Retention of the Antibiotic Cefuroxime onto Agricultural and Forest Soils

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Abstract: Antibiotics in wastewater, sewage sludge, manures, and slurries constitute a risk for the environment when spread on soils. This work studies the adsorption and desorption of the antibiotic cefuroxime (CFX) in 23 agricultural and forest soils, using batch-type experiments. Our results show that the adsorption values were between 40.75 and 99.57% in the agricultural soils, while the range was lower (from 74.57 to 93.46%) in forest soils. Among the Freundlich, Langmuir, and Linear models, the Freundlich equation shows the best fit for the adsorption results. In addition, agricultural soils with higher pH are the ones that present the highest adsorption. Further confirmation of the influence of pH on adsorption is given by the fact that Freundlich’s $K_F$ parameter and the Linear model $K_D$ parameter shows a positive correlation with pH and with the exchangeable Ca and Mg values, which are known to affect the charges of the soil colloids and the formation of cationic bridges between adsorbents and adsorbate. In addition, Freundlich’s $n$ parameter shows a positive and significant correlation with the organic matter content, related to the high adsorption taking place on forest soils despite their pH < 5. Regarding desorption, in most cases, it is lower than 1%, which indicates that CFX is adsorbed in a rather irreversible way onto these soils. Overall, these results can be considered relevant regarding their potential impact on environmental quality and public health.

Keywords: adsorption; desorption; emerging pollutants; soils

1. Introduction

Antibiotics have been widely used for the treatment of infectious diseases, both in veterinary and human medicine. Regarding antibiotics for human use, Kovalakova [1] indicates that their worldwide consumption increased by around 65% between 2000 and 2015, when expressed in defined daily doses (DDD). In the case of Europe, 3821 tons of antibiotics were used in human medicine in 2014, of which 9% were consumed in Spain [2]. To note that the most recent data available indicate that “in 2019, the average total (community and hospital sector combined) consumption of antibiotics for systemic use in the EU/EEA was 19.4 DDD per 1000 inhabitants per day (country range: 9.5–34.1), evidencing that during the period 2010–2019, a statistically significant decrease was observed for the EU/EEA overall” [3].

Once the antibiotics are administered, a significant proportion (between 28% and 90%, depending on the type of antibiotic) is excreted as parent compounds or metabolites through feces and urine [4,5]. After their excretion, these compounds reach the environ-
ment, and the subsequent potential impact has been causing increasing concerns in recent years, as previously occurred for some inorganic pollutants [6,7].

In fact, Kim et al. [8] indicate that since the beginning of the 21st century a growing number of studies has revealed the presence of a wide range of persistent pharmaceuticals in soil and water, and its relevance has been confirmed [9]. The main entry of human-medicine antibiotics into the environment takes place through wastewater and sewage sludge, after domestic use. In fact, it has been reported that the direct application of wastewater in irrigation, or the application of sewage sludge as fertilizer in agricultural soils, can be the main source of antimicrobials to the edaphic environment [10–13], as wastewater treatment plants usually do not eliminate these pollutants [14–17]. Excessive concentrations of these drugs in the soil could affect food quality, the safety of crop production, and the health of the environment, bearing in mind that these contaminants move through environmental compartments and the food chain, especially after being absorbed by plants [18–20].

Once the antibiotics reach soils, they are subjected to different physicochemical and biological processes in the soil-water system, mainly adsorption/desorption, degradation, transportation, and uptake by crops, depending on the properties of the antibiotic, the characteristics of the soil, and climatic conditions. The magnitude of each of these processes will strongly determine the fate and persistence of these compounds in the environment [21,22].

Among antibiotics, cefuroxime (CFX) is a compound belonging to the cephalosporin group, and it has become one of the most consumed worldwide [23]. It is frequently used to treat diseases like pneumonia, otitis, sinusitis, and urinary tract infection [24]. Regarding its presence in the environment, in a study dealing with antibiotics in treated wastewater, Latrou et al. [25] found that CFX was the one with the highest concentrations, reaching around 6.6 µg L⁻¹. Moreover, regarding CFX in the environment, Li et al. [26] found that the application of manure increased the levels of this and other antibiotics in greenhouse soils. Furthermore, as regards its effects on microbiota in the environment, Orlewska et al. [27] reported a low initial resistance of soil microbial communities to CFX, but these authors concluded that despite a short-term negative effect, the balance of the soil ecosystem could be clearly disturbed. The chemical structure of the antibiotic CFX (shown in Figure 1) has relevance as regards its potential interactions with various soil compounds [22], which would need further attention, and should need additional discussion.

Figure 1. Chemical structure of the antibiotic cefuroxime.
Overall, there is a lack of studies providing results on CFX retention/release on/from soils, and additional research would be needed to elucidate the fate of this compound in the soil, and other environmental compartments.

Taking all this background into account, the main objective of the current study is to evaluate the eventual influence of soil characteristics on the behavior of CFX in the edaphic environment. For this, the adsorption and desorption of the antibiotic were studied in 23 forest and agricultural soils presenting a variety of physicochemical properties. The results of this research could be relevant to increase the knowledge on the evolution and potential repercussions of this pollutant in the environment, and specifically in the edaphic system, from which it could undergo transport towards water bodies and enter the food chain.

2. Materials and Methods

2.1. Soils

A total of 23 soils were sampled in different areas of Galicia (NW Spain). Table S1 (Supplementary Materials) shows some basic details on these sampling areas. Within these samples, 20 corresponded to agricultural soils as follows: Thirteen vineyard soils, with five in Ourense province—VO1 to VO5, and 8 in Pontevedra province—VP1 to VP8, while the other 7 were corn (or maize) soils—M1 to M7. In addition, the three forest soils sampled were: One of them under Pinus—FP, another one under oak (Q. robur)—FC, and the third one under Eucalyptus—FE.

In each plot, 10 sub-samples were collected in a zig-zag, in the surface layer of the soil (0–20 cm), and these sub-samples were then grouped to make a composite sample for each of the plots. Subsequently, in the laboratory, they were dried at 40 °C, sieved through a 2 mm mesh, and stored until analysis.

2.2. Soils Analyses

Different physicochemical parameters were determined in the soil samples. Specifically, these parameters were: Soil texture, pH values in water and in KCl, total C, total N, exchangeable Ca, Mg, Na, K and Al, effective cation exchange capacity (eCEC), available phosphorus, total non-crystalline Fe and Al, and finally, Fe and Al bound to organic matter. The methods used for the characterization of the soils are indicated in the Supplementary Materials, as well as the results obtained (Table S2).

2.3. Adsorption and Desorption Experiments

The adsorption and desorption experiments were carried out using batch-type tests performed with the different soil samples. Specifically, amounts of 2 g of soil (taken from those previously dried at 40 °C and sieved through a 2 mm mesh) were mixed with 5 mL of solutions containing different concentrations of the antibiotic (2.5, 5, 10, 20, 30, 40, or 50 µmol L⁻¹) and 0.005 M CaCl₂ as background electrolyte. The suspensions were shaken for 48 h (time enough for reaching equilibrium, as demonstrated by kinetic studies previously performed—data not shown) in the dark, using a rotary shaker, and then centrifuged at 4000 rpm for 15 min, using a Model 5810R Centrifuge (Eppendorf, Hamburg, Germany). The pH values of the equilibrium solutions were determined with a pH meter (MultiMeter MM41 model, Crison, Barcelona, Spain). The resulting supernatants were filtered through 0.45 µm nylon syringe filters (Fisher scientific, Madrid, Spain), and the antibiotic concentration of the filtered liquids was determined by HPLC-UV.

2.4. Chemical Reagents and Quantification of CFX

Cefuroxime (purity ≥ 95%) was supplied by Sigma-Aldrich (Barcelona, Spain). Phosphoric acid (85% extra pure) and acetonitrile (purity ≥ 99.9%) used for HPLC were supplied by Fisher Scientific (Madrid, Spain), while Ca₂Cl₂ (95% purity) was provided by Panreac (Barcelona, Spain). All solutions used during HPLC determinations were prepared with milliQ water (Millipore, Madrid, Spain). The HPLC determinations were carried out with a
Model LPG 3400 SD equipment (Thermo Fisher Scientific, Waltham, MA, USA). A Luna C18 column (150 mm × 4.6 mm, 5 µm) and a precolumn (4 mm × 2 mm, 5 µm), packed with the same material as the column, was also used; both provided by Phenomenex (Madrid, Spain). During the HPLC analysis, the injection volume was 50 µL, and the flow rate was 1.5 mL min⁻¹, with the mobile phase being acetonitrile (phase A) and 0.01 M 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. The wavelength used for detection was 212 nm. The amounts of antibiotic adsorbed were calculated by the difference between the concentrations in the added solutions and those in the solutions at equilibrium.

Once the adsorption experiments were carried out, desorption was also studied, which determines the degree of reversibility of the process. For this, 5 mL of 0.005 M CaCl₂ (without antibiotic) were added to the soil materials resulting from the adsorption process, and then the same process used for adsorption was repeated.

All determinations corresponding to adsorption and desorption experiments were made in triplicate. Selected chromatograms are presented in Figure S1 (Supplementary Materials).

2.5. Fitting to Adsorption Models and Statistical Treatment

The experimental data obtained in the adsorption tests were adjusted to the Freundlich (1), Langmuir (2), and Linear (3) models [6,7].

\[
q_e = K_F C_{eq}^n
\]

(1)

\[
q_e = \frac{q_m K_L C_{eq}}{1 + K_L C_{eq}}
\]

(2)

\[
K_d = \frac{q_e}{C_{eq}}
\]

(3)

where \(q_e\) is the amount of antibiotic retained by the soil; \(C_{eq}\) is the concentration of antibiotic present in the solution at equilibrium; \(K_F\) is the Freundlich parameter related to the adsorption capacity; \(n\) is a parameter of the Freundlich model related to the nonlinearity of the adsorption; \(K_L\) is the Langmuir adsorption constant; and \(q_m\) is the maximum adsorption capacity according to the Langmuir model. \(K_d\) is the partition coefficient in the linear model.

For the adjustments of the adsorption experiments to the Langmuir, Freundlich, and Linear models, as well as for performing statistical correlation analyses, the SPSS Statistics 21 software was used.

3. Results and Discussion

3.1. Characteristics of the Soil Samples

The physicochemical properties of the soils used are shown in Table S2 (Supplementary Materials). Regarding the particle size distribution, most soils are sandy loam, in correspondence with the dominance of silicic original material, with sand contents between 43.42% and 69.35%, and the highest percentages generally corresponding to forest soils. The clay fraction ranges between 12.36 and 24.5%, with agricultural soils showing higher values. The range of pH in water (pH_{H2O}) is very wide, going from 4.68 to 8.02, with the most acidic values corresponding to forest soils. There is also a high variability in the organic C content, ranging between 0.63 and 9.78%, while the N content ranges between 0.06 and 0.67%. For both C and N, the highest levels correspond to forest soils.

The effective cationic exchange capacity (eCEC) values also show a wide oscillation (Table S2, Supplementary Materials), between 5.43 and 42.81 cmolₐ kg⁻¹, with Ca being the cation that dominates in most agricultural soils, while Al dominates in forest soils. The non-crystalline forms of Fe and Al also show high variability. Specifically, total non-crystalline Fe (Fe_{ox}) is between 1695 and 6990 mg kg⁻¹, with the highest values generally corresponding to soils on amphibolite, while total non-crystalline Al (Al_{ox}) oscillates between 484 and
11,651 mg kg$^{-1}$, with the lowest values corresponding to soils on schist/slate. Regarding Fe bound to organic matter ($\text{Fe}_{\text{pir}}$), the range goes from 715 to 9239 mg kg$^{-1}$, while Al bound to organic matter ($\text{Al}_{\text{pir}}$) ranges from 484 to 14,857 mg kg$^{-1}$, with generally higher values in forest soils (FP, FE, and FC), and in those with more organic carbon (M5 and VP4) within agricultural soils.

In fact, previous studies have shown that these soil characteristics are very relevant as regards retention/release of a variety of pollutants [7], and specifically antibiotics [12], which will be further discussed below.

### 3.2. Adsorption of CFX and Modeling

#### 3.2.1. Adsorption Data

Table S3 (Supplementary Materials) shows CFX adsorption (in $\mu$mol kg$^{-1}$ and percentage) as a function of the concentration of antibiotic added.

In the soils with corn cultivation, when the highest dose of CFX was added, the adsorption values oscillate between 71.36 and 123.91 $\mu$mol kg$^{-1}$ (Table S3, Supplementary Materials), while in the vineyard soils on schist and slate adsorption is between 101.05 and 122.86 $\mu$mol kg$^{-1}$, and in vineyard soils on granite is between 54.39 and 125 $\mu$mol kg$^{-1}$. Forest soils show a scarce oscillation, between 109.9 and 116.71 $\mu$mol kg$^{-1}$. Analyzing the data expressed as a percentage, a large part of the soils adsorbed more than 75% of the CFX added. In this sense, the range of variation was small in all vineyard soils on schist and slate, and in forest soils (from 79.26 to 96.24%, and between 74.57 and 93.46%, respectively), while a wide oscillation was observed within corn soils (ranging 49.49–99.2%) and vineyard soils on granite (ranging 40.75–99.57%). In other words, some of the soils under study adsorb almost 100% of the maximum concentration of the antibiotic added, while others do not absorb even half of that concentration.

In the agricultural soils of the current study, whose pH values vary between 5.01 and 8.02, the differences in adsorption would be mainly related to these pHs. In fact, those soils having the highest pH (M1, M5, VP6, and VP7) show higher adsorption. Similar results were reported by Fakhri and Adami [28] when studying the adsorption of various cephalosporine antibiotics on magnesium oxide nanoparticles and carbon nanotubes, finding higher adsorption when the pH of the medium was >8. pH is one of the parameters having the highest influence on antibiotic-adsorbent interactions, since it simultaneously affects the chemical speciation of antibiotics and adsorbent surfaces [29]. Both antibiotics and soil components, have functional groups that can undergo protonation/deprotonation reactions, depending on the pH of the solution. The CFX molecule is amphoteric, having two dissociation constants ($\text{pK}_a$ $1 3.15$ and $\text{pK}_a$ $2 10.97$), which can have a positive or negative charge, or be in the form of a zwitterion, depending on the pH of the medium [30].

At pH above 10.97, CFX is in anionic form, while at pH below 3.97, it is in cationic form, and between both pH values, it is a zwitterion. Regarding the soils in this study, since most have a pH above 5.5, the components with variable charge (1:1 clays, organic matter, and non-crystalline minerals) will preferably be negatively charged. At these pH values, CFX would be as a zwitterion, meaning the positively charged amino groups of the antibiotic would interact electrostatically with the negatively charged adsorbent surfaces of the soils, while the anionic groups (COO-) of CFX would bind to these surfaces through a cationic bridge [31]. The higher the pH of the soil, the more negative charges would be produced in its components, which would explain the influence of pH on these adsorption processes.

In the case of forest soils, the adsorption of CFX is generally above 70% (Figure S1, Supplementary Materials), despite having a clearly acidic pH (<5). This relevant score for adsorption could be related to the high content of organic matter in these soils (between 12.32 and 16.86%), much higher than that of the agricultural soils of the study. Organic components have a pH-dependent charge and are highly involved in antibiotic adsorption processes [32], giving that at pH < 5, the –COOH groups of organic matter...
begin to dissociate [33], and then could interact electrostatically with the positively charged groups of CFX.

3.2.2. Fitting to Adsorption Models

Figure 2 shows the adsorption curves of the 23 soils used in this work, plotting the amount of antibiotic adsorbed versus its concentration in the equilibrium solution.

Figure 2. Adsorption curves for CFX on the various soils were studied. M, maize (corn) soils; VO, vineyard soils (Ourense province); VP, vineyard soils (Pontevedra province); F, forest soils; CM and CV, control soils in maize and vineyard areas. Average values (n = 3), with coefficients of variation always <5%.
In addition, Table 1 shows the parameters of the adsorption equations obtained from the adjustments of the experimental data to the Freundlich, Langmuir, and Linear models. The adsorption data of most of the soils adjusted better to the Freundlich equation, as indicated by the values of the coefficient of determination obtained for most of the soils \( (R^2 \text{ above } 0.9) \). In the Linear and Langmuir models, \( R^2 \) higher than 0.9 was obtained in a smaller number of soils. In addition, this last model was the most affected by high errors (mean squared errors—MSE) associated with the fitting, making it the least adequate for the soils in this study. The values of the distribution coefficient \( (K_d) \) of the linear model show wide variation in corn soils \((3.08–247.33 \text{ L kg}^{-1})\) and vineyard soils on granite \((2.01–201.92 \text{ L kg}^{-1})\), while the range is lower in vineyard soils on schist and slate \((11.48–51.39 \text{ L kg}^{-1})\), and especially in forest soils \((20.43–33.43 \text{ L kg}^{-1})\). To be noted that, using mean squared errors, only the MSE of different fits to the same data should be compared, as it will depend on the magnitude of the data (larger values tend to have higher variability). Future more detailed treatment of these data could be made using more sophisticated, weighted nonlinear regression, as well as modeling comparison based on likelihood ratio tests and/or Akaike’s Information Criteria (AIC) and Bayesian Information Criteria (BIC).

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

| Soil | \(K_F\) | Error | \(n\) | Error | \(R^2\) | \(K_L\) | Error | \(q_m\) | Error | \(R^2\) | \(K_d\) | Error | \(R^2\) |
|------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| M1   | 478.866 | 152.237 | 1.575 | 0.29 | 0.893 | - | - | - | - | 247.337 | 29.375 | 0.797 |
| M2   | 5.133 | 0.958 | 0.881 | 0.07 | 0.988 | 0.013 | 0.008 | 341.167 | 174.072 | 0.989 | 3.699 | 0.122 | 0.983 |
| M3   | 22.027 | 11.843 | 0.41 | 0.23 | 0.57 | - | - | - | - | 4.735 | 1.169 | 0.978 |
| M4   | 3.234 | 1.002 | 0.983 | 0.11 | 0.979 | - | - | - | - | 3.084 | 0.113 | 0.978 |
| M5   | 470.333 | 140.326 | 1.655 | 0.3 | 0.917 | - | - | - | - | 233.145 | 26.194 | 0.816 |
| M6   | 32.85 | 8.286 | 1.013 | 0.25 | 0.894 | - | - | - | - | 33.257 | 2.798 | 0.894 |
| CM   | - | - | - | - | - | - | - | - | - | - | - | - |
| VO1  | 36.079 | 9.37 | 0.782 | 0.21 | 0.808 | - | - | - | - | 27.873 | 3.461 | 0.779 |
| VO2  | 40.898 | 10.846 | 0.83 | 0.28 | 0.746 | - | - | - | - | 35.283 | 4.932 | 0.728 |
| VO3  | 32.17 | 13.084 | 0.855 | 0.35 | 0.603 | - | - | - | - | 27.53 | 4.932 | 0.593 |
| VO4  | 42.584 | 6.548 | 1.378 | 0.26 | 0.943 | - | - | - | - | 51.391 | 3.805 | 0.917 |
| VO5  | 21.681 | 4.085 | 0.685 | 0.1 | 0.948 | 0.113 | 0.037 | 193.418 | 37.659 | 0.957 | 11.48 | 1.085 | 0.863 |
| VP1  | 228.797 | 25.578 | 1.589 | 0.18 | 0.971 | - | - | - | - | 157.328 | 13.55 | 0.888 |
| VP2  | 327.646 | 63.461 | 1.54 | 0.23 | 0.941 | - | - | - | - | 201.923 | 19.545 | 0.861 |
| VP3  | 10.877 | 3.319 | 0.458 | 0.1 | 0.895 | 0.15 | 0.095 | 58.473 | 11.744 | 0.876 | 2.018 | 0.266 | 0.693 |
| VP4  | 20.2 | 5.829 | 0.944 | 0.19 | 0.947 | - | - | - | - | 18.56 | 1.088 | 0.947 |
| VP5  | 10.842 | 3.289 | 0.459 | 0.1 | 0.896 | 0.15 | 0.094 | 58.46 | 11.649 | 0.878 | 2.017 | 0.265 | 0.696 |
| VP6  | 207.294 | 19.519 | 1.451 | 0.15 | 0.975 | - | - | - | - | 157.181 | 11.182 | 0.923 |
| VP7  | 164.232 | 5.17 | 1.099 | 0.05 | 0.996 | - | - | - | - | 156.031 | 3.176 | 0.993 |
| CV   | - | - | - | - | - | - | - | - | - | - | - | - |
| FP   | 21.07 | 3.307 | 0.978 | 0.11 | 0.971 | - | - | - | - | 20.43 | 0.876 | 0.971 |
| FE   | 24.905 | 2.618 | 1.323 | 0.1 | 0.986 | - | - | - | - | 33.435 | 1.836 | 0.954 |
| FC   | 20.149 | 3.368 | 1.251 | 0.14 | 0.971 | - | - | - | - | 26.738 | 1.548 | 0.949 |

The \( K_d \) values are linked to soil characteristics, as indicated by the statistical results that show positive and significant correlation \( (p < 0.05) \) with pH in water \( (r = 0.50; R^2 = 0.25) \), with the concentrations of exchangeable Ca and Mg \( (r = 0.58 \text{ and } 0.43; R^2 = 0.34 \text{ and } 0.18, \text{ respectively}) \), and with eCEC \( (r = 0.57; R^2 = 0.32) \). To note that bivariate correlations were calculated using the Pearson’s correlation method, in which the obtained “r” values indicate the degree of correlation (values closer to 1 indicate that more relation exists between the parameters) and “\( p \)” is the level of significance. The squared values of \( r \) \((R^2, \text{coefficients of determination})\) indicate the fraction of the variability explained by the respective soil property.
Regarding the Freundlich model, to consider the higher the values of the $K_F$ parameter, the greater the adsorption capacity of the adsorbent [34]. In the present study, $K_F$ values also show high variability in corn soils ($3.23–478.86 \text{ L}^n \mu \text{mol}^{1-n} \text{ kg}^{-1}$) and VP vineyards ($0.84–327.64 \text{ L}^n \mu \text{mol}^{1-n} \text{ kg}^{-1}$), with lower oscillation for vineyard soils on schist and slate and for forest soils ($21.6–42.58$ and $20.14–24.90 \text{ L}^n \mu \text{mol}^{1-n} \text{ kg}^{-1}$, respectively). Considering the whole set of soils used in this work, $K_F$ showed a positive and significant correlation ($p < 0.05$) with the same soil parameters as $K_d$, specifically with pH in water ($r = 0.56; R^2 = 0.31$), pH and in KCl ($r = 0.56; R^2 = 0.31$), concentrations of exchangeable Ca ($r = 0.71; R^2 = 0.50$), exchangeable Mg ($r = 0.45; R^2 = 0.20$), and with eCEC ($r = 0.49; R^2 = 0.24$).

Kodešová et al. [35] also found high correlations among these soil properties and values of the Freundlich’s $K_F$ coefficient corresponding to adsorption of various types of antibiotics onto soils. As previously indicated, these results show the importance of pH in the adsorption processes, mainly due to affecting the charge of both antibiotics and soil components, as well as the possible intervention of cationic bridges. The values of Freundlich’s $n$ parameter (related to the reactivity and heterogeneity of the active sites of the sorbent) [36,37] were highly variable for the different soils. The highest oscillations were observed in crop soils (between 0.011 and 1.655 in corn soils, between 0.21 and 1.589 in granite vineyard soils, and between 0.685 and 1.378 in vineyard soils on schist and slate), while the variability was lower, and the values were relatively high, in forest soils (from 0.978 to 1.323).

3.3. Desorption

Table 2 shows the amounts of CFX desorbed (in $\mu \text{mol kg}^{-1}$ and percentage), as a function of the concentration of antibiotic added. Desorption values were low, never exceeding $1.87 \mu \text{mol kg}^{-1}$, regardless of the concentrations of antibiotic added. In maize (corn) and vineyard soils on schist and slates, the maximum desorption value was $0.53 \mu \text{mol kg}^{-1}$. The score was slightly higher in vineyard soils on granite ($0.73 \mu \text{mol kg}^{-1}$). Forest soils showed the maximum desorption values among the whole set of samples in the study ($1.87 \mu \text{mol kg}^{-1}$).
Table 2. CFX desorption, expressed in µmol kg\(^{-1}\) (and in a percentage, between brackets), from the various studied soils, as a function of the concentration of antibiotic added (C\(_0\), in µmol L\(^{-1}\)). M, maize (corn) soils; VO, vineyard soils (Ourense province); VP, vineyard soils (Pontevedra province); F, forest soils. Average values (\(n=3\)), with coefficients of variation always < 5%.

| Soil | C\(_0\) (µmol L\(^{-1}\)) | 2.5 | 5 | 10 | 20 | 30 | 40 | 50 |
|------|----------------------------|-----|---|----|----|----|----|----|
| M1   | 0 (0)                      | 0.37 (1.5) | 0.37 (0.8) | 0.39 (0.8) | 0.51 (0.7) | 0.51 (0.5) | 0.53 (0.4) |
| M2   | 0 (0)                      | 0.36 (3.0) | 0.35 (1.4) | 0.36 (0.7) | 0.39 (0.5) | 0.36 (0.4) | 0.48 (0.4) |
| M3   | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0.11 (2.7) |
| M4   | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0.48 (0.4) |
| M5   | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0.48 (0.4) |
| M6   | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0.01 (0.0) |
| M7   | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0.01 (0.0) |
| VO1  | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      |
| VO2  | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      |
| VO3  | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      |
| VO4  | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      |
| VO5  | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      |
| VP1  | 0.39 (6.64)                | 0.41 (3.35) | 0.43 (1.77) | 0.50 (1.02) | 0.49 (0.67) | 0.59 (0.60) | 0.49 (0.48) |
| VP2  | 0.38 (6.45)                | 0.38 (3.15) | 0.41 (1.67) | 0.46 (0.92) | 0.66 (0.89) | 0.65 (0.66) | 0.73 (0.59) |
| VP3  | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      |
| VP4  | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      |
| VP5  | 0 (0)                      | 0 (0)     | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      | 0 (0)      |
| VP6  | 0 (0)                      | 0 (0)     | 0.37 (1.55) | 0.34 (0.69) | 0.47 (0.64) | 0.42 (0.43) | 0.49 (0.40) |
| VP7  | 0.44 (7.98)                | 0.42 (3.07) | 0.39 (1.66) | 0.33 (0.67) | 0.27 (0.37) | 0.30 (0.33) | 0.51 (0.40) |
| VP8  | 0.36 (6.27)                | 0.35 (2.90) | 0.33 (1.34) | 0.11 (0.23) | 0.32 (0.43) | 0.31 (0.43) | 0.46 (0.37) |
| FP   | 0.14 (3.12)                | 0.33 (3.22) | 0.73 (3.33) | 1.13 (2.53) | 1.22 (1.81) | 0.41 (0.47) | 0 (0)      |
| FE   | 0.11 (2.32)                | 0.26 (2.42) | 0.58 (2.53) | 1.17 (1.81) | 0.96 (1.38) | 0.66 (0.72) | 0.49 (0.42) |
| FC   | 0.15 (3.53)                | 0.35 (4.85) | 1.05 (4.85) | 1.87 (3.79) | 0.77 (1.11) | 0.58 (0.64) | 0.33 (0.29) |

A statistical test focusing on eventual relations among the maximum desorption values and the properties of the different soils showed a significant and positive correlation with sand content (\(r = 0.45, p < 0.05\)), and a negative correlation with clay content (\(r = -0.43, p < 0.05\)). Therefore, clays would have an important role in the intensity of the adsorption, reducing the reversibility of the process.

Analyzing desorption data presented in percentage (Table 2), CFX desorption was always below 8% (and below 1% in most cases), evidencing that adsorption has low reversibility in the soils of the current study, as previously observed in other Galician soils for tetracycline antibiotics [40], and contrary to what was found for sulfonamides, in which desorption exceeded 50% in some cases [41]. The marked differences among adsorption and desorption scores indicate the relevance of hysteresis affecting these processes.

4. Conclusions

In the agricultural soils included in this study, the adsorption of the antibiotic cefuroxime (CFX) was dependent on the pH of the soil, with the highest adsorption corresponding to those soils having higher pH values. In the case of forest soils, which had a very acidic pH, their high organic matter contents would explain the high CFX adsorption obtained. Regarding desorption, it was below 1% in most cases, indicating the low reversibility of the
adsorption process, especially in soils with a higher proportion of clay. Adsorption data fitted better to the Freundlich than to the Linear and Langmuir models. The correlations of Freundlich’s $K_F$ parameter and the $K_d$ parameter of the Linear model with soil characteristics indicate that the most important factors in adsorption are pH and the concentrations of exchangeable Ca and Mg, probably due to their influence on the electric charges of colloids and the formation of cationic bridges. These results can be considered relevant in terms of the evaluation of the possible evolution of the antibiotic CFX when it reaches the soil as a contaminant, affecting its retention/release. Therefore, there is a probability that it will be mobilized into water bodies or absorbed by plants, entering the food chain, with have consequent environmental and public health repercussions.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/app11104663/s1, Table S1: Basic details corresponding to the 23 soils sampled for this study. M, maize (corn) soils; VO, vineyard soils (Ourense province); VP, vineyard soils (Pontevedra province); F, forest soils; CM and CV, control soils in maize and vineyard areas; Table S2: Values corresponding to the basic parameters determined in the various studied soils. M, maize (corn) soils; VO, vineyard soils (Ourense province); VP, vineyard soils (Pontevedra province); F, forest soils; CM and CV, control soils in maize and vineyard areas. Average values ($n = 3$), with coefficients of variation always <5%; Table S3: CFX adsorption, expressed in $\mu$mol kg$^{-1}$ (and in a percentage, between brackets), onto the various studied soils, as a function of the concentration of antibiotic added. M, maize (corn) soils; VO, vineyard soils (Ourense province); VP, vineyard soils (Pontevedra province); F, forest soils; CM and CV, control soils in maize and vineyard areas. Average values ($n = 3$), with coefficients of variation always <5%; Figure S1: Selected chromatograms corresponding to the quantification of the antibiotic cefuroxime.

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