

## Article

# Efficacy of Different Waste and By-Products from Forest and Food Industries in the Removal/Retention of the Antibiotic Cefuroxime

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**Abstract:** Environmental pollution due to antibiotics is a serious problem. In this work, the adsorption and desorption of the antibiotic cefuroxime (CFX) were studied in four by-products/residues from the forestry and food industries. For this, batch-type experiments were carried out, adding increasing concentrations of CFX (from 0 to 50  $\mu\text{mol L}^{-1}$ ) to 0.5 g of adsorbent. The materials with a pH higher than 9 (mussel shell and wood ash) were those that presented the highest adsorption percentages, from 71.2% (23.1  $\mu\text{mol kg}^{-1}$ ) to 98.6% (928.0  $\mu\text{mol kg}^{-1}$ ). For the rest of the adsorbents, the adsorption was also around 100% when the lowest concentrations of CFX were added, but the percentage dropped sharply when the highest dose of the antibiotic was incorporated. Adsorption data fitted well to the Langmuir and Freundlich models, with  $R^2$  greater than 0.9. Regarding desorption, the materials that presented the lowest values when the highest concentration of CFX was added were wood ash (0%) and mussel shell (2.1%), while pine bark and eucalyptus leaves presented the highest desorption (26.6% and 28.6%, respectively). Therefore, wood ash and mussel shell could be considered adsorbents with a high potential to be used in problems of environmental contamination by CFX.

**Keywords:** antibiotics; eucalyptus leaves; mussel shell; pine bark; pine needles; retention/release; wood ash



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## 1. Introduction

From 2000 to 2015, the worldwide consumption of antibiotics in humans and in veterinary medicine increased by almost 65% [1,2], due to the increase in the world population, and to the higher demand for protein, which intensified animal production, requiring a higher use of antibiotics [3,4].

Among these drugs, cephalosporins, belonging to the group of beta-lactams, are widely used in the treatment of bacterial infections, as they have good tolerance and few side effects [5,6]. In human medicine, they are used mainly in specific infections of the human genital tract, as well as in serious infections such as meningitis [7,8]. In veterinary medicine, cephalosporins are widely used in infections of the respiratory tract and mammary glands [8–10].

Among the second-generation cephalosporins, cefuroxime (CFX) is the most prescribed, representing more than 50% of the total administration of cephalosporins in most European countries [11]. These antimicrobials are poorly absorbed by the intestine and a significant proportion (up to 90%) are excreted through feces and urine as the parent

compound [12–14], being incorporated into wastewater in the case of humans, and passing to slurry pits or directly into the environment in the case of farm animals. These wastewaters reach treatment plants, but many of these facilities have not been designed to eliminate antibiotics [14,15], removing between 20 and 90% of the pollutants, either through its accumulation in sewage sludge [16], or by degradation processes, which affect antibiotics such as penicillin [17]. However, other antimicrobials such as cephalosporins, fluoroquinolones, and tetracyclines are more resistant to natural degradation [17,18].

As an example, a study conducted in Greece on the presence of antibiotics in wastewater detected high concentrations of amoxicillin, clarithromycin, CFX, and ciprofloxacin [19]. The incorporation of antibiotics into the soil, through wastewater or fertilization with sewage sludge or livestock manure, can cause the appearance of bacterial resistance, contamination of underground or surface water bodies, and the passage of these pollutants to the food chain, both through drinking water and animal or vegetable products, as different crops can absorb the antibiotics present in the soils [20], constituting a threat to human health [21].

Recently, Cela-Dablanca et al. [22] studied the retention of CFX in various soils, finding adsorption values between 40.8% and 99.6% (between 54.39 and 125  $\mu\text{mol kg}^{-1}$ ) in those devoted to agricultural production, and between 74.6% and 93.5% (between 109.9 and 116.71  $\mu\text{mol kg}^{-1}$ ) in forest soils. However, taking into account that the presence of antibiotics both in soils and other environmental compartments is considered a matter of real concern, growing research is focusing on the design of systems and procedures to remove/retain these molecules, with special emphasis on wastewater, which is often used as irrigation waters [2,23], and also in soils [24–26].

The methods generally used for the removal of antibiotics include advanced oxidation, biological technology, and membrane separation, but they can be excessively expensive and even produce toxic by-products [14,24,27]. Adsorption technologies have the advantages of being relatively simple, low-cost, long-lasting, and renewable, and they do not generate toxic by-products [25,26]. The most common adsorbents include activated carbon, mineral materials, and biological materials [13]. Within these, the most used for the removal of antibiotics is activated carbon, but its high cost and difficulty of regeneration are considered relevant disadvantages [28]. In view of that, it would be clearly interesting to determine the adsorption capacity and potential effectivity of alternative low-cost adsorbent materials. In this line, bio-adsorbents derived from a wide variety of sources, many of them residual materials that need to be recycled, can be a viable option for the retention/removal of antibiotics present as contaminants in environmental compartments [29].

In view of the above background, this work focused on studying the adsorption/desorption characteristics of the antibiotic CFX when it interacts with different residues/by-products generated by the forestry industry (eucalyptus leaf, pine bark, pine needles, and wood ash), and of a waste from the food industry (mussel shell), in order to evaluate their potential suitability to be used in processes of removal/retention of this antibiotic, which could be very relevant for environmental protection and preservation of public health.

## 2. Materials and Methods

### 2.1. Sorbent Materials

The following materials were used: (a) four residues and by-products derived from the forestry industry, specifically eucalyptus leaves from plantations in the province of Lugo (Spain), pine bark (a commercial product of Geolia, Madrid), pine needles (from plantations located in the province of Lugo, Spain), and wood ash from a combustion boiler in Lugo (Spain); and (b) a waste/by-product from the food industry: crushed mussel shell (<1 mm in diameter), provided by Abonomar S.L. (Pontevedra, Spain). It should be noted that Galicia is one of the geographic areas with a higher production related to the forest industry, as well as in relation to mussel processing, which generates high amounts of by-products and wastes needing recycling.

The characterization of these sorbents was carried out following the methods detailed in the Supplementary Material.

## 2.2. Chemical Reagents

The CFX used (purity  $\geq 95\%$ ) was supplied by Sigma-Aldrich (Barcelona, Spain). Phosphoric acid (85% extra pure) and acetonitrile (purity  $\geq 99.9\%$ ) used for HPLC were supplied by Fisher Scientific (Madrid, Spain), and  $\text{Ca}_2\text{Cl}$  (95% purity) by Panreac (Barcelona, Spain). To carry out HPLC determinations, all solutions were prepared with milliQ water (Millipore, Madrid, Spain).

## 2.3. Adsorption and Desorption Experiments

Batch-type experiments were carried out to study the adsorption/desorption of CFX on/from the different bio-adsorbents. For this, 0.5 g of bio-adsorbent was weighed, and 10 mL of a solution with different concentrations of the antibiotic (2.5, 5, 5, 10, 20, 30, 40, and  $50 \mu\text{mol L}^{-1}$ ) was added, also containing 0.005 M of  $\text{CaCl}_2$  as a background electrolyte. The suspensions were shaken for 48 h in the dark by means of a rotary shaker (this time being enough to reach equilibrium, according to previous kinetic tests, data not shown). These suspensions were then centrifuged at 4000 rpm for 15 min. The resulting supernatants were filtered through  $0.45 \mu\text{m}$  nylon syringe filters, and the antibiotic concentration in the filtered liquids was determined by HPLC-UV with LPG 3400 SD equipment (Thermo-Fisher, Waltham, MA, USA).

For this, a Luna C18 column (150 mm long, 4.6 mm internal diameter,  $5 \mu\text{m}$  particle size) was used, provided by Phenomenex (Madrid, Spain), as well as a pre-column (4 mm long, 2 mm in diameter,  $5 \mu\text{m}$  particle size) packed with the same material as the column. The injection volume was  $50 \mu\text{L}$  and the flow rate was  $1.5 \text{ mL min}^{-1}$ . The mobile phase consisted of acetonitrile (phase A) and 0.01 M of phosphoric acid (phase B). A linear gradient was used varying from 5% to 32% of phase A and from 95% to 68% of phase B. The initial conditions were re-established in 2 min and maintained for 2.5 min. The total analysis time was 15 min, with a retention time of 8.69 min, and the wavelength used for detection was 212 nm. The amounts of antibiotic adsorbed were calculated by the difference between the concentrations initially present in the added solutions and those remaining in the solutions at equilibrium. All determinations were made in triplicate. Figure S1 (Supplementary Material) shows some selected chromatograms corresponding to the quantification of CFX.

Once the adsorption experiments were carried out, desorption was studied, allowing the evaluation of the reversibility of the process. For this, a volume of 10 mL of 0.005 M of  $\text{CaCl}_2$  (without antibiotic) was added to the material resulting from the adsorption process, and then the subsequent procedure carried out for adsorption was repeated. All determinations were made in triplicate.

## 2.4. Data Treatment

The experimental data obtained in the adsorption/desorption tests were adjusted to the Freundlich (Equation (1)), Langmuir (Equation (2)), and Linear (Equation (3)) models.

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

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

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

where  $q_e$  is the amount of antibiotic retained by the bio-sorbent (calculated as the difference between the concentration added and that remaining in the equilibrium solution);  $C_{eq}$  is the concentration of antibiotic present in the solution at equilibrium;  $K_F$  is the Freundlich constant related to the adsorption capacity;  $n$  is a parameter of the Freundlich model associated with the degree of heterogeneity of the adsorption;  $K_L$  is the Langmuir adsorption

constant;  $q_m$  is the maximum adsorption capacity according to the Langmuir model; and  $K_d$  is the partition coefficient in the linear model.

The SPSS Statistics 21 software was used to carry out the adjustment of the data derived from the adsorption experiments to the Langmuir, Freundlich, and Linear models, as well as statistical correlation studies among parameters of the bio-adsorbent materials and adsorption.

### 3. Results and Discussion

#### 3.1. Characteristics of the Sorbent Materials

The bio-adsorbents used in this study showed some marked differences in their physicochemical properties (Table 1). The pH in water ranged from highly acidic values, such as that of pine needles (pH = 3.68), to clearly alkaline values, such as that of wood ash (pH = 11.31). The total C content also presented a wide range, going from 13.26% in wood ash to more than 50% in eucalyptus leaves and pine needles. Regarding the total N content, it ranged between 0.08% in pine bark and 1.35% in eucalyptus leaves.

**Table 1.** Characteristics of the bio-adsorbent materials. C: total carbon; N: total nitrogen;  $Ca_e$ ,  $Mg_e$ ,  $Na_e$ ,  $K_e$ ,  $Al_e$ : elements in the exchange complex; Sat. Al: Al-saturation in the exchange complex; eCEC: effective cation exchange capacity;  $X_T$ : total content of the element (X);  $Al_o$ ,  $Fe_o$ : noncrystalline Al and Fe. Average values (n = 3), with coefficients of variation always <5%.

Parameter	Unit	Eucalyptus Leaves	Pine Bark	Pine Needles	Wood Ash	Mussel Shell
C	%	53.05	48.70	50.31	13.23	11.43
N	%	1.35	0.08	1.08	0.22	0.21
C/N		39.18	608.75	46.76	60.14	55.65
pH <sub>water</sub>		4.88	3.99	3.68	11.31	9.39
pH <sub>KCl</sub>		4.81	3.42	3.51	13.48	9.04
$Ca_e$	cmol <sub>c</sub> kg <sup>-1</sup>	7.95	5.38	2.13	95.0	24.75
$Mg_e$	cmol <sub>c</sub> kg <sup>-1</sup>	8.53	2.70	7.15	3.26	0.72
$Na_e$	cmol <sub>c</sub> kg <sup>-1</sup>	1.36	0.46	1.42	12.17	4.37
$K_e$	cmol <sub>c</sub> kg <sup>-1</sup>	12.93	4.60	11.09	250.65	0.38
$Al_e$	cmol <sub>c</sub> kg <sup>-1</sup>	0.13	1.78	2.15	0.07	0.03
eCEC	cmol <sub>c</sub> kg <sup>-1</sup>	30.90	14.92	23.94	361.15	30.25
Sat Al	%	0.42	11.93	8.98	0.02	0.10
Available-P	mg kg <sup>-1</sup>	262.84	70.45	217.95	462.83	54.17
$Na_T$	mg kg <sup>-1</sup>	242.31	68.92	271.54	2950	5174.00
$Mg_T$	mg/kg	840.96	473.55	653.40	26,171	980.66
$Al_T$	mg kg <sup>-1</sup>	80.58	561.50	246.95	14,966	433.24
$K_T$	mg kg <sup>-1</sup>	4464.10	737.84	4123.44	99,515	202.07
$Ca_T$	mg kg <sup>-1</sup>	2262.96	2318.81	538.96	136,044	280,168
$Cr_T$	mg kg <sup>-1</sup>	0.13	1.88	0.74	36.28	4.51
$Mn_T$	mg kg <sup>-1</sup>	614.92	30.19	356.28	10,554	33.75
$Fe_T$	mg kg <sup>-1</sup>	43.13	169.78	47.27	12,081	3535
$Co_T$	mg kg <sup>-1</sup>	0.03	0.20	0.38	17.25	1.02
$Ni_T$	mg kg <sup>-1</sup>	2.17	1.86	0.93	69.25	8.16
$Cu_T$	mg kg <sup>-1</sup>	2.80	<LD	3.81	146.33	6.72
$Zn_T$	mg kg <sup>-1</sup>	7.66	6.98	5.78	853.00	7.66
$As_T$	mg kg <sup>-1</sup>	0.02	<LD	0.02	8.36	1.12
$Cd_T$	mg kg <sup>-1</sup>	0.0	0.13	0.05	19.93	0.07
$Al_o$	mg kg <sup>-1</sup>	45.0	315.0	169.0	8323	178.33
$Fe_o$	mg kg <sup>-1</sup>	77.0	74.0	15.0	4233	171.0

The effective cation exchange capacity (eCEC) values also varied greatly depending on the type of bio-adsorbent, from 23.94 cmol<sub>c</sub> kg<sup>-1</sup> for pine needles to 361.15 cmol<sub>c</sub> kg<sup>-1</sup> for wood ash. In pine bark and mussel shell, the predominant exchangeable cation was Ca<sup>2+</sup>, while it was K<sup>+</sup> in wood ash, eucalyptus leaves, and pine needles. In addition, noteworthy are the high values of available P present in wood ash, followed by eucalyptus leaves

and pine needles (always higher than  $200 \text{ mg kg}^{-1}$ ). The total contents of heavy metals were clearly higher in wood ash compared to the other bio-adsorbents, also presenting the highest concentrations of noncrystalline Fe and Al ( $\text{Fe}_o$ ,  $\text{Al}_o$ ), followed by mussel shell (Table 1).

### 3.2. Adsorption and Desorption of CFX

#### 3.2.1. Adsorption

Figure 1 shows the adsorption curves of CFX for the different adsorbents. Table S1 (Supplementary Material) shows the values of the adsorbed amounts and adsorption percentages as a function of the concentration of antibiotic added. The maximum adsorption values were between  $551.62 \text{ } \mu\text{mol kg}^{-1}$  of pine bark and  $927.95 \text{ } \mu\text{mol kg}^{-1}$  of wood ash.

A statistical analysis showed that the maximum adsorption values for CFX were significantly and positively correlated with the eCEC of the adsorbents ( $r = 0.927$ ,  $p < 0.05$ ), with its Ca contents ( $r = 0.918$ ,  $p < 0.05$ ), its K contents ( $r = 0.927$ ,  $p < 0.05$ ), and its Na contents ( $r = 0.903$ ,  $p < 0.05$ ).

Comparing CFX adsorption data for the five adsorbents, wood ash showed the highest adsorption percentages, retaining practically 100% of the amount added, even for the highest concentration ( $50 \text{ } \mu\text{mol L}^{-1}$ ). For pine bark and pine needles, percentage adsorption values decreased as the CFX concentration added increased, going from 100% (for the lowest concentration added) to around 55% (for the highest concentration added). Eucalyptus leaves also presented a higher CFX adsorption percentage (94.26%) when low concentrations of the antibiotic were added, compared with a value of 67.29% reached when higher CFX concentrations were used, which is probably due to the progressive saturation of the adsorption sites. In the case of mussel shell, adsorption percentages varied to a lesser extent depending on the concentration of antibiotic added, ranging between 71.19% and 85.02%.

Comparing the results obtained for the different adsorbents, it is clear that the materials with the highest pH (mussel shell and wood ash) are those with the highest adsorption values, especially when the highest concentrations of the antibiotic are added. Similarly, Fakhri and Adami [30] pointed out that the parameter that most influences the adsorption of cephalosporins is pH, as it simultaneously affects the chemical speciation of the antibiotics and the adsorbent surfaces, making the adsorption of cephalosporins low at  $\text{pH} < 6$ , while a basic or alkaline medium favors the adsorption processes for these compounds. These same authors also studied the adsorption of CFX in different materials (magnesium oxide nanoparticles and carbon nanotubes), finding that sorbents with  $\text{pH} > 8$  presented a higher adsorption, as has occurred in the present study with wood ash. The acid dissociation constant ( $\text{pK}_a$ ) is an important parameter that determines the mobility/retention of organic compounds, and therefore their distribution in environmental compartments [8,31]. Cephalosporins have at least two dissociation constants ( $\text{pK}_{a1} = 3.15$  and  $\text{pK}_{a2} = 10.97$ ) [32,33], and their molecules can have a positive or negative charge, as well as behave as a zwitterion, depending on the pH of the medium. At pH above 10.97, they are in anionic form, while they are cations when the pH is below 3.15, and they will be zwitterions between these two pH values. In view of that, CFX would be a zwitterion in all the adsorbents used in this work (except wood ash), so the positively charged groups ( $\text{NH}_4^+$ ) of the antibiotic will interact electrostatically with the surfaces of the negatively charged adsorbents, which are more abundant in adsorbents with a higher pH, while the anionic groups ( $\text{COO}^-$ ) of CFX will bind to these surfaces through a cationic bridge [34]. In the case of wood ash, the pH value is higher than that of the  $\text{pK}_{a2}$  value of the antibiotic (10.97), so CFX would be negatively charged, as would certain components of the ash, specifically noncrystalline Fe and Al minerals (Table 1), favoring adsorption taking place through a cationic bridge, an interaction that will be also favored by the high concentration of changeable  $\text{Ca}^{2+}$  present in the ash.

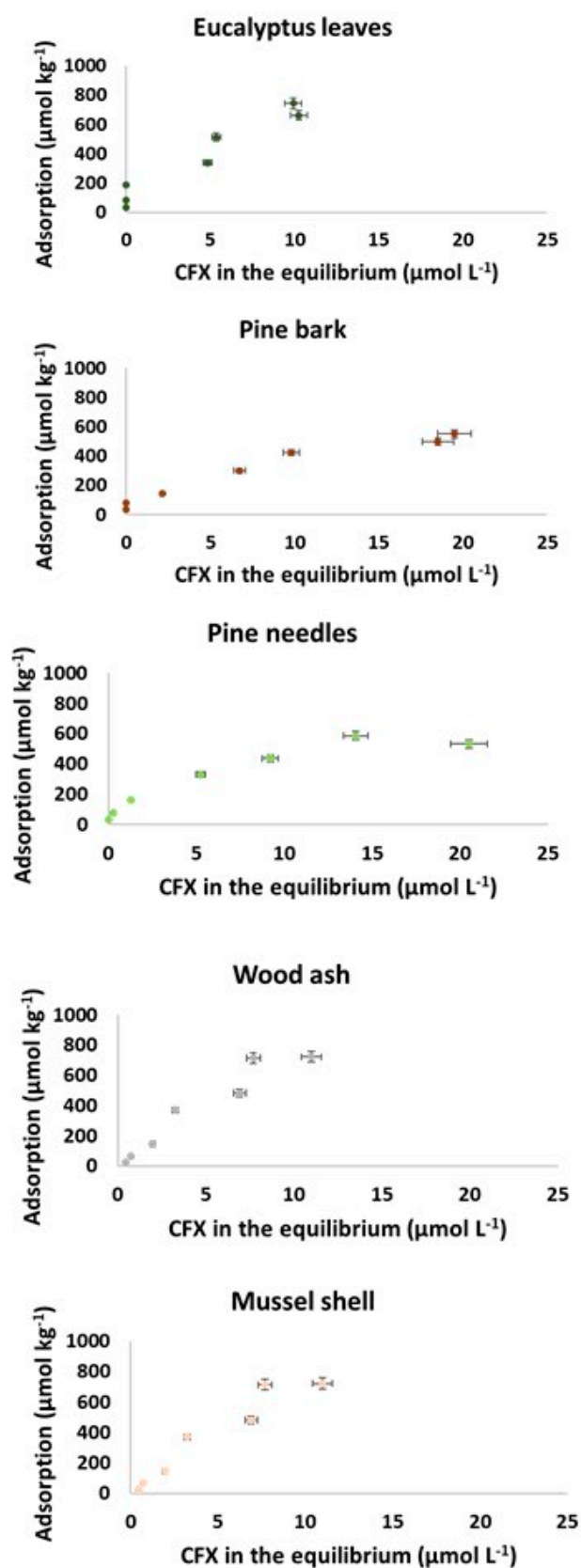


Figure 1. Adsorption curves for CFX and the five sorbent materials used.

When all five adsorbents were considered together, significant correlations were obtained between the amount of CFX adsorbed when the highest concentration of this



antibiotic was added and the exchangeable cations (with values of  $r = 0.918, 0.903,$  and  $0.927$ , for Ca, Na, and K, respectively;  $p < 0.05$ ). This suggests their participation in bonds taking place by means of cationic bridges.

For three of the materials used in this study (wood ash, pine bark, and mussel shell), Conde-Cid et al. [35,36] studied in previous works their adsorption capacity for three tetracycline antibiotics (oxytetracycline, chlortetracycline, and tetracycline) and for three sulfonamides (sulfadiazine, sulfamethazine, and sulfachloropyridazine). In the case of tetracyclines, a high adsorption capacity was also obtained for wood ash, with pine bark also showing a high capacity to retain tetracyclines (unlike what was observed in the present study for CFX and pine bark), while the mussel shell was not suitable for the removal of these substances. Regarding the results of sulfonamide adsorption on those materials, Conde-Cid et al. [36] also obtained results showing differences in relation to the current work, with pine bark retaining practically 100% of the added sulfonamide, while wood ash and mussel shell were not effective in retaining these antibiotics.

Several authors have studied the adsorption of different cephalosporins on other materials [37–41]. For example, activated carbon obtained from different plant remains showed an adsorption capacity higher than 80% for cephalexin present in an aqueous solution [38,39,41]. In a study by Samarghandi et al. [42], the natural zeolites used retained 28% of the added cephalexin at pH 7, but the adsorption increased to 89% when these zeolites were coated with manganese oxide nanoparticles. Biochar made from pine wood showed a very high adsorption for different antibiotics and, therefore, can be considered promising in terms of treating contamination by these substances [14,43,44]. This kind of biochar reaches and even exceeds the adsorption capacity of powdered activated carbon biochar, a product that is commercially available but is very expensive [14,44]. It should be noted that, in the present study, residual materials such as mussel shell and especially wood ash showed high potentials to adsorb CFX, without performing additional modification treatments.

### 3.2.2. Modeling of Adsorption Data

The Langmuir isotherm assumes that the adsorption is homogeneous and in a single layer, with no interaction among the molecules of the sorbate. It is recognized that each sorbate molecule occupies a site, and no further adsorption can take place on it [45]. Unlike Langmuir's model, the Freundlich's model assumes that adsorption can occur in multiple layers, and that the adsorption sites are heterogeneous, with those with the highest energy being the first to be occupied, which means that there may be different functional groups involved in adsorption on the surface of the sorbent, with the intervention of different binding energies [45].

In the present study, the experimental adsorption data obtained were adjusted to the Freundlich (Equation (1)), Langmuir (Equation (2)), and Linear (related to the Henry's isotherm equation) (Equation (3)) models. Table 2 shows the parameters of the adsorption equations obtained from the adjustments to the three models. Figure 2 shows graphically the fitting to the adsorption models used.

**Table 2.** Fitting of the adsorption data to the Freundlich, Langmuir, and Linear models.  $K_F$  ( $L^n \mu\text{mol}^{1-n} \text{kg}^{-1}$ );  $K_L$  ( $L \mu\text{mol}^{-1}$ );  $n$  (dimensionless);  $q_m$  ( $\mu\text{mol kg}^{-1}$ );  $K_d$  ( $L \text{kg}^{-1}$ ). -: standard error values too high for fitting.

Adsorbent	Freundlich					Langmuir					Linear Model		
	$K_F$	Error	$n$	Error	$R^2$	$K_L$	Error	$q_m$	Error	$R^2$	$K_d$	Error	$R^2$
Eucalyptus leaves	66.94	18.00	0.72	0.13	0.955	0.067	0.056	862.05	458.17	0.951	36.41	2.45	0.929
Pine bark	110.86	27.94	0.54	0.09	0.965	0.096	0.038	817.67	140.82	0.971	30.41	2.70	0.867
Pine needles	161.98	27.35	0.43	0.07	0.967	0.202	0.067	700.09	75.87	0.974	34.25	4.31	0.748
Wood ash	-	-	-	-	-	-	-	-	-	-	597.15	181.51	0.145
Mussel shell	93.25	34.91	0.77	0.18	0.909	0.077	0.067	1223.47	666.70	0.923	56.83	5.09	0.884

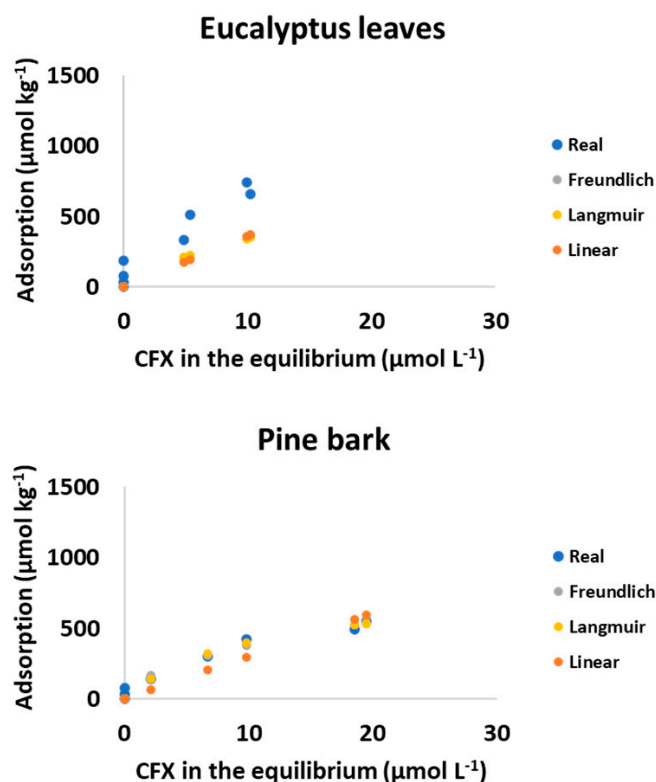


Figure 2. Adsorption curves for CFX also including data of fitting to the adsorption models used.

For the linear model, the  $R^2$  values were lower than 0.90 in all materials (with the exception of eucalyptus leaves,  $R^2 = 0.929$ ), with  $R^2$  being very low in the case of wood ash. On the contrary, in the Freundlich and Langmuir models,  $R^2$  values were higher than 0.9, with the exception of wood ash (bearing in mind that for this material, it was not possible to adjust both models, due to the existence of too high an error). In fact, CFX adsorption onto wood ash did not fit any model, as it adsorbed 100% of the concentrations of CFX added, which prevents the adjustment of the experimental data to the adsorption models used.

The Freundlich's  $K_F$  parameter, related to the adsorption capacity, varied between 66.9 and 162.0  $L^n \mu\text{mol}^{1-n} \text{kg}^{-1}$ . The dimensionless Freundlich's  $n$  parameter, related to the heterogeneity of the active sites of the sorbent [46], showed values between 0.43 and 0.77, with the highest corresponding to mussel shell. All the adsorbents used in this study presented values of  $n < 1$ , which indicates a heterogeneous adsorption surface, where the highest energy sites are occupied first. This means that the adsorption energy decreases exponentially as the available surface is smaller [46,47]. It is also relevant that, the closer  $n$  is to zero, the more heterogeneous the adsorption surface will be [46,48,49].

### 3.2.3. Desorption

Table 3 shows data corresponding to CFX desorption from the different adsorbents, expressed in  $\mu\text{mol kg}^{-1}$  (and as a percentage, between parentheses). The adsorbents presenting the highest desorption values were eucalyptus leaves (ranging between 6.4 and 212.2  $\mu\text{mol kg}^{-1}$ ) and pine bark (ranging between 8.4 and 157.0  $\mu\text{mol kg}^{-1}$ ). Regarding the rest of the adsorbents (pine needles, mussel shell, and wood ash), the desorbed quantities did not exceed 20.7  $\mu\text{mol kg}^{-1}$  in any case.

With desorption data expressed as percentages, it is confirmed that eucalyptus leaves and pine bark were the materials showing the highest desorption, with values ranging between 19.5 and 28.6% for eucalyptus leaves, and between 25.9 and 59.1% for pine bark. In the rest of the materials, desorption was less than 20.6% for pine needles, 12.3% for mussel shell, and 0% for wood ash. The lower desorption values of mussel shell and wood ash



correspond to the presence of higher contents of noncrystalline Al and/or Fe compounds ( $Al_0$ ,  $Fe_0$ ) in these bio-adsorbents (Table 1).

**Table 3.** CFX desorption, expressed in  $\mu\text{mol kg}^{-1}$  (and in a percentage, between brackets), for the five different sorbents, as a function of the concentration of antibiotic added ( $C_0$ , in  $\mu\text{mol L}^{-1}$ ). -: no data. Average values ( $n = 3$ ), with coefficients of variation always  $<5\%$ .

Sorbent	$C_0$ ( $\mu\text{mol L}^{-1}$ )						
	2.5	5	10	20	30	40	50
Eucalyptus leaves	6.4(19.8)	16.3(20.2)	41.1(22.2)	65.9(19.5)	141.1(27.5)	164.5(24.9)	212.2(28.6)
Pine bark	8.4(25.9)	36.2(44.8)	84.0(59.1)	133.3(44.5)	157.0(37.1)	141.8(28.6)	146.5(26.6)
Pine needles	0(0)	15.4(20.5)	20.7(13.0)	19.5(5.9)	-	-	-
Wood ash	0(0)	-	-	0(0)	-	0(0)	0(0)
Mussel shell	0.3(12.2)	0.6(8.4)	1.6(10.7)	1.5(3.9)	1.4(2.9)	1.5(2.1)	1.5(2.1)

In three of these materials (oak ash, pine bark, and mussel shell), previous works studied the desorption of other groups of antibiotics, specifically three tetracyclines and three sulfonamides. For the former, Conde-Cid et al. [35] also obtained a low desorption from wood ash, but (unlike what was observed in the present study with CFX) these authors found that pine bark adsorbed tetracyclines in a way that was practically irreversible, while desorption from mussel shell was high (up to 44% of what was adsorbed). In the case of sulfonamides, Conde-Cid et al. [36,50] (2021, 2020) reported that only pine bark retained irreversibly high concentrations of these antibiotics, while wood ash and mussel shell had a low adsorption capacity and desorbed a high percentage of what was previously retained.

Considering together data on CFX adsorption and desorption for the five different adsorbents used, wood ash presented the best results, with the highest adsorption and the lowest desorption values. In previous studies, this material was also found to be very effective for the irreversible adsorption of tetracyclines [35]. Mussel shell also has potential utility for retaining CFX present in polluted media. However, pine bark could not be recommended for the adsorption of CFX, as it had low adsorption and high desorption, especially for the highest concentrations added, despite the fact that in previous studies, it showed great effectiveness to strongly retain tetracyclines and sulfonamides [35].

#### 4. Conclusions

Among the five sorbents evaluated, the most effective for the adsorption of the antibiotic cefuroxime (CFX) were wood ash and mussel shell. Both materials were those with the highest pH values and were also characterized by their richness in noncrystalline compounds. Both sorbents would be of high interest for being used in CFX retention/removal processes, which would contribute to their recycling. The rest of the materials studied (pine bark, pine needles, and eucalyptus leaves) could not be recommended for retention/removal of this antibiotic, as they showed low adsorption and high desorption when the highest concentrations of CFX were added.

CFX adsorption generally showed a good fit to the Langmuir isotherm, and especially to the Freundlich model. Furthermore, in these materials, the Freundlich's  $n$  values were always lower than 1, which would indicate the relevance of heterogeneous adsorption sites, with those with the highest energy being the first to be occupied. Future additional studies could focus on delving into the retention mechanisms of CFX and other antibiotics (especially cephalosporins) in the sorbents that showed better results in the current work. Likewise, the influence of the simultaneous presence of several antibiotics, or of antibiotics and other contaminants, both organic and inorganic, could be evaluated, as well as the impact of modifying the values of different variables that could affect the final effectivity in the retention/release of the pollutants. Globally, the results of this study can be considered relevant at an environmental level, in relation to the potential promotion of waste and by-product recycling, protection against pollution, and its potential repercussions on aspects that affect public health.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/pr9071151/s1>, Table S1: Adsorption amounts ( $\mu\text{mol kg}^{-1}$ ) and percentages for the five adsorbents used, after adding the different initial concentrations ( $C_0$ ) of the antibiotic CFX; Figure S1. Selected chromatograms corresponding to the detection of CFX after adding various concentrations of the antibiotic to the different adsorbents used in the study.

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