituyente En El Anillo Aromático En Las Interacciones Carbón Activado-Adsorbato. Afnidad Rev. Quím. Teórica Appl. 2017, 74, 194–201.

(86) Okman, I.; Karagöz, S.; Tay, T.; Erdem, M. Activated Carbons from Grape Seeds by Chemical Activation with Potassium Carbonate and Potassium Hydroxide. Appl. Surf. Sci. 2014, 293, 138–142.

(87) Ruiz, H.; Zambrano, M.; Giraldo, L.; Sierra, R.; Moreno-Piraján, J. C. Production and Characterization of Activated Carbon from Oil-Palm Shell for Carboxylic Acid Adsorption. Orient. J. Chem. 2015, 31, 753–762.

(88) de Franco, M. A. E.; de Carvalho, C. B.; Bonetto, M. M.; Soares, R.; de, P.; Félix, L. A. Removal of Amoxicillin from Water by Adsorption onto Activated Carbon in Batch Process and Fixed Bed Column: Kinetics, Isotherms, Experimental Design and Breakthrough Curves Modelling. J. Cleaner Prod. 2017, 161, 947–956.

(89) Tran, H. N.; You, S.-J.; Hosseini-Bandegharaei, A.; Chao, H.-P. Mistakes and Inconsistencies Regarding Adsorption of Contaminants from Aqueous Solutions: A Critical Review. Water Res. 2017, 120, 88–116.

(90) Alajrani, M. N.; Alsgaer, O. A. Removal of Antibiotics from Water by Polymer of Intrinsic Microporosity: Isotherms, Kinetics, Thermodynamics, and Adsorption Mechanism. Sci. Rep. 2020, 10, No. 794.

(91) Benjedin, S.; Romero-Can, L. A.; Pérez-Cadenas, A. F.; Bautista-Toledo, M. I.; Lotfi, E. M.; Carrasco-Marin, F. Removal of Emerging Pollutants Present in Water Using an E. Coli Biofilm Supported on Activated Carbons Prepared from Argan Wastes: Adsorption Studies in Batch and Fixed Bed. Sci. Total Environ. 2020, 720, No. 137491.

(92) Ren, L.; Zhou, D.; Wang, J.; Zhang, T.; Peng, Y.; Chen, G. Biomaterial-Based Flower-like MnO2@Carbon Microspheres for Rapid Adsorption of Amoxicillin from Wastewater. J. Mol. Liq. 2020, 309, No. 110374.

(93) Lima, E. C.; Cestari, A. R.; Adebayo, M. A. Comments on the Paper: A Critical Review of the Applicability of Avrera Fractional Kinetic Equation in Adsorption-Based Water Treatment Studies. Desalin. Water Treat. 2016, 57, 19566–19571.

(94) Lima, E. C.; Adebayo, M. A.; Machado, F. In Chapter 3. Kinetic and Equilibrium Models of Adsorption. Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications; Springer International Publishing: New York, 2015; pp 33–70.

(95) Tran, H. N.; You, S.-J.; Hosseini-Bandegharaei, A.; Chao, H.-P. Mistakes and Inconsistencies Regarding Adsorption of Contaminants from Aqueous Solutions: A Critical Review. Water Res. 2017, 120, 88–116.

(96) Volesky, B. Biosorption and Me. Water Res. 2007, 41, 4017–4029.

(97) Jaramillo, J.; Alvarez, P. M.; Gómez-Serrano, V. Oxidation of Activated Carbon by Dry and Wet Methods Surface Chemistry and Textural Modifications. Fuel Process. Technol. 2010, 91, 1768–1775.

(98) Boehm, H. P. Some Aspects of the Surface Chemistry of Carbon Blacks and Other Carbons. Carbon 1994, 32, 759–769.

(99) Pawlicka, A.; Doczekalska, B. Determination of Surface Oxygen Functional Groups of Active Carbons According to the Boehm’s Titration Method. Ann. Warsaw Univ. Life Sci.–SGGW, Anim. Sci. 2013, 84, 11–14.

(100) Abukhadra, M. R.; Adlii, A.; Bakry, B. M. Green Fabrication of Bentonite/Chitosan@cobalt Oxide Composite (BE/CH@Co) of Enhanced Adsorption and Advanced Oxidation Removal of Congo Red Dye and Cr (VI) from Water. Int. J. Biol. Macromol. 2019, 126, 402–408.

(101) Mojiri, A.; Vakili, M.; Farray, H.; Aziz, S. Q. Combined Oxide Oxidation Process and Adsorption Methods for the Removal of Acetaminophen and Amoxicillin from Aqueous Solution; Kinetic and Optimisation. Environ. Technol. Innov. 2019, 15, No. 100404.

(102) Ramírez-Franco, J. H.; Galeano, L.-A.; Vicente, M.-A. Fly Ash as Photo-Fenton Catalyst for the Degradation of Amoxicillin. J. Environ. Chem. Eng. 2019, 7, No. 103274.

(103) Yasmeen, S.; Kabiraz, M. K.; Saha, B.; Qadri, M. R.; Gafur, M. A.; Masum, S. M. Chromium (VI) Ions Removal from Tannery Effluent Using Chitosan-Microcrystalline Cellulose composite as Adsorbent. Int. J. Pure Appl. Chem. 2016, 10, 1–14.

(104) Singh, J.; Kumar, S.; Dhaliwal, A. S. Controlled Release of Amoxicillin and Antioxidant Potential of Gold Nanoparticles-Xanthan Gum/Poly (Acrylic Acid) Biodegradable Nanocomposite. J. Drug Delivery Sci. Technol. 2020, SS, No. 101384.

(105) Bebu, A.; Szabó, L.; Leopold, N.; Berindean, C.; David, L. IR, Raman, SERS and DFT Study of Amoxicillin. J. Mol. Struct. 2011, 993, 52–56.

(106) Zha, X. S.; Zhou, Y.; Jin, X.; Chen, Z. The Removal of Amoxicillin from Wastewater Using Organobentonite. J. Environ. Manage. 2013, 129, 569–576.

(107) Guo, X.; Zhang, L.; Wang, Z.; Sun, Y.; Liu, Q.; Dong, W.; Hao, A. Fluorescent Carbon Dots Based Sensing System for Detection of Enrofloxacin in Water Solutions. Spectrochim. Acta, Part A 2019, 219, 15–22.

(108) Yang, C.; Wang, L.; Yu, Y.; Wu, P.; Wang, F.; Liu, S.; Luo, X. Highly Efficient Removal of Amoxicillin from Water by Mg-Al Layered Double Hydroxide/Cellulose Nanocomposite Beads Synthesized through in-Situ Coprecipitation Method. Int. J. Biol. Macromol. 2020, 149, 93–100.

(109) ASTMInternational. ASTM D1509 - 18 Standard Test Methods for Carbon Black—Heating Loss, 2018, Vol. I.

(110) Kim, K. C.; Yoon, T.-U.; Bae, Y.-S. Applicability of Using CO2 Adsorption Isotherms to Determine BET Surface Areas of Porous Materials. Microporous Mesoporous Mater. 2016, 224, 294–301.

(111) Yuan, T.; He, W.; Yin, G.; Xu, S. Comparison of Bio-Chars Formation Derived from Fast and Slow Pyrolysis of Walnut Shell. Fuel 2020, 261, 569–576.

(112) Dong, J.; Tang, Y.; Nzhou, A.; Chi, Y.; Weiss-Hortala, E.; Ni, M. Life Cycle Assessment of Pyrolysis, Gasification and Incineration Waste-to-Energy Technologies: Theoretical Analysis and Case Study of Commercial Plants. Sci. Total Environ. 2018, 626, 744–753.

(113) Adnana, D.; Wan Daud, W. M. A.; Aroua, M. K. Preparation and Characterization of Activated Carbon from Palm Shell by Chemical Activation with K2CO3. Bioresour. Technol. 2007, 98, 145–149.

(114) Ospona-guarín, V. M.; Buttrago-sierra, R.; López-lópez, D. P. Preparación y Caracterización de Carbón Activado a Partir de Torta de Higuerilla Preparation and Characterization of Activated Carbon from Castor De-Oiled Cake. Tecno Lóg. 2014, 17, 75–84.