






## Article

# Removal of Cefuroxime from Soils Amended with Pine Bark, Mussel Shell and Oak Ash

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**Abstract:** The global increase in antibiotics consumption has caused hazardous concentrations of these antimicrobials to be present in soils, mainly due to the spreading of sewage sludge (or manure or slurry) and wastewater, and they could enter the food chain, posing serious risks to the environment and human health. One of these substances of concern is cefuroxime (CFX). To face antibiotics-related environmental pollution, adsorption is one of the most widely used techniques, with cost-effective and environmentally friendly byproducts being of clear interest to retain pollutants and increase the adsorption capacity of soils. In light of this, in this work, three low-cost bioadsorbents (pine bark, oak ash, and mussel shell) were added to different soil samples (at doses of 12 and 48 t/ha) to study their effects on the adsorption of CFX. Specifically, batch experiments were carried out for mixtures of soils and bioadsorbents, adding a range of different antibiotic concentrations at a fixed ionic strength. The results showed that the addition of pine bark (with pH = 3.99) increased the adsorption to 100% in most cases, while oak ash (pH = 11.31) and mussel shell (pH = 9.39) caused a clearly lower increase in adsorption (which, in some cases, even decreased). The Freundlich and linear models showed rather good adjustment to the experimental data when the bioadsorbents were added at both doses, while the Langmuir model showed error values which were too high in many cases. Regarding desorption, it was lower than 6% for the soils without bioadsorbents, and there was no desorption when the soils received bioadsorbent amendments. These results show that the addition of appropriate low-cost bioadsorbents to soils can be effective for adsorbing CFX, helping in the prevention of environmental pollution due to this emerging contaminant, which is a result of clear relevance to environmental and human health.

**Keywords:** adsorption; antibiotics; byproducts; desorption; soil



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## 1. Introduction

Pharmaceuticals are broadly used worldwide, generating high concentrations of substances such as antibiotics in wastewaters, which can be released to different environmental compartments [1]. The massive use of antibiotics has caused their widespread presence in the environment, with derived pollution detected in soils, sediments, sludges, water, plants, and aquatic animals [2,3]. The time required for the degradation of antibiotics in the environment depends on many factors, such as the concentration and chemical structure of the pollutant, as well as the characteristics of the affected soils or sediments (including the humic acid content, humidity, pH, temperature, sorption capacity, presence of inorganic matter, and availability of oxygen and microorganisms that support the biodegradation

process) [4,5]. We note that between 20% and 97% of any dose of most antibiotics administered to humans and animals is excreted as active substances [6,7]. Specifically, the incomplete absorption of antibiotics by humans entails the discharge of large quantities of these pharmaceuticals in municipal wastewater treatment plants (WWTPs) [1] which, together with their inefficiency at removing antibiotics [8], is the main cause of this pollution problem. These WWTP coexist with and contact relevant amounts of microorganisms and antibiotic residues for prolonged periods of time, triggering the additional problem of increasing antibiotic resistance [9–11]. The increase in antibiotic-resistant bacteria (ARB) is a major problem for public health due to the fact that infections caused by these resistant microbes are difficult to treat, with COVID-19 deriving an additional rise in antibiotic consumption [12], also affecting the general levels of antimicrobial resistance (AMR) [13].

The removal of antibiotics in WWTPs by means of conventional treatments is limited to 50–80%, depending on the antibiotics' physicochemical properties [14–16]. In this regard, the antibiotic CFX has been detected in wastewater at  $\mu\text{g/L}$  and  $\text{ng/L}$  levels [17] as well as in surface waters, with the highest concentration reaching 210  $\mu\text{g/L}$  for wastewater from the pharmaceutical industry and hospitals around the world [18,19]. A study carried out in multiple urban wastewaters in Germany showed CFX concentrations up to 6196  $\text{ng/L}$  and 1957  $\text{ng/L}$  in influent and effluent samples, respectively [20].

The spreading of wastewater and sewage sludge is a potential way to introduce pharmaceutical compounds into waterbodies and soils [21,22]. The use of reclaimed wastewater for the irrigation of crops is an important source of ARB and antibiotic resistant genes (ARGs) in agricultural soils [23]. Furthermore, it is quite common that annual fertilization with repeated applications of inappropriate doses of sewage sludge is carried out to provide soil nutrients and organic matter [24,25]. In Europe, for many years, more than 50% of produced sewage sludge is used in agriculture [26–29]. However, the application of sewage sludge to soils may pose a problem for the environment, due to their contents including a wide variety of toxic pollutants [29–32]. Furthermore, emerging pollutants pose an important risk if they are transferred to groundwater because it is a source of drinking water [33–35], and degradation will likely be extremely limited in these aquatic systems [36,37].

Antibiotic residues have different persistence times and transport types in agricultural soils, affected by factors such as adsorption, degradation, and lixiviation [38,39]. Their dissipation rates, expressed as half-lives, can range from 18.6 to 21.3 days for sulfonamide antibiotics, whereas for tetracyclines, they can be up to 1–2 months, and for enrofloxacin, they can be approximately 7–8 months [40]. Conde-Cid et al. [41] observed no degradation for three sulfonamides in the dark, while under simulated sunlight, after 2 h of exposure, sulfachloropyridazine and sulfadiazine degraded by 90%, and sulfamethazine degraded by 80% after 8 h. Rodríguez-López et al. [42] studied the degradation of clarithromycin, ciprofloxacin, and trimethoprim under different conditions, observing that after 1 h of exposure to light radiation, 85% of the ciprofloxacin degraded. They also reported that clarithromycin degradation was pH-dependent, obtaining the highest degradation percentage (30%) at  $\text{pH} = 4$ , whereas trimethoprim reached less than 5%. A study carried out in China's Xuanwu Lake found four cephalosporins degraded abiotically in the surface water in the dark, with half-lives between 2.7 and 18.7 days, while the time decreased by up to 2.2–5 days under exposure to simulated sunlight [43].

Adsorption is widely used to remove antibiotics due to its simple design and because it is environmentally friendly, economic, and versatile [44]. Its efficiency depends on the type of adsorbent, adsorbate properties, and waste stream (in the case of waste liquids) composition [45,46]. Depending on the pH of the medium and the  $\text{pK}_a$  of the pollutant, sorption is also affected by the charges of the molecular forms of the sorbates, (i.e., neutral, cationic, anionic, or zwitterionic) [47]. Furthermore, developing cost-effective and environmentally friendly treatment techniques for the remediation of specific contaminants (such as antibiotics) present in soils is imperative [48,49]. The need to deal with agricultural and industrial wastes or byproducts has drawn additional attention to the adsorption field,

due to the eco-friendly approach and advantages of using these materials, such as their easy access, high availability, and low cost compared with synthetic or other high-cost materials [50]. Some examples were shown by Ahmed et al. [51], whereas other specific previous studies showed that the addition of pine bark to soils increased the retention of three sulfonamides [52]. Also, in a previous work, we studied the effectiveness of the byproducts pine bark, oak ash, and mussel shell as bioadsorbents for the antibiotics amoxicillin, ciprofloxacin, and trimethoprim, with good results [53], and other studies focused on the retention of CFX in soils [54] and onto the same byproducts [55], although no research was performed dealing with the retention or release of CFX on or from soils amended with these sorbents.

In light of the above background, the objective of this work was to characterize the potential of three bioadsorbents (pine bark, oak ash, and mussel shell) to retain or remove the antibiotic cefuroxime (CFX) after the amendment of six different soils at two doses (12 and 48 t/ha). The results of the investigation could be of relevance regarding the management of soils contaminated with this emerging pollutant as well as the recycling of byproducts, potentially facilitating sustainability and a circular economy.

## 2. Materials and Methods

### 2.1. Soils and Bioadsorbents

To carry out this research, six different soil samples were selected, with all of them coming from different agricultural areas in Galicia (northwest Spain). These soils are devoted to vineyards (named VP1, VP2, and VO), and corn production (denoted as C1, C2, and C3). In a previous work [54], we studied CFX adsorption onto 23 different soils, and we selected among them the 6 soils with the lowest CFX adsorption capacities for use in the current research. The selected soils were amended with various bioadsorbents to assess the eventual modification of CFX adsorption onto these soils. The methods used for their characterization are presented in the Supplementary Materials, with the results shown in Table S1.

Three byproducts were used as bioadsorbents, with two of them coming from the forestry industry—pine bark, provided by Geolia (Madrid, Spain), and oak ash from a combustion boiler in Lugo (Spain)—while the third one was from the canning industry: mussel shell, provided by Abonomar S.L (Pontevedra, Spain).

Table 1 shows the results corresponding to the characterization of different parameters for the three bioadsorbents. The pH values were determined using a soil-to-liquid ratio of 1:2.5. The contact time for the pH in water was 10 min, while for the pH in KCl, it was 2 h [55]. The measurements were made with a CRISON pH meter, model 2001 (Crison, Barcelona, Spain). The available phosphorous was determined by the Olsen method [56]. To carry out this method, 2.5 grams of bioadsorbent was weighted, and 50 mL of the extracting solution (sodium bicarbonate at pH = 8.5) was added. This mixture was subjected to shaking for 30 min before utilizing visible spectrophotometry for P quantification. Determination of the total C and N was carried out using an elemental analysis method with a LECO TRUSPEC CHNS instrument (Leco, St. Joseph, MI, USA). The exchangeable cations ( $Ca_e$ ,  $Mg_e$ ,  $Na_e$ ,  $K_e$ , and  $Al_e$ ) were displaced using a 1 M  $NH_4Cl$  solution in a 1:10 sorbent:solution ratio, with subsequent quantification by means of atomic absorption spectrophotometry using a Perkin Elmer AAnalyst 200 apparatus (Perkin Elmer, Waltham, MA, USA). The total contents of the elements analyzed were determined through the EPA 3051 method using acid digestion with a 65%  $HNO_3$  solution. The measurements were performed by means of an ICP-MS (Perkin-Elmer, USA). To determine the total non-crystalline Fe and Al contents, a specific type of extraction was performed using ammonium oxalate buffered at a pH level of 3, followed by stirring for 4 h in the dark, adding 5 drops of 0.25% superfloc to the resulting extract, centrifuging at 2000 rpm for 10 min, and filtering and diluting the supernatant to a 1:5 ratio. Finally, Fe and Al in non-crystalline form ( $Fe_o$  and  $Al_o$ ) were quantified with atomic absorption spectrophotometry (Perkin-Elmer, USA).

**Table 1.** Characteristics of the bioadsorbent materials.  $Ca_e$ ,  $Mg_e$ ,  $Na_e$ ,  $K_e$ , and  $Al_e$  = elements in the exchange complex; Sat. Al = Al saturation in the exchange complex; eCEC = effective cation exchange capacity; XT = total content of the element (X); and  $Al_o$  and  $Fe_o$  = non-crystalline Al and Fe, respectively. Average values ( $n = 3$ ) with coefficients of variation always <5%.

| Parameter           | Unit                               | Pine Bark | Oak Ash | Mussel Shell |
|---------------------|------------------------------------|-----------|---------|--------------|
| C                   | %                                  | 48.70     | 13.23   | 11.43        |
| N                   | %                                  | 0.08      | 0.22    | 0.21         |
| C/N                 |                                    | 608.75    | 60.14   | 55.65        |
| pH <sub>water</sub> |                                    | 3.99      | 11.31   | 9.39         |
| pH <sub>KCl</sub>   |                                    | 3.42      | 13.48   | 9.04         |
| $Ca_e$              | cmol <sub>c</sub> kg <sup>-1</sup> | 5.38      | 95.0    | 24.75        |
| $Mg_e$              | cmol <sub>c</sub> kg <sup>-1</sup> | 2.70      | 3.26    | 0.72         |
| $Na_e$              | cmol <sub>c</sub> kg <sup>-1</sup> | 0.46      | 12.17   | 4.37         |
| $K_e$               | cmol <sub>c</sub> kg <sup>-1</sup> | 4.60      | 250.65  | 0.38         |
| $Al_e$              | cmol <sub>c</sub> kg <sup>-1</sup> | 1.78      | 0.07    | 0.03         |
| eCEC                | cmol <sub>c</sub> kg <sup>-1</sup> | 14.92     | 361.15  | 30.25        |
| Sat Al              | %                                  | 11.93     | 0.02    | 0.10         |
| Available P         | mg kg <sup>-1</sup>                | 70.45     | 462.83  | 54.17        |
| $Na_T$              | mg kg <sup>-1</sup>                | 68.92     | 2950    | 5174.00      |
| $Mg_T$              | mg/kg                              | 473.55    | 26,171  | 980.66       |
| $Al_T$              | mg kg <sup>-1</sup>                | 561.50    | 14,966  | 433.24       |
| $K_T$               | mg kg <sup>-1</sup>                | 737.84    | 99,515  | 202.07       |
| $Ca_T$              | mg kg <sup>-1</sup>                | 2318.81   | 136,044 | 280,168      |
| $Cr_T$              | mg kg <sup>-1</sup>                | 1.88      | 36.28   | 4.51         |
| $Mn_T$              | mg kg <sup>-1</sup>                | 30.19     | 10554   | 33.75        |
| $Fe_T$              | mg kg <sup>-1</sup>                | 169.78    | 12,081  | 3535         |
| $Co_T$              | mg kg <sup>-1</sup>                | 0.20      | 17.25   | 1.02         |
| $Ni_T$              | mg kg <sup>-1</sup>                | 1.86      | 69.25   | 8.16         |
| $Cu_T$              | mg kg <sup>-1</sup>                | <LD       | 146.33  | 6.72         |
| $Zn_T$              | mg kg <sup>-1</sup>                | 6.98      | 853.00  | 7.66         |
| $As_T$              | mg kg <sup>-1</sup>                | <LD       | 8.36    | 1.12         |
| $Cd_T$              | mg kg <sup>-1</sup>                | 0.13      | 19.93   | 0.07         |
| $Al_o$              | mg kg <sup>-1</sup>                | 315.0     | 8323    | 178.33       |
| $Fe_o$              | mg kg <sup>-1</sup>                | 74.0      | 4233    | 171.0        |

Other details related to additional previously published characteristics are provided in the Supplementary Materials.

These bioadsorbents were added to soil samples in doses of 12 and 48 t/ha. The mixtures reached the pH values that are shown in Table S2 (Supplementary Materials).

## 2.2. Chemicals and Reagents

The antibiotic cefuroxime (CFX) was provided by Sigma Aldrich (Barcelona, Spain) and was of >95% purity. Phosphoric acid (85% extra pure) was supplied by Acros Organics (Barcelona, Spain), acetonitrile (purity  $\geq 99.9\%$ ) was supplied by Fisher Scientific (Madrid, Spain), and  $CaCl_2$  (95% purity) was supplied by Panreac (Barcelona, Spain). All of the reagents needed for the quantification of antibiotics were of HPLC grade.

## 2.3. Adsorption and Desorption Experiments

Batch experiments were carried out to study the adsorption capacity of the mixtures of soil and bioadsorbents. To accomplish this, 5 mL of a 0.005 M  $CaCl_2$  solution (which served as the background electrolyte to maintain a constant ionic strength) received the appropriate amount of antibiotics to achieve different specific CFX concentrations (0, 2.5, 5, 10, 20, 30, 40, and 50  $\mu\text{mol/L}$ ). Then, each of these solutions was added to 2 g of the corresponding mixtures of soil and bioadsorbent. Afterward, the samples were subjected to shaking for 48 h and centrifugated at 4000 rpm for 15 min, with the resulting supernatants being passed

through 0.45  $\mu\text{m}$  nylon-type syringe filters. Previous kinetic studies demonstrated that 48 h is enough time to reach equilibrium.

Quantification of the antibiotic concentrations was performed using HPLC equipment, with all the details provided in the Supplementary Materials.

Figure S1 shows some select chromatograms corresponding to the quantification of CFX.

After the adsorption phase, the desorption experiments were carried out. For this, 5 mL of  $\text{CaCl}_2$  was added to the remaining post-adsorption materials. The samples were shaken for 48 h, centrifugated, filtered, and analyzed in the same conditions as those during the adsorption process.

#### 2.4. Modeling and Statistics

The experimental adsorption data were fitted to the Freundlich (Equation (1)), Langmuir (Equation (2)), and linear (Equation (3)) models [57]:

$$q_e = K_F C_{eq}^n \quad (1)$$

$$q_e = \frac{q_m K_L C_{eq}}{1 + K_L C_{eq}} \quad (2)$$

$$K_d = q_e / C_{eq} \quad (3)$$

where  $q_e$  is the amount of CFX retained (concentration added minus concentration in the equilibrium);  $C_{eq}$  is the CFX concentration in equilibrium;  $K_F$  is the Freundlich adsorption capacity parameter;  $n$  is a parameter related to heterogeneity in adsorption;  $K_L$  is the Langmuir adsorption constant;  $q_m$  is the Langmuir maximum adsorption capacity; and  $K_d$  is the linear model's partition coefficient.

All of the experimental determinations were made in triplicate.

The fitting of the experimental data to the Langmuir, Freundlich, and linear models was performed by means of SPSS Statistics 21 software.

The studies carried out for this research can be seen as the first steps within an overall broader strategy which will need further future works to be completed, both with classic and new scientific tools [58,59].

### 3. Results and Discussion

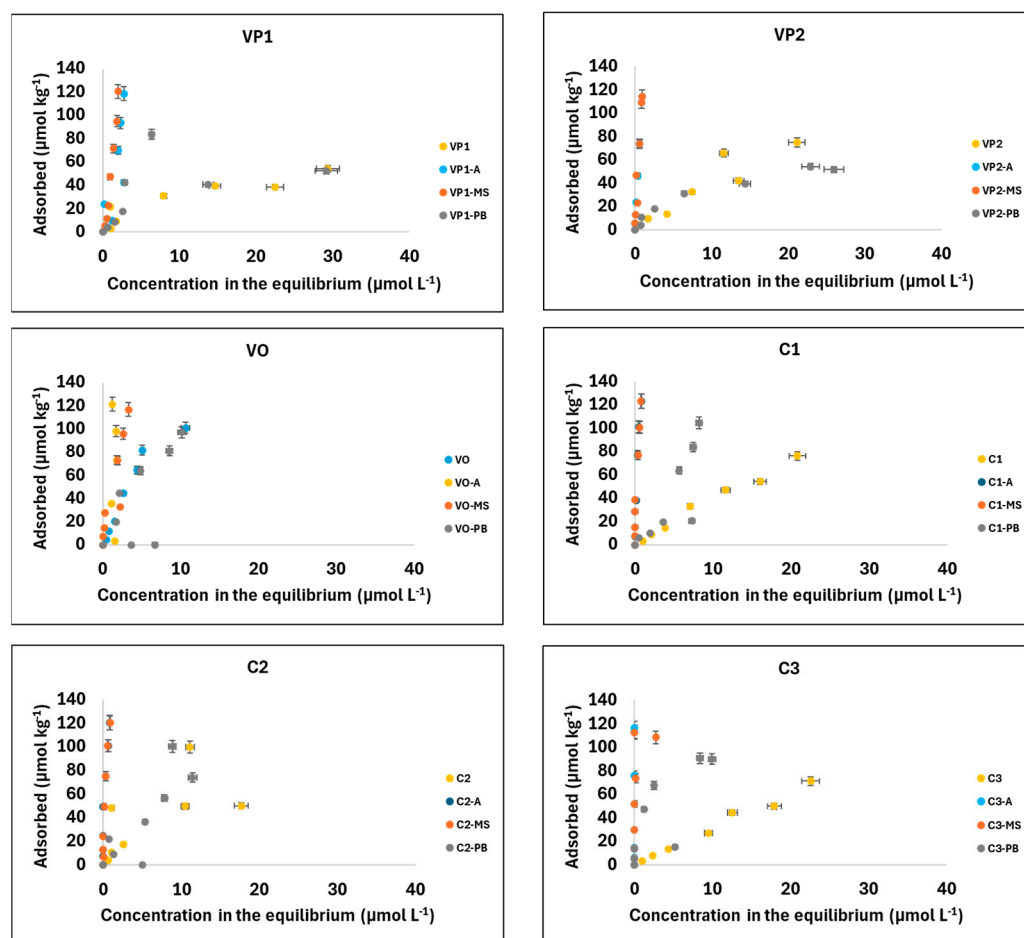
#### 3.1. CFX Adsorption

Figures 1 and 2 show the adsorption curves corresponding to the different soils amended with doses of 12 and 48 t/ha of each of the three bioadsorbents.

Both figures show that, overall, mussel shell (pH = 9.39) was the sorbent with the greatest positive effect on the increase in CFX adsorption for any of the soils receiving both doses of the amendments. In fact, with this byproduct, the concentrations in the antibiotic's equilibrium (expressed in  $\mu\text{mol/L}$ ) were the lowest, being associated with the highest adsorption levels (expressed in  $\mu\text{mol/kg}$ ). In contrast, pine bark (pH = 3.99) showed the weakest effects as an amendment intended to increase CFX adsorption for the soils treated with the three byproducts.

Compared with previous studies [54,60] focused on retention of the same antibiotic on equivalent soils and byproducts but performed for soils and sorbents separately (not mixing the soils and sorbents, which was performed for the first time in the present study), the following comments can be presented. Regarding the adsorption of CFX onto the bioadsorbents (without soil), based on a previous publication by Cela-Dablanca et al. [60], the influence of the pH level was confirmed, with oak ash (pH = 11.31) showing the highest adsorption values (927.95  $\mu\text{mol/kg}$  when a concentration of 50  $\mu\text{mol/L}$  was added), followed by mussel shell (pH = 9.39), with maximum adsorption of 721.65  $\mu\text{mol/kg}$  when a concentration of 50  $\mu\text{mol/L}$  was added, and finally pine bark (pH = 3.99), which presented the lowest adsorption (551.62  $\mu\text{mol kg}^{-1}$  when a concentration of 50  $\mu\text{mol/L}$  was added). Furthermore, in another previous study [54] focused on CFX adsorption by soils (without

bioadsorbents) with different pH values, the authors confirmed that soils with an alkaline pH presented the highest CFX adsorption, with scores oscillating between  $74.86 \mu\text{mol kg}^{-1}$  (for soil with pH = 5.7) and  $123.88 \mu\text{mol/kg}$  (for soil with pH = 8.02).

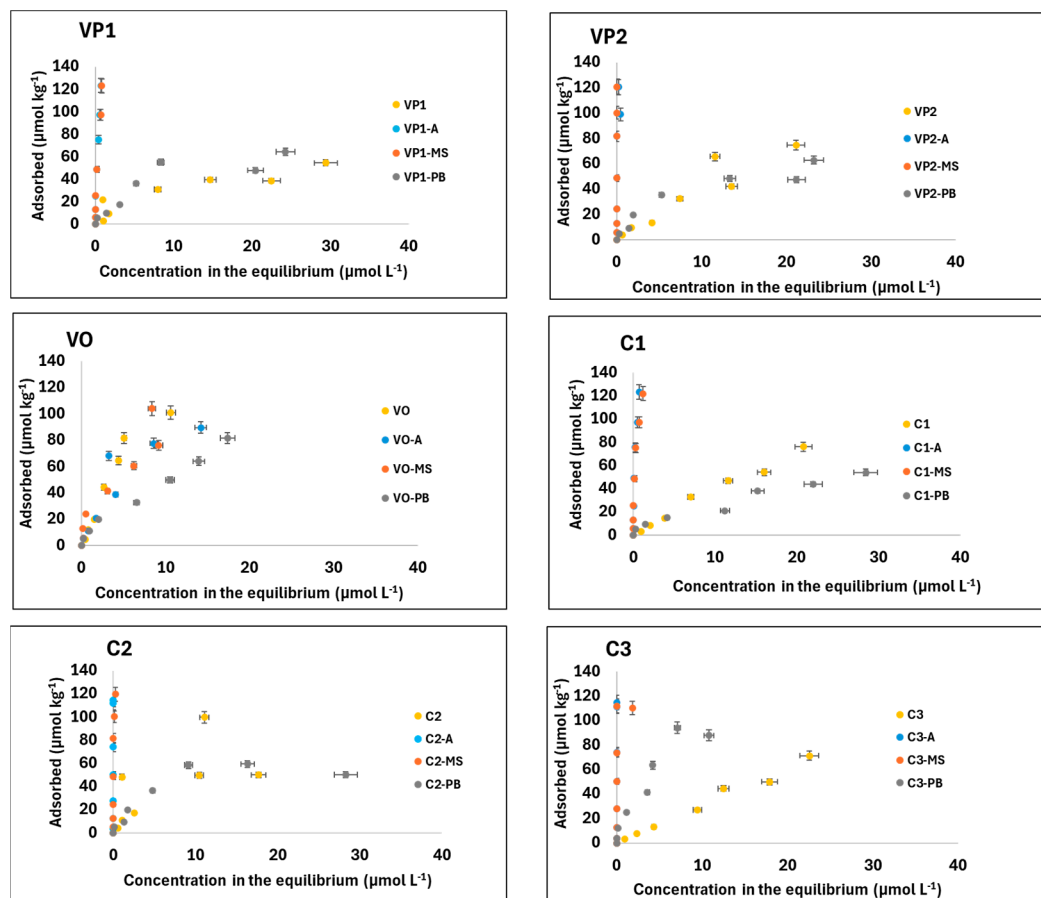


**Figure 1.** Adsorption curves for CFX corresponding to soils without and with bioadsorbents (amended with a dose of 12 t/ha). Average values ( $n = 3$ ) are with coefficients of variation always lower than 5%. Bars indicate standard deviation. C = corn soils; VO and VP = vineyard soils; A = oak ash; MS = mussel shell; and PB = pine bark.

Figures 3 and 4 show the CFX adsorption (as a percentage) for the different antibiotic concentrations added to the soils ( $2.5\text{--}50 \mu\text{mol/L}$ ) without and with the amendment of the three bioadsorbents, which were applied in doses of 12 t/ha (Figure 3) and 48 t/ha (Figure 4).

As shown in Figure 3, when the bioadsorbents were added to soils at a dose of 12 t/ha, the behaviors were different as a function of the byproduct used. Specifically, the addition of mussel shell and oak ash generated an increase in CFX adsorption, reaching values of 100% retention in most cases. However, when pine bark was added to soils, the adsorption increase was significantly lower, and adsorption even decreased in some cases.

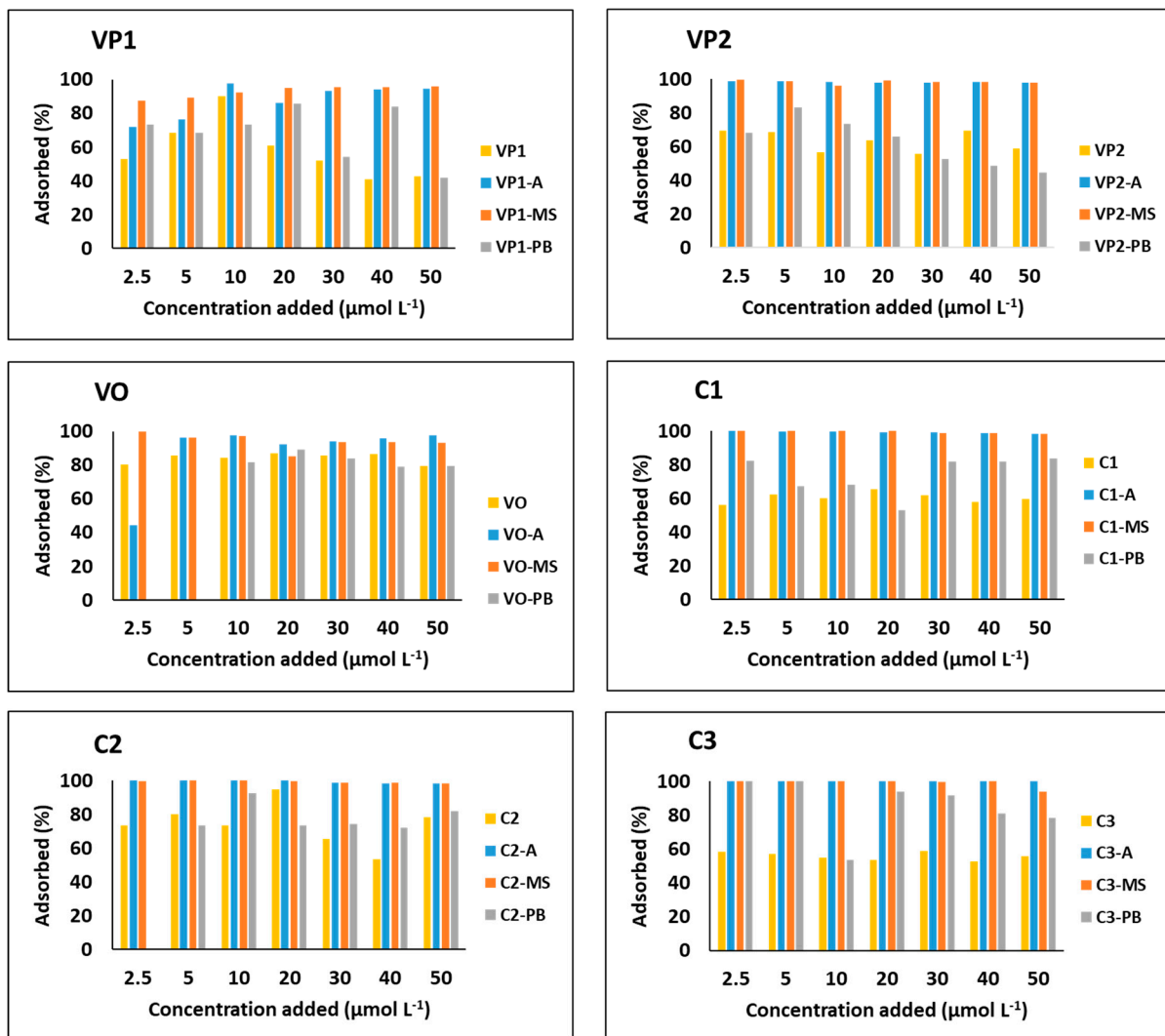




**Figure 2.** Adsorption curves for CFX corresponding to soils without and with bioadsorbents (amended at a dose of 48 t/ha). Average values ( $n = 3$ ) are with coefficients of variation always lower than 5%. Bars indicate standard deviation. C = corn soils; VO and VP = vineyard soils; A = oak ash; MS = mussel shell; and PB = pine bark.

Despite this, in a previous work carried out for other antibiotics (three sulfonamides), Conde-Cid et al. [52] found that adding pine bark to soils increased the adsorption capacity to 99.6%. Once again, it should be noted that mussel shell and oak ash present alkaline pH values (9.39 and 11.31, respectively), while pine bark has a pH level of 3.99. This would suggest that CFX adsorption is pH-dependent. These results were confirmed by the abovementioned previous studies performed separately for soils and bioadsorbents [54,60]. We note that the dissociation constant ( $pK_a$ ) is a parameter having marked relevance regarding the environmental fate of organic compounds [4]. In this sense, the pH level affects the behavior of antibiotics when they are cationic, anionic, or neutral molecules, and it also affects the activity of functional groups in a solution [61]. According to El-Shaboury et al. [62], Lin et al. [63], and Ribeiro and Schmidt [64], cephalosporin structures generally have two or more ionization centers. In the case of CFX, the dissociation constants are  $pka_1 = 3.15$  and  $pka_2 = 10.97$  [64]. At pH values below 3.15, CFX will be in its cationic form, and above pH 10.97, it will be in its anionic form. In the pH range 3.15–10.97 (in which our samples were placed), CFX would be zwitterionic. In this case, the positive charges of the antibiotic ( $NH_4^+$ ) will bind to the negative charges of the sorbents due to electrostatic interactions, while the negative charges of CFX ( $COO^-$ ) could make use of a cationic bridge with negative charges present on the surface of the sorbent materials [65]. Calcium was the predominant cation in most samples used in this study, and it would be the most probable binding element acting as a cationic bridge between the adsorbents and the adsorbate. Soils amended with the bioadsorbents used here generally reach a pH level above 5.5, with the highest values corresponding to amendments with mussel shell and the lowest ones

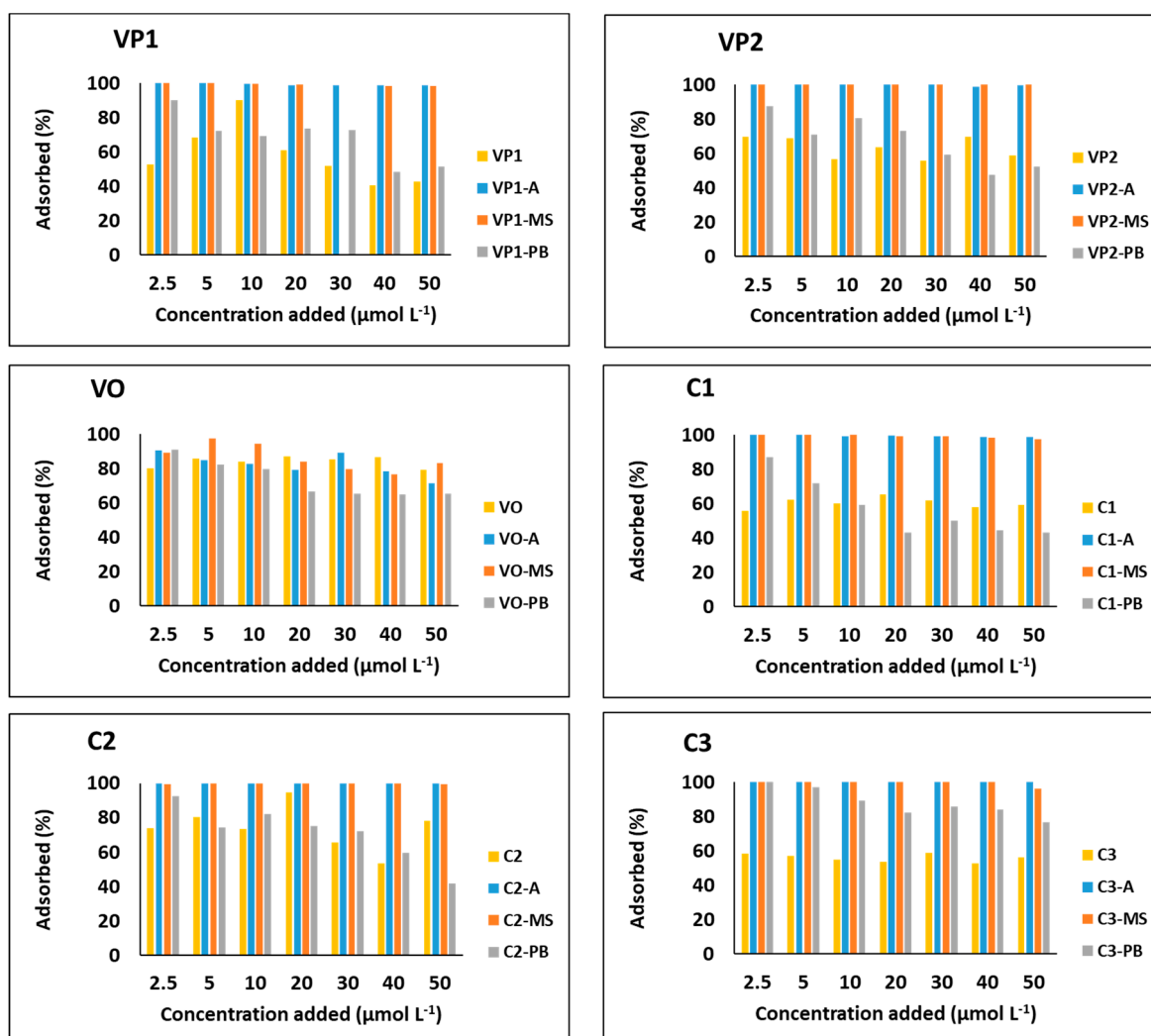
associated with pine bark (which has a pH lower than that of the used soils), particularly for those at doses of 48 t/ha (Table S2, Supplementary Materials). The variable charge components of the soils used in this study (mainly kaolinite, non-crystalline Al and Fe minerals, and organic matter) and non-crystalline minerals of the bioadsorbents (extremely abundant in the case of oak ash) would exhibit a negative charge at these pH values. This negative charge in the soil and bioadsorbent mixture would be greater for higher pH levels (soil with mussel shell and soil with oak ash), favoring electrostatic interactions between these negative charges and the positively charged groups of CFX, or through cationic bridges with the anionic groups of this antibiotic [65]. In contrast, the soils amended with pine bark showed lower CFX adsorption since the pH level was lower than those of the other mixtures, as the high amount of organic matter they provided would present few negative charges. Additionally, pine bark had a lower content of non-crystalline minerals, which provide a negative charge at  $\text{pH} > 6$ , and a lower Ca content to establish cationic bridges between CFX and the soils amended with this byproduct. All of this would explain why this bioadsorbent was less effective in CFX retention than the other two. Furthermore, in acidic conditions, free  $\text{H}^+$  in the medium could contribute to the formation of hydrogen bonds between the adsorbent's surface and the antibiotic [66].



**Figure 3.** Adsorption of CFX (as a percentage) by soils without and with bioadsorbents amended at a dose of 12 t/ha as a function of the concentration of antibiotics added. Average values ( $n = 3$ ) are with coefficients of variation always lower than 5%. C = corn soils; VO and VP = vineyard soils; A = oak ash; MS = mussel shell; and PB = pine bark.



Figure 4 shows the CFX adsorption by soils without bioadsorbents and amended with the three bioadsorbents at a dose of 48 t/ha.



**Figure 4.** Adsorption of CFX (as a percentage) by soils without and with bioadsorbents amended at a dose of 48 t/ha as a function of the concentration of antibiotics added. Average values ( $n = 3$ ) are with coefficients of variation always lower than 5%. C = corn soils; VO and VP = vineyard soils. A = oak ash; MS = mussel shell; and PB = pine bark.

The data obtained corresponding to the addition of the bioadsorbents to the six soils at a dose of 48 t/ha (Figure 4) confirmed an equivalent behavior to that found for the dose of 12 t/ha. The addition of bioadsorbents with alkaline pH levels (oak ash and mussel shell) was associated with the highest increase in adsorption, while the addition of pine bark (with an acidic pH) caused a lower increase (and decreased adsorption in several cases). These results would confirm that CFX adsorption onto these sorbents depends on the pH level. In this regard, a previous study dealing with the adsorption of one cephalosporin (cefixime) by a porous, aluminum-based metal–organic framework–aminoclay nanocomposite reported an increase in antibiotic adsorption when the pH oscillated from 3 to 7, obtaining the maximum adsorption at a pH level of seven [67]. To further evidence the potential relation, statistical analyses were performed, obtaining a significant and positive correlation between adsorption and pH ( $r = 0.440$ ,  $p < 0.05$ ). In a previous study in which the adsorption of amoxicillin by mixtures equivalent to those used here was studied, it was observed that the organic matter content also influenced the adsorption of the antibiotic [68]. Furthermore, previous studies focused on CFX adsorption for soils varying within a wide range of pH

level (4.62–8.02) and organic matter contents (1.09–16.87), showing a clear influence of these two parameters on retention of the antibiotic [54]. However, in the current research, all soil samples had a moderate organic matter content, with the pH level being the most influential characteristic affecting CFX adsorption for the mixtures of soil and bioadsorbent. In addition to the pH level, other properties of the bioadsorbent materials, such as the higher exchangeable Ca content in mussel shell and oak ash and the non-crystalline Al and Fe contents in oak ash, would contribute to explaining the higher increase in CFX adsorption caused by these two materials compared with pine bark [60].

### 3.2. Adsorption Isotherms for Soils and Mixtures of Soil and Bioadsorbents

The fitting of the experimental adsorption results to adsorption equations was evaluated for the Freundlich, Langmuir, and linear models. Table 2 shows the results of the parameters of the adjustments, considering soils without and with bioadsorbents added at a dose of 12 t/ha.

**Table 2.** Parameters of adsorption isotherms for cefuroxime in soils without and with bioadsorbents at a dose of 12 t/ha ( $K_F$  expressed in  $L^n \text{ kg}^{-1} \mu\text{mol}^{1-n}$ ;  $n$  = dimensionless;  $K_L$  expressed in  $L \mu\text{mol}^{-1}$ ;  $q_m$  expressed in  $\mu\text{mol kg}^{-1}$   $K_d$  expressed in  $L \text{ kg}^{-1}$ ; - = error value too high for fitting). C = corn soils; VO and VP = vineyard soils; A = oak ash; MS = mussel shell; and PB = pine bark.

| Sample | Freundlich |        |       |       |       | Langmuir |       |          |         |       | Linear Model |        |       |
|--------|------------|--------|-------|-------|-------|----------|-------|----------|---------|-------|--------------|--------|-------|
|        | $K_F$      | Error  | $n$   | Error | $R^2$ | $K_L$    | Error | $q_m$    | Error   | $R^2$ | $K_d$        | Error  | $R^2$ |
| VP1    | 10.877     | 3.319  | 0.458 | 0.104 | 0.895 | 0.15     | 0.095 | 58.473   | 11.744  | 0.876 | 2.018        | 0.266  | 0.693 |
| VP1-A  | 22.781     | 17.403 | 1.345 | 0.826 | 0.661 | -        | -     | -        | -       | -     | 30.783       | 5.082  | 0.648 |
| VP1-MS | 41.676     | 3.52   | 1.483 | 0.142 | 0.982 | -        | -     | -        | -       | -     | 52.343       | 3.516  | 0.932 |
| VP1-PB | 22.04      | 10.863 | 0.308 | 0.195 | 0.49  | -        | -     | 65.554   | 20.877  | 0.608 | -            | -      | -     |
| VP2    | 6.365      | 3.11   | 0.815 | 0.18  | 0.907 | -        | -     | 225.213  | 188.987 | 0.912 | 3.838        | 0.323  | 0.892 |
| VP2-A  | 120.162    | 2.58   | 0.909 | 0.048 | 0.996 | 0.129    | 0.118 | 1053.162 | 875.508 | 0.995 | 122.871      | 2.444  | 0.994 |
| VP2-MS | 122.858    | 12.836 | 0.959 | 0.235 | 0.916 | -        | -     | -        | -       | -     | 124.267      | 9.223  | 0.916 |
| VP2-PB | 10.765     | 1.548  | 0.499 | 0.049 | 0.98  | 0.13     | 0.03  | 67.645   | 5.521   | 0.983 | 2.345        | 0.241  | 0.811 |
| C1     | 5.135      | 0.958  | 0.881 | 0.068 | 0.988 | 0.013    | 0.008 | 341.167  | 174.058 | 0.989 | 3.699        | 0.122  | 0.983 |
| C1-A   | 137.408    | 7.386  | 0.52  | 0.054 | 0.979 | 2.742    | 0.896 | 174.487  | 24.936  | 0.973 | 169.606      | 18.516 | 0.824 |
| C1-MS  | 122.905    | 14.431 | 0.329 | 0.126 | 0.904 | -        | -     | 211.46   | 172.105 | 0.848 | 169.582      | 18.416 | 0.826 |
| C1-PB  | -          | -      | -     | -     | -     | -        | -     | -        | -       | -     | 9.249        | 1.523  | 0.671 |
| VO     | 21.681     | 4.085  | 0.685 | 0.096 | 0.948 | 0.113    | 0.037 | 193.42   | 37.656  | 0.975 | 11.48        | 1.085  | 0.863 |
| VO-A   | 52.829     | 16.977 | -     | -     | 0.359 | -        | -     | -        | -       | -     | 43.309       | 11.013 | 0.314 |
| VO-MS  | 33.059     | 15.12  | 0.979 | 0.456 | 0.823 | -        | -     | -        | -       | -     | 32.377       | 3.568  | 0.823 |
| VO-PB  | -          | -      | 1.285 | 0.754 | 0.495 | -        | -     | -        | -       | -     | 7.981        | 1.72   | 0.487 |
| C2     | 22.027     | 11.843 | 0.410 | 0.225 | 0.57  | -        | -     | 80.688   | 28.959  | 0.6   | 4.735        | 1.169  | 0.328 |
| C2-A   | 132.409    | 31.22  | 0.511 | 0.408 | 0.77  | -        | -     | -        | -       | -     | 161.564      | 22     | 0.727 |
| C2-MS  | 131.114    | 11.877 | 0.490 | 0.104 | 0.94  | 3.548    | 1.866 | 153.98   | 29.786  | 0.94  | 160.503      | 18.222 | 0.807 |
| C2-PB  | -          | -      | 1.324 | 0.65  | 0.671 | -        | -     | -        | -       | -     | 7.276        | 1.218  | 0.655 |
| C3     | 3.219      | 0.817  | 0.985 | 0.088 | 0.985 | -        | -     | -        | -       | -     | 3.084        | 0.095  | 0.985 |
| C3-A   | -          | -      | -     | -     | -     | -        | -     | -        | -       | -     | -            | -      | -     |
| C3-MS  | -          | -      | -     | -     | -     | -        | -     | -        | -       | -     | -            | -      | -     |
| C3-PB  | 37.349     | 18.209 | 0.330 | 0.258 | 0.661 | -        | -     | 83.349   | 29.002  | 0.624 | 9.619        | 1.828  | 0.517 |

The results indicate that when the bioadsorbents were added at a dose of 12 t/ha, the Freundlich model showed the best adjustment, because 45% of the samples obtained an  $R^2$  value  $> 0.9$ , whereas in the case of the Langmuir and linear models, the values decreased to 25% and 20%, respectively.

The Freundlich affinity coefficient ( $K_F$ ) values ranged between 2.396 and 137.408  $L^n \text{ kg}^{-1} \mu\text{mol}^{1-n}$ , while the  $n$  values oscillated between 0.308 and 1.693. Some authors postulated that when  $n < 1$ , adsorption is carried out in a heterogeneous matrix, with the highest energy sites being occupied first [69]. Meanwhile, when  $n > 1$ , a deviation from the Freundlich equation would occur, such as the eventual existence of irreversible reactions like precipitation [70] or cooperative adsorption [71]. The values of the distribution constant of the linear model ( $K_d$ ) ranged between 2.018 and 169.606  $L \text{ kg}^{-1}$ , whereas those of the Langmuir adsorption constant ( $K_L$ ) were between 0.013 and 3.548  $L \mu\text{mol}^{-1}$ .

Table 3 shows the results of the parameters of the adjustments to the adsorption models considering soils without and with bioadsorbents added at a dose of 48 t/ha. In this case, 62.5% of the samples obtained an  $R^2$  value  $>0.9$  when adjusted to the Langmuir model. This percentage decreased to 54% and 25% when adjusted to the Freundlich and linear models, respectively (Table 3). In this regard, Jafari et al. [72] studied the adsorption of two cephalosporins (cephalexin and cefixime) onto multi-walled carbon nanotubes and obtained a better adjustment to the Freundlich model for the adsorption of cefixime, while cephalexin adsorption fit better to the Langmuir equation.

**Table 3.** Parameters of adsorption isotherms for cefuroxime in soils without and with bioadsorbents at a dose of 48 t/ha ( $K_F$  expressed in  $L^n \text{ kg}^{-1} \mu\text{mol}^{1-n}$ ;  $n$  = dimensionless;  $K_L$  expressed in  $L \mu\text{mol}^{-1}$ ;  $q_m$  expressed in  $\mu\text{mol kg}^{-1}$   $K_d$  expressed in  $L \text{ kg}^{-1}$ ; - = error value too high for fitting). C = corn soils; VO and VP = vineyard soils; A = oak ash; MS = mussel shell; and PB = pine bark.

|        | Freundlich |        |       |       |       | Langmuir |       |         |         |       | Linear Model |         |       |
|--------|------------|--------|-------|-------|-------|----------|-------|---------|---------|-------|--------------|---------|-------|
|        | $K_F$      | Error  | $n$   | Error | $R^2$ | $K_L$    | Error | $q_m$   | Error   | $R^2$ | $K_d$        | Error   | $R^2$ |
| VP1    | 10.877     | 3.319  | 0.458 | 0.104 | 0.895 | 0.150    | 0.095 | 58.473  | 11.744  | 0.876 | 2.018        | 0.266   | 0.693 |
| VP1-A  | 148.757    | 10.363 | 0.714 | 0.094 | 0.979 | 0.848    | 0.567 | 308.951 | 140.343 | 0.972 | 174.349      | 9.055   | 0.958 |
| VP1-MS | 129.954    | 8.905  | 0.592 | 0.102 | 0.973 | 1.635    | 1.073 | 200.034 | 63.88   | 0.961 | 149.227      | 11.307  | 0.933 |
| VP1-PB | 14.658     | 4.505  | 0.455 | 0.112 | 0.879 | 0.157    | 0.071 | 76.091  | 12.693  | 0.918 | 2.922        | 0.463   | 0.606 |
| VP2    | 6.365      | 3.11   | 0.815 | 0.18  | 0.907 | -        | -     | -       | -       | -     | 3.838        | 0.323   | 0.892 |
| VP2-A  | -          | -      | -     | -     | -     | -        | -     | -       | -       | -     | -            | -       | -     |
| VP2-MS | -          | -      | -     | -     | -     | -        | -     | -       | -       | -     | -            | -       | -     |
| VP2-PB | 13.248     | 2.902  | 0.473 | 0.078 | 0.947 | 0.169    | 0.056 | 70.367  | 7.659   | 0.962 | 2.79         | 0.334   | 0.754 |
| C1     | 5.133      | 0.958  | 0.881 | 0.068 | 0.988 | 0.013    | 0.008 | 341.167 | 174.058 | 0.989 | 3.699        | 0.122   | 0.983 |
| C1-A   | 140.678    | 12.98  | 0.511 | 0.091 | 0.951 | 3.499    | 1.444 | 161.637 | 27.525  | 0.949 | 183.897      | 20.641  | 0.814 |
| C1-MS  | 112.159    | 8.731  | 0.414 | 0.107 | 0.935 | 2.905    | 1.403 | 151.631 | 26.71   | 0.935 | 116.45       | 15.809  | 0.737 |
| C1-PB  | 5.254      | 1.399  | 0.691 | 0.088 | 0.972 | 0.023    | 0.015 | 134.903 | 61.572  | 0.961 | 2.036        | 0.121   | 0.937 |
| VO     | 21.681     | 4.085  | 0.685 | 0.096 | 0.948 | 0.113    | 0.037 | 193.42  | 37.656  | 0.975 | 11.48        | 1.085   | 0.863 |
| VO-A   | 22.164     | 5.979  | 0.550 | 0.123 | 0.887 | 0.169    | 0.089 | 128.494 | 30.869  | 0.909 | 7.728        | 1.082   | 0.71  |
| VO-MS  | 23.636     | 6.952  | 0.591 | 0.147 | 0.918 | -        | -     | 162.823 | 89.866  | 0.9   | 10.285       | 0.928   | 0.872 |
| VO-PB  | 8.756      | 1.668  | 0.764 | 0.073 | 0.986 | 0.018    | 0.016 | 326.384 | 235.677 | 0.976 | 4.728        | 0.196   | 0.971 |
| C2     | 22.027     | 11.843 | 0.41  | 0.225 | 0.57  | -        | -     | 80.688  | 28.959  | 0.6   | 4.735        | 1.169   | 0.328 |
| C2-A   | -          | -      | -     | -     | -     | -        | -     | -       | -       | -     | -            | -       | -     |
| C2-MS  | 53.205     | 27.298 | -     | -     | 0.402 | -        | -     | -       | -       | -     | 571.086      | 153.561 | 0.229 |
| C2-PB  | 18.948     | 5.349  | 0.361 | 0.104 | 0.84  | 0.261    | 0.107 | 67.821  | 8.438   | 0.93  | 2.675        | 0.593   | 0.304 |
| C3     | 3.219      | 0.817  | 0.985 | 0.088 | 0.985 | -        | -     | -       | -       | -     | 3.084        | 0.095   | 0.985 |
| C3-A   | -          | -      | -     | -     | -     | -        | -     | -       | -       | -     | -            | -       | -     |
| C3-MS  | -          | -      | -     | -     | -     | -        | -     | -       | -       | -     | -            | -       | -     |
| C3-PB  | 26.541     | 5.886  | 0.544 | 0.112 | 0.94  | 0.158    | 0.085 | 150.68  | 40.312  | 0.944 | 10.352       | 1.104   | 0.824 |

The values of the  $K_F$  parameter ranged between 3.219 and 148.757  $L^n \text{ kg}^{-1} \mu\text{mol}^{1-n}$ . These scores are similar to those previously obtained for another antibiotic (amoxicillin) in equivalent soil-bioadsorbent mixtures [68]. Focusing on the data, the  $K_F$  values were significantly higher when mussel shell or oak ash was added, indicating stronger adsorption when the soils were amended with these alkaline adsorbents. Regarding Freundlich's  $n$  values, they were lower than one in all cases, suggesting the presence of heterogeneous adsorption sites and a nonlinear and concave curve, which was frequently interpreted. This suggests that the sites with high adsorption energy are occupied first, indicating chemical adsorption [71,73]. The  $K_d$  values ranged between 2.018 and 571.086  $L \mu\text{mol}^{-1}$ , while the Langmuir adsorption constant ( $K_L$ ) ranged between 0.013 and 10.917  $L \text{ kg}^{-1}$ . These values are lower than those previously obtained for amoxicillin in equivalent mixtures [68].

### 3.3. Comparison with Previously Studied Bioadsorbents

Other authors previously studied the capacity of different bioadsorbents to retain or remove CFX. Awwad et al. [74] used activated carbon and a micelle-clay complex to retain this antibiotic, achieving adsorption values of 26.31  $\text{mg g}^{-1}$  and 31.25  $\text{mg g}^{-1}$ , respectively, for a CFX-added concentration of 20  $\text{mg L}^{-1}$ . Ma et al. [75] studied CFX adsorption with a cationic *Enteromorpha prolifera* polysaccharide-based hydrogel, obtaining adsorptions of 5  $\text{mg g}^{-1}$  for a concentration of 50  $\text{mg L}^{-1}$  and 25–30  $\text{mg g}^{-1}$  for a concentration of

400 mg L<sup>-1</sup>. In addition, different bioadsorbents have been previously studied regarding their adsorption of other antibiotics of the cephalosporins group. Among them, biochar derived from fiber residues of palm oil were used to remove cephalixin, obtaining adsorption values of 57.47 mg g<sup>-1</sup> [76]. Cephalixin adsorption was also studied for natural zeolite and zeolite coated with manganese oxide nanoparticles, reaching adsorption values of 16.1 and 24.5 mg g<sup>-1</sup>, respectively [77]. When comparing these results with the data obtained in the current study, the bioadsorbents used here showed lower adsorption capacities in the specific experimental conditions of the present research (which are not identical to those of the other investigations). However, expressed as a percentage, adsorption was above 80% for the mussel shell and oak ash in most cases. We note that the adsorbent materials evaluated in the referred previous research are not low-cost materials. In light of this, in case of requiring better adsorption performance associated with the low-cost byproducts employed here, one might suggest assessing the effect of carrying out different chemical modifications in this regard. Table 4 shows the results corresponding to each of the compared bioadsorbents.

**Table 4.** Comparison of antibiotics' adsorption capacities for various bioadsorbents.

| Bioadsorbent  | Antibiotic | Initial Concentration  | Adsorption (mg g <sup>-1</sup> ) | Reference                |
|---|------------|------------------------|----------------------------------|--------------------------|
| Activated carbon  | Cefuroxime | 20 mg L <sup>-1</sup>  | 26.31                            | Awad et al., 2015 [74]   |
| Micelle-clay complex  | Cefuroxime | 20 ppm                 | 31.25                            | Awad et al., 2015 [74]   |
| <i>Enteromorpha prolifera</i> polysaccharide-based hydrogel | Cefuroxime | 50 mg L <sup>-1</sup>  | 5                                | Ma et al., 2022 [75]     |
| <i>Enteromorpha prolifera</i> polysaccharide-based hydrogel | Cefuroxime | 400 mg L <sup>-1</sup> | 25–30                            | Ma et al., 2022 [75]     |
| Fiber residues of palm oil                                  | Cephalexin | 20 mg L <sup>-1</sup>  | 57.47                            | Acelas et al., 2021 [76] |
| Natural zeolite   | Cephalexin | 10 mg L <sup>-1</sup>  | 16.1                             | Samarghandi, 2015 [77]   |
| MnO zeolite   | Cephalexin | 10 mg L <sup>-1</sup>  | 24.5                             | Samarghandi, 2015 [77]   |
| Pine bark   | Cefuroxime | 21 mg L <sup>-1</sup>  | 0.037                            | This study               |
| Mussel shell  | Cefuroxime | 21 mg L <sup>-1</sup>  | 0.052                            | This study               |
| Oak ash   | Cefuroxime | 21 mg L <sup>-1</sup>  | 0.052                            | This study               |

### 3.4. Desorption

Desorption was always lower than 10% for the soils without bioadsorbents and decreased to 0% when the bioadsorbents were added, indicating strong retention. Similar results were previously obtained for amoxicillin in equivalent mixtures, where desorption decreased from 17% to 6% after adding bioadsorbent amendments to the soils [68].

## 4. Conclusions

The two bioadsorbents we investigated which had alkaline pH levels (mussel shell and oak ash) were highly effective at increasing CFX adsorption after being applied to the studied soils, resulting in strong and practically irreversible retention. The bioadsorbent amendment at 12 t/ha was sufficient to achieve these effects and did not require higher doses. In contrast, the bioadsorbent having an acidic pH, pine bark, was less effective, in some cases (high CFX concentrations and a dose of 48 t/ha of the bioadsorbent) even causing a decrease in CFX adsorption compared with the unamended soil. These facts suggest that among the different characteristics of the soils and bioadsorbents studied here, the pH level would be the one with the highest influence on adsorption of the antibiotic CFX. These results could be useful to manage soils and other environmental compartments affected by pollution episodes due to the antibiotic CFX, which can clearly be seen as relevant. For future research, it would be interesting to carry out equivalent experiments focusing on the efficacy of the bioadsorbents studied here and other low-cost

bioadsorbents to retain combinations of different antibiotics simultaneously present in the medium. In addition, complementary studies to shed further light on the retention and release mechanisms would be of relevance, as well as investigating low-cost procedures to increase the efficacy of raw adsorbents in cases where they would be needed.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr12071335/s1>. Table S1: Values corresponding to the basic parameters determined in the soils. C = corn soils; VO = vineyard soils (Ourense province); and VP = vineyard soils (Pontevedra province). Average values (n = 3) with coefficients of variation always <5%. Table S2: pH values of soils amended with the bio-adsorbents in doses of 12 and 48 t/ha. C = corn soils; VO = vineyard soils (Ourense province); VP = vineyard soils (Pontevedra province); A = ash; MS = mussel shell; and PB = pine bark. Figure S1: Example chromatograms corresponding to CFX adsorption onto soils amended with bio-adsorbents.

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