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Simultaneous presence of antibiotics in the environment: competition for soil adsorption sites and risk mitigation by bioadsorbents

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Antibiotics are poorly absorbed and largely excreted through feces and urine, entering the environment. Although previous research focused on the adsorption of cefuroxime (CFX), amoxicillin (AMX) and azithromycin (AZM) onto soils and bio-adsorbents, the effect of the simultaneous presence of these antibiotics was not investigated, although being common in the environment. Hence, this work studied the adsorption of these antibiotics when added together to six soils and to three bio-adsorbents (oak ash, pine bark and mussel shell), and compared the results with those obtained for each antibiotic individually in previous studies. AZM exhibited the highest adsorption on soil. AMX adsorption by soils increased in the presence of CFX and AZM (from 76% to 88%). However, the adsorption of the other two antibiotics decreased in ternary systems: CFX dropped from 99% to 96%, and AZM from 100% to 42%. Regarding bio-adsorbents, oak ash demonstrated the highest adsorption efficiency for the three antibiotics, exceeding 90% in the ternary system. Pine bark and mussel shell showed lower adsorption efficiencies. The Freundlich model best described adsorption in soils, while only mussel shell fits well this model among the bio-adsorbents. Desorption from soils increased when antibiotics were applied simultaneously, with AMX showing the highest desorption. For bio-adsorbents, desorption was higher in the single-compound systems. Overall, AMX adsorption was enhanced by the presence of CFX and AZM, while both CFX and AZM adsorption were negatively affected by the presence of other antibiotics, suggesting competitive interactions.

Environmental significance

The increased consumption of antibiotics in recent years has led to their presence becoming more common in various environmental compartments, including wastewater, drinking water sources, soils, and even plants. This can lead to these pollutants entering into the food chain and posing significant risks to both environmental and human health. As soil acts as a natural filter, investigating the retention of these contaminants and preventing their transfer to other systems is particularly important to understand how antibiotics behave in soil and their environmental fate. This study evaluates the capacity of soils with different physicochemical properties to retain three commonly used human antibiotics – amoxicillin, cefuroxime, and azithromycin – when they reach the edaphic environment simultaneously. Additionally, the adsorption capacity of low-cost waste materials or by-products is assessed as a potential mitigation strategy for antibiotic contamination. All these aspects are of clear environmental relevance.

1 Introduction

Emerging pollutants include pharmaceuticals and their transformation products, personal care products, pesticides, certain biological materials, and others.[1] In recent years, low concentrations of these contaminants have been detected in wastewater, surface water, groundwater and drinking water, which can generate great risks to human health and natural ecosystems due to short- and long-term toxicity.[2–4] Golchin *et al.*[5] detected amoxicillin in concentrations between 4.7 and 16.25 g L^{-1} in treated effluents.

Regarding antibiotics, in 2021 the population weighed average consumption in the EU/EEA, measured in mg of active substance per kg of estimated biomass, was 125.0 mg kg^{-1} in humans and 92.6 mg kg^{-1} in food-producing animals,[6] representing a 53% reduction in the latter between 2011 and 2022.[7] Regarding humans, the average total consumption of systemic antibacterial agents used in Europe in 2023 was estimated to be 20 daily doses per 1000 inhabitants per day, considering both

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hospital and no-hospital use, while non-hospital consumption, was 18.3 daily doses per 1000 inhabitants per day.[8]

Approximately, 60–85% of antibiotics consumed are excreted in feces and urine as parent compounds or transformation products.[9–11] After excretion, these antimicrobials may end up retained in sludge and/or eliminated by biotic and abiotic degradation in wastewater disposal systems. However, molecular breakdown is often incomplete, and antibiotics and their metabolites end up entering the environment.[12] Moreover, sewage sludge that contains antibiotics is used as organic amendment in agricultural soils, with repeated applications contributing to the entry of antimicrobials to terrestrial ecosystems.[13–16]

Soil is often the main sink for pollutants and can potentially reduce environmental risks related to antibiotics, as physical and chemical processes could immobilize these molecules. The retention of antibiotics onto soils depends on soil characteristics (pH, organic matter, clays, metal oxides, *etc.*), as well as on characteristics of the antibiotics (photo-stability, biodegradation, solubility in water, electrical charge, *etc.*).[17] However, soil can also become a source of emissions when its capacity to retain the affected pollutants is exceeded.[18] Biel-Maeso *et al.*[19] detected antibiotics in concentrations up to 5.45 ng g^{-1} in soil samples collected in Spain. In the same geographic area of the current study, Conde-Cid *et al.*[20] reported the presence of various tetracyclines and sulfonamides in soils at concentrations of up to 600 ng g^{-1}. In addition, Barreiro *et al.*[21] detected amoxicillin (AMX) and cefuroxime (CFX) in soil samples, with concentrations reaching up to 57 ng g^{-1} and 276 ng g^{-1}, respectively, while azithromycin was not detected. However, Topp *et al.*[22] detected azithromycin, in concentrations between 100 and 10 000 ng g^{-1}, in soils after consecutive application of sewage sludge for five years.

Techniques such as adsorption, coagulation–flocculation, membrane filtration, chemical oxidation, and electrochemical processes are considered effective methods for removing contaminants. However, due to its simple design and operation, along with the advantage of not introducing undesirable byproducts into the system, adsorption has been deemed a promising method for removing pharmaceuticals in the fields of pollution control and waste management.[23,24] Additionally, it is interesting to study the capacity of different materials to adsorb antibiotics, as good results could make them a viable option for incorporation into WWTP or soils with low adsorption capacity to increase pollutants removal. Several studies have documented the interaction and adsorption mechanisms of antibiotic pollutants on various adsorbent materials. Examples of these adsorbents include activated carbon, graphene oxide, bamboo biochar,[25–27] and hybrid magnetic composite sorbents.[28]

Among the most widely used antibiotic types, β-lactams represent the largest proportion of consumption in human and veterinary medicine, being the most common antibiotics found in wastewater and surface waters.[29] Quinolones and their subgroup fluoroquinolones, sulfonamides and macrolides are also emerging groups of antibiotics in the environment due to their slow and difficult biodegradation.[30] To carry out this work two β-lactams, amoxicillin and cefuroxime, and one macrolide, azithromycin, were selected. Fig. 1 shows the chemical structure of these three antibiotics.

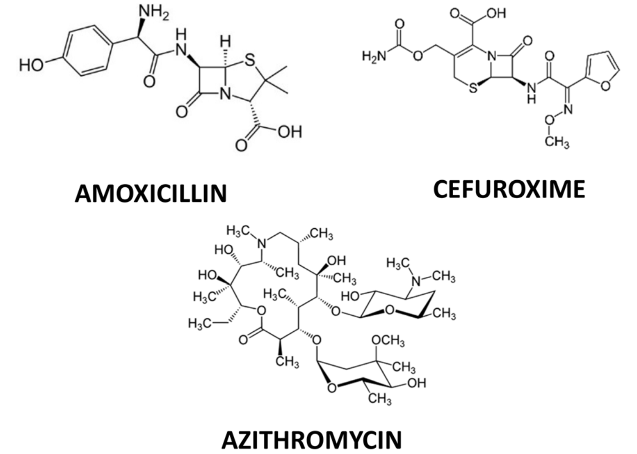

Fig. 1 Chemical structure of amoxicillin, cefuroxime and azithromycin.

Previous studies have investigated the individual adsorption of two β-lactam antibiotics, cefuroxime (CFX) and amoxicillin (AMX), as well as one macrolide antibiotic, azithromycin (AZM), onto various soils and bio-adsorbents.[31–36] However, usual environmental conditions are more complex, often involving the simultaneous presence of multiple contaminants, which may result in competitive interactions.[37,38] Such interactions can involve competition for sorption sites, leading to sorption inhibition, physical displacement of one compound by another, decreased adsorption efficiency, and increased mobility or release.[39]

To date, no studies have evaluated the competitive adsorption and desorption behavior of AMX, CFX and AZM when present simultaneously in a polluted environment. Therefore, the objective of the present work is to investigate the competitive adsorption of these three antibiotics (AMX, CFX, and AZM) onto six soils with varying physicochemical characteristics, as well as onto three low-cost adsorbents (mussel shell, pine bark, and oak ash) which could be used to enhance soil adsorption capacity and in water decontamination processes, which could be of relevance for human and environmental health.

2 Material and methods

2.1 Soil and bio-adsorbents

2.1.1 Soils. Six soils with different physicochemical properties were selected, including one forest soil and five agricultural soils (four vineyard soils and one corn soil). Table S1 (SI) shows the detailed physicochemical properties of the soils. The pH values ranged between 4.68 and 8.02, whereas organic carbon content oscillated from 1.77% to 7.15%, and cationic exchange capacity (eCEC) varied between 7.42 cmol$_c$ kg^{-1} and 42.81 cmol$_c$ kg^{-1}.

2.1.2 Bio-adsorbents. Three bio-adsorbents were selected, two of them from the forestry industry (pine bark and oak ash), and the third one from the food industry (mussel shell). All of them were previously characterized,[32] showing very different physicochemical properties. Pine bark has an acid pH (3.99), while mussel shell and oak ash present an alkaline pH (9.39 and 11.31). Organic carbon ranged between 11.43% (mussel shell) and 48.70% (pine bark), while eCEC values oscillated from 14.92 $\text{cmol}_c\ \text{kg}^{-1}$ (pine bark) to 361.15 $\text{cmol}_c\ \text{kg}^{-1}$ (oak ash). Table S2 (SI) shows the detailed physicochemical properties of the bio-adsorbents.

2.2 Chemical reagents

Cefuroxime (purity ≥ 95%), amoxicillin (with ≥ 95% of purity) and azithromycin (neat) were supplied by Sigma-Aldrich (Barcelona, Spain). Phosphoric acid (being 85% extra pure) was from Acros Organics (Barcelona, Spain), potassium phosphate (purity ≥ 99.5%), acetonitrile (with ≥99.9% of purity) were from Fisher Scientific (Madrid, Spain) and $CaCl_2$ (with purity of 95%) was provided by Panreac (Barcelona, Spain). Milli-Q water (Millipore, Madrid, Spain) was used for preparing all solutions needed for HPLC quantification procedures.

2.3 Adsorption and desorption experiments

Batch-type experiments, consisting of equilibrium tests performed in static and closed systems with a fixed amount of adsorbent and solution under controlled conditions, were carried out to study the adsorption/desorption of CFX, AMX and AZM by six soils and three bioadsorbents, each tested separately, in ternary systems (with the three antibiotics added simultaneously). Two g of each soil were weighed and then 5 mL of a solution with different concentrations of each antibiotic (0; 2.5; 5; 10; 20; 30; 40; 50 $\mu\text{mol L}^{-1}$) were added, using 0.005 M $CaCl_2$ as background electrolyte. In the case of the bioadsorbents, the relation adsorbent to solution used was 0.5 : 10 (0.5 g of each bioadsorbent and 10 mL of antibiotic solution). The suspensions were shaken in the dark for 48 h (time enough to reach equilibrium, according to previous kinetic tests) using a rotary shaker. These suspensions were then centrifuged at 4000 rpm for 15 min (G force: 1931.91). The resulting supernatants were filtered through 0.2 μm nylon syringe filters. Finally, the antibiotic concentrations in the equilibrium solution were determined by HPLC-UV with a LPG 3400 SD equipment (Thermo Fisher, Waltham, MA, USA). After finalizing the adsorption phase, desorption experiments were carried out by adding 0.005 M $CaCl_2$ solution (5 mL for soils and 10 mL for bioadsorbents), which promotes the breaking of the bond between the antibiotic and the adsorbent. Desorption was performed following the same procedure as described for adsorption.

2.4 Data treatment

The experimental data obtained in the adsorption/desorption tests were adjusted to the Freundlich (eqn (1)) and linear (eqn (2)) models.[40]

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

$$K_d = q_e / C_{eq} \quad (2)$$

where q_e (expressed in $\mu\text{mol kg}^{-1}$) is the amount of antibiotic retained in the adsorbent (calculated as the difference between the concentration added and that remaining in the equilibrium solution); K_F ($\text{L}^n\ \mu\text{mol}^{1-n}\ \text{kg}^{-1}$) is the Freundlich constant related to the adsorption capacity; C_{eq} ($\mu\text{mol L}^{-1}$) is the concentration of antibiotic present in the solution at equilibrium; n (dimensionless) is a parameter of the Freundlich model associated with the degree of heterogeneity of the adsorption, and K_d (L kg^{-1}) is the partition coefficient in the linear model.

Freundlich and linear models were adapted for competitive systems (eqn (3) and (4), respectively).

$$(q_{e\ AMX} + q_{e\ CFX} + q_{e\ AZM}) = K_F(C_{eq\ AMX} + C_{eq\ CFX} + C_{eq\ AZM})^n \quad (3)$$

$$(q_{e\ AMX} + q_{e\ CFX} + q_{e\ AZM}) = K_d(C_{eq\ AMX} + C_{eq\ CFX} + C_{eq\ AZM}) \quad (4)$$

In addition, soil properties were correlated with the parameters obtained in the adjustments to the adsorption models, determining the Pearson correlation coefficients.

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 any further statistical analysis.

3 Results and discussion

3.1 Soil adsorption

Fig. 2 shows adsorption curves for AMX, AZM and CFX in the six soils studied, for both the simple system (when one antibiotic was added alone) and the ternary system (when three antibiotics were added simultaneously). Fig. 3 shows the percentage of adsorption for all antibiotics in simple and ternary systems.

The figures show that AZM was the antibiotic that generally presented the highest adsorption percentages in the simple system, followed by CFX and finally AMX. Furthermore, comparing the adsorption values obtained for the six soils, several differences have been observed. This is due to, both antibiotics (Fig. 1) and soil components, contain functional groups (carboxyl, amine, phenol, hydroxyls on Fe and Al oxides…) that can undergo protonation or deprotonation depending on the pH of the solution.

In the case of AZM, comparing the adsorption values obtained for the six soils, in simple system were not observed differences between soils, however, in ternary system, it was observed an influence of pH in the adsorption. This is due to AZM has one pK_a approximately between 8.6 and 9.5,[41] so in the range of the soils included in this study (4.68–8.02), AZM has positively charged functional groups, favoring the electrostatic interactions with the negative charges of minerals and organic matter. In higher-pH soils (C and VO), AZM adsorption remained unaffected by the presence of the other two antibiotics, with adsorption percentages of 100% in all cases. In contrast, the remaining soils exhibited a pronounced reduction

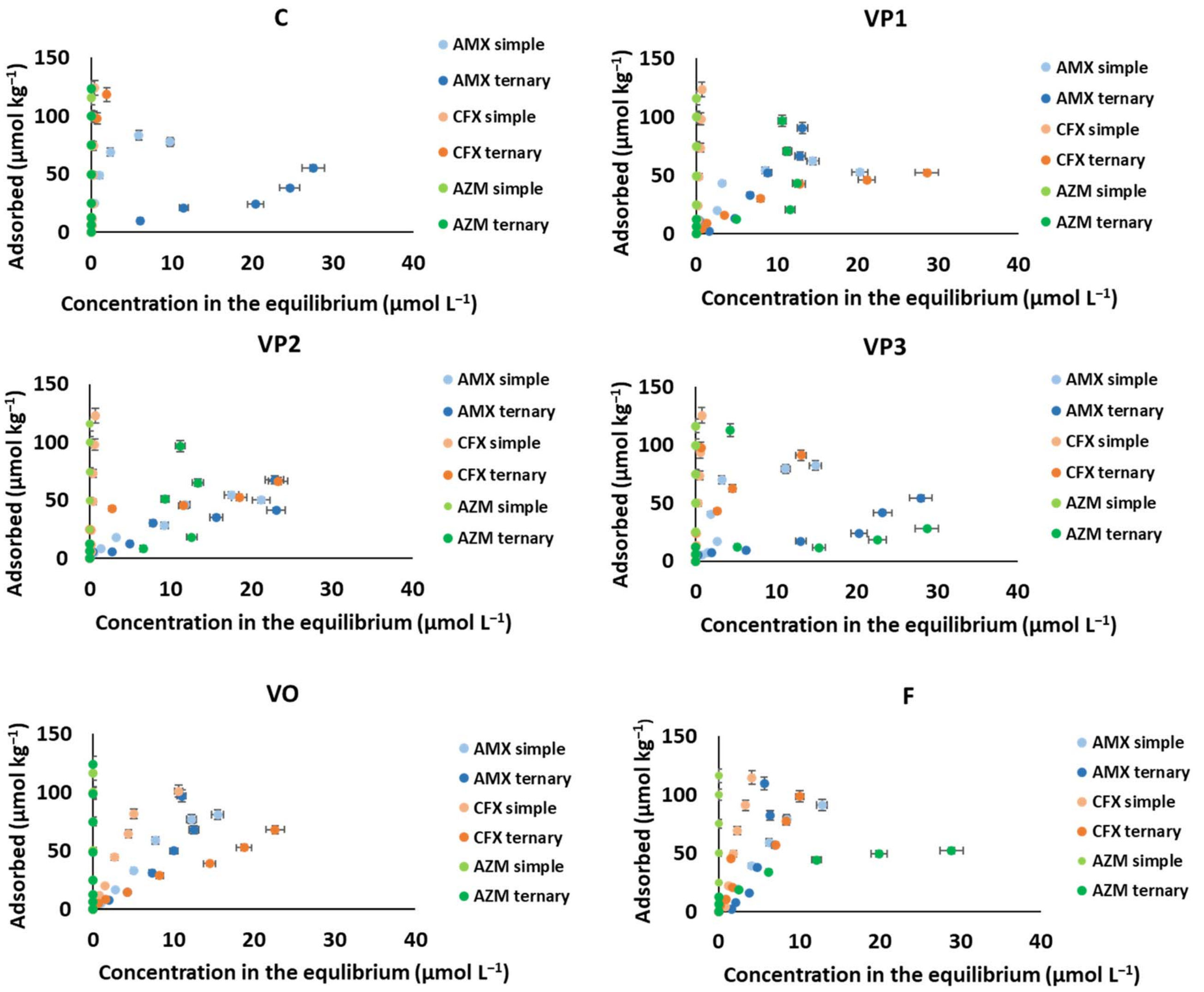

Fig. 2 Adsorption curves for each antibiotic obtained from simple and ternary systems. AMX: amoxicillin; CFX: cefuroxime; AZM: azithromycin; C: corn soil; VP: vineyard soil (Pontevedra province); VO: vineyard soil (Ourense province); F: forest soil.

in AZM adsorption relative to the simple system, indicating potential competitive interactions for adsorption sites. Among the soils evaluated, F exhibited the lowest AZM adsorption percentages in the ternary system (42% when 50 μmol L^{-1} of AZM were added). This is the soil with the lowest pH value, and at the pH level of soil F (pH = 4.68) the non-crystalline components, abundant in this soil, will be positively charged, as well as azithromycin AZM. Therefore, under these conditions, the low-crystallinity components would not contribute to the retention of this antibiotic, but the –COOH groups of the organic matter would begin to deprotonate, facilitating electrostatic interactions with the positively charged groups of AZM. In the ternary system, AZM adsorption showed a negative and significant correlation with exchangeable Al ($r = -0.867$, $p < 0.05$), Fe_{pir} ($r = -0.916$, $p < 0.05$) and Al_{pir} ($r = -0.927$, $p < 0.01$). However, the overall negative charge at the pH value of soil F is still limited, resulting in lower adsorption in more acidic soil compared to those with higher pH, so the other two antibiotics may compete with AZM for adsorption sites, leading to a reduction in its adsorption compared to the simple system. In the other soils (with adsorption values exceeding 80% in the ternary system), the content of non-crystalline minerals is lower than in soil F. However, due to their higher pH range (6.04–8.02, except for VP1), these compounds exhibit negative charges. This, combined with the increased negative charge of organic matter at elevated pH levels, reduced competition for adsorption sites among antibiotics, resulting in a minimal decrease in AZM adsorption compared to the single-component system. Additional mechanisms may also contribute to AZM adsorption in the studied soils, including hydrogen bonding with organic matter and van der Waals forces. Balarak *et al.*[41] also observed a gradual increase in AZM adsorption as pH increased, using activated porous carbon derived from *Azolla filiculoides*, with maximum adsorption at pH values between 9 and 11.

Regarding CFX, similar to AZM, competition among antibiotics was evident, as adsorption percentages were consistently

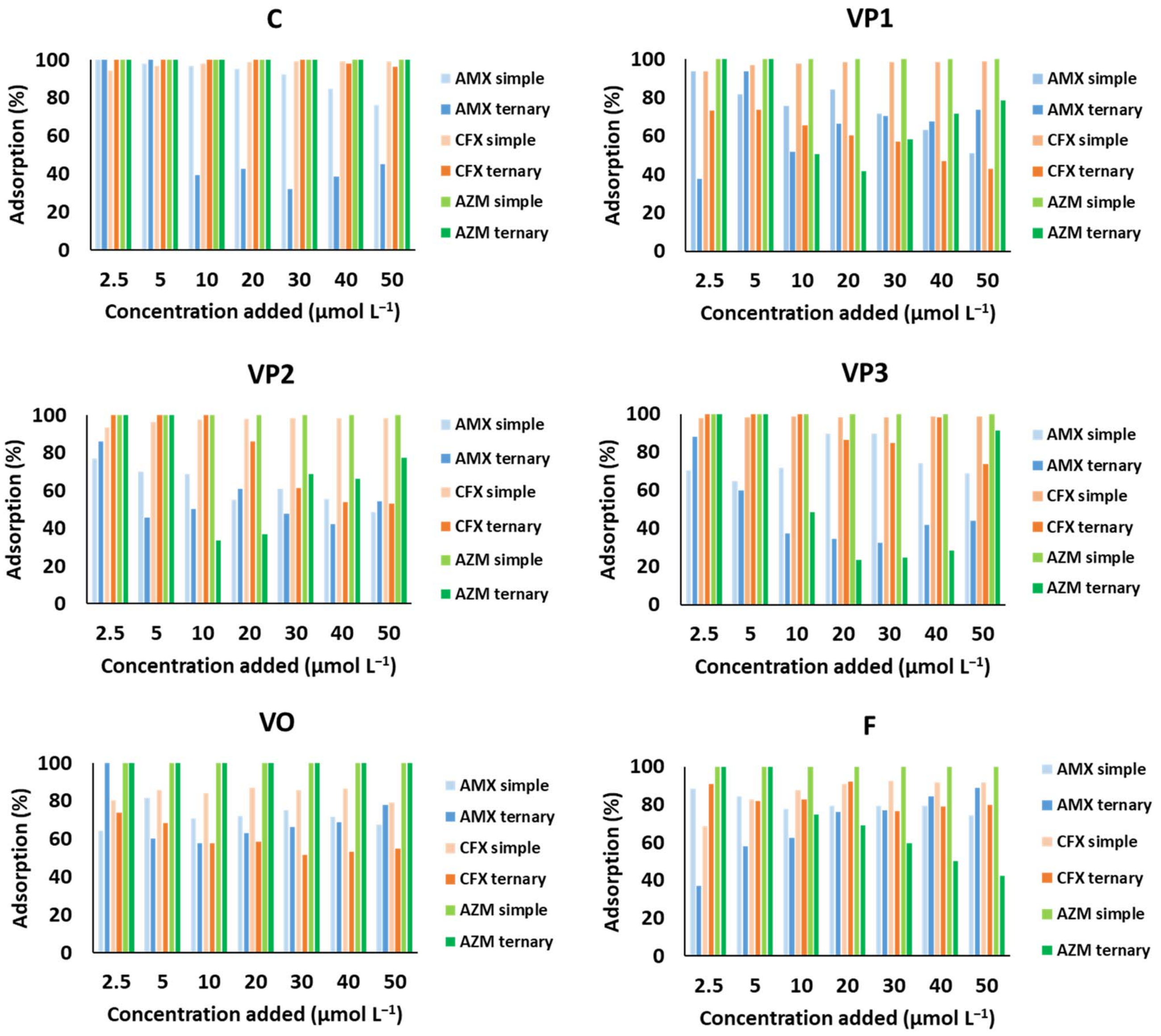

Fig. 3 Adsorption (in percentages) for each antibiotic (amoxicillin, cefuroxime and azithromycin) obtained from simple and ternary systems, as a function of the antibiotic concentrations added. AMX: amoxicillin; CFX: cefuroxime; AZM: azithromycin; C: corn soils; VP: vineyard soil (Pontevedra province); VO: vineyard soil (Ourense province); F: forest soil.

higher in the single systems compared to the ternary system. Furthermore, minimal differences were observed among the different soils when this antibiotic was added individually. However, in the ternary system (AMX + CFX + AZM), differences in adsorption among the different soils were observed. CFX has two dissociation constants ($pK_{a1} = 3.15$ and $pK_{a2} = 10.97$) and can carry a positive or negative charge or exist as a zwitterion, depending on the pH of the medium.[42] Within the pH range of the studied soils, CFX will exist as a zwitterion, with both negative and positive charges. Soils with high pH values (soil C has pH 8.02, being 7.27 for soil VP3) presented the highest adsorption scores for CFX (between 73 and 100%) for all the concentrations added, especially in the ternary system. At these pH values, CFX exists in zwitterionic form, meaning that the positively charged amino groups of the antibiotic interact electrostatically with the negatively charged adsorbent surfaces of the soils, while the anionic groups (COO^-) of CFX bind to these negatively charged surfaces *via* a cation bridge.[43] The lower adsorption in ternary system compared with simple system may be due to the higher antibiotic concentrations, probably as a result of increased ionic strength, which attenuates electrostatic interactions and thereby intensifies the competition for negative charges on the soil surface. This may be due to in the case of soil F, it showed a rather high adsorption percentage (80%), despite having a pH of 4.68. This elevated value for adsorption could be related to the high content of organic matter in this soil (12.33%) and non-crystalline compounds (Table S1), because at pH < 5, same –COOH groups of the organic matter can dissociate[44] and could interact with the positive charges of CFX by electrostatic interactions. It is also possible that protonated amino groups in the soil organic matter and positively charged non-crystalline components interact with anionic groups of the antibiotic. In contrast, the VO soil presents a relatively low adsorption considering its pH (6.04), which is probably justified by being the soil with the lowest organic matter content (3.05%) and also with the lowest concentrations of non-crystalline compounds (Table S1).

Regarding AMX, in the single system, AMX it was generally the least adsorbed compared to the other two antibiotics, particularly at the highest concentration tested (50 μmol L^{-1}), where adsorption values ranged between 50% and 80% (Fig. 3). In the ternary system, AMX also exhibited the lowest adsorption among the three antibiotics, with values ranging from 40% to 90% (Fig. 3). When comparing the single-compound system to the ternary one, synergistic or antagonistic effects of the other antibiotics on AMX adsorption were observed, depending on the soil. In the two soils with the highest pH values (C and VP3), the presence of the other antibiotics had an antagonistic effect, reducing AMX adsorption, possibly due to competition for adsorption sites, an effect that becomes more pronounced at higher concentrations, as the increased ionic strength attenuates electrostatic interactions, as previously described for CFX. In contrast, in the remaining four soils, the effect was synergistic, with CFX and AZM enhancing AMX adsorption. In a previous study on the adsorption competition between AMX and ciprofloxacin (CIP), a synergistic effect between the two antibiotics was observed, with the adsorption of AMX being enhanced by the presence of CIP.[45] This was attributed to a cooperative adsorption, pointed out by several authors.[46–48] According to this cooperative model, when a solute is retained by a site on a homogeneous adsorbent surface, it can influence the consecutive active sites of that surface, promoting new adsorptions and stronger retentions.

Statistical analyses were conducted, revealing a highly significant negative correlation ($r = -0.953$; $p < 0.01$) between pH and AMX adsorption in the ternary system. This antibiotic has three dissociation constants, due to the presence of different functional groups such as carboxyl (with $pK_{a1} = 2.68$), amino ($pK_{a2} = 7.49$) and phenolic ($pK_{a3} = 9.63$),[49] causing that in most of the studied soils it would be found as a zwitterion. In the forest soil (pH < 5), deprotonated carboxyl groups of AMX can bind to the positive charges in the soil (non-crystalline minerals and amino groups of the organic matter) through electrostatic interactions, and also $-COO^-$ groups of the organic matter could interact with the positive charges of AMX. Soils with pH between 5 and 6.5 (VO and VP1) will present more negative charge than soil F, which can interact with protonated groups of AMX. In soils with pH > 7 (C, VP2 and VP3), negative charges will predominate, especially in soil C (pH = 8.02) and AMX will have more deprotonated groups, favoring adsorption through a cationic bridge, and under these conditions there is competition between AMX and the other two antibiotics for the adsorption sites.

Table 1 Parameters of the linear and Freundlich models for amoxicillin, cefuroxime and azithromycin adsorption onto soils in simple and ternary systems[a]

		Freundlich					Linear		
Soil	Antibiotic	K_F	Error	n	Error	R^2	K_d	Error	R^2
C	AMX	44.17	4.64	0.31	0.06	0.940	10.72	2.30	0.370
	CFX	478.87	152.34	1.58	0.29	0.893	247.34	29.38	0.797
	AZM	95.99	50.52	0.39	0.10	0.890	3.40	0.55	0.670
	AMX + CFX + AZM	**8.62**	**4.42**	**1.03**	**0.16**	**0.969**	**9.55**	**0.42**	**0.969**
VP1	AMX	99.53	20.66	1.09	0.28	0.840	93.63	0.67	0.480
	CFX	228.80	25.58	1.59	0.18	0.971	157.03	11.18	0.923
	AZM	—	—	—	—	—	1.08	0.13	0.790
	AMX + CFX + AZM	**0.53**	**0.43**	**1.54**	**0.22**	**0.968**	**4.07**	**0.29**	**0.927**
VP2	AMX	—	—	—	—	—	—	—	—
	CFX	207.30	19.52	1.45	0.15	0.975	157.18	11.18	0.923
	AZM	10.24	0	1.33	0.08	0.360	33.87	9.59	0.360
	AMX + CFX + AZM	**—**	**—**	**1.25**	**0.29**	**0.926**	**3.38**	**0.25**	**0.917**
VP3	AMX	116.05	9.89	0.93	0.13	0.970	120.34	5.63	0.970
	CFX	164.23	5.17	1.10	0.05	0.996	156.03	3.18	0.990
	AZM	—	—	—	—	—	8.58	2.56	0.300
	AMX + CFX + AZM	**—**	**—**	**0.84**	**0.78**	**0.553**	**2.99**	**0.611**	**0.551**
VO	AMX	19.29	5.08	0.66	0.14	0.900	9.68	1.15	0.790
	CFX	21.68	4.09	0.69	0.1	0.948	11.48	1.09	0.863
	AZM	8.87	0	1.07	0.07	0.270	11.99	3.78	0.270
	AMX + CFX + AZM	**3.63**	**1.93**	**1.22**	**0.16**	**0.977**	**7.53**	**0.33**	**0.970**
F	AMX	13.44	1.89	0.79	0.07	0.990	8.49	0.38	0.970
	CFX	20.15	3.37	1.25	0.14	0.971	26.74	1.55	0.949
	AZM	—	—	—	—	—	0.47	0.11	0.100
	AMX + CFX + AZM	**12.54**	**2.81**	**0.79**	**0.06**	**0.988**	**6.08**	**0.26**	**0.971**

[a] K_F expressed in $L^n\ kg^{-1}\ \mu mol^{1-n}$; n = dimensionless; K_d expressed in L kg^{-1}; — = error value too high for fitting. C = corn soil; VP and VO = vineyard soils; AMX: amoxicillin; CFX: cefuroxime; AZM: azithromycin.

3.2 Adjustment of AMX, CFX and AZM adsorption onto soils to adsorption models

Adsorption results were adjusted to the linear and Freundlich models. The linear and Freundlich models are the most common methods of establishing equilibrium relationships between an adsorbent and an adsorbate, or between the amount of substance adsorbed onto a solid phase and the amount remaining in solution at a given temperature under equilibrium conditions.[50] The Freundlich model assumes that adsorption has no predictable limit and that it occurs on a heterogeneous surface with adsorption sites of different energy, as is the case with soils.[51] On the contrary, the linear model assumes that adsorption is proportional to the concentration in solution, with adsorption sites being abundant and uniform. Table 1 shows the values obtained for the different parameters of these models.

As shown in Table 1, the adsorption of AMX, CFX and AZM in the ternary system presented a rather acceptable adjustment to the linear and Freundlich models in most cases, with R^2 values higher than 0.9, except for soil VP3.

Regarding the Freundlich model, the K_F parameter, which is related to the adsorption capacity, ranged between 0.526 and 12.543 L^n kg^{-1} μmol^{1-n}, values lower than those obtained for simple systems corresponding to each antibiotic. This difference is especially evident for CFX, which shows the most significant decrease in adsorption within the ternary system. K_F values also were lower than those obtained by Conde-Cid *et al.*[52] for tetracyclines in a ternary system, and by Cela-Dablanca *et al.*[45] in a binary system with AMX and CIP. However, these values were similar to those obtained in a ternary system for three sulfonamides.[53] K_F was significantly and positively correlated ($p < 0.05$) with different properties of the soils: with C ($r = 0.881$), N ($r = 0.897$) and Fe_{pir} ($r = 0.828$). The observation of strong correlations with non-crystalline Fe contents in the soils may indicate high adsorption energy for certain antibiotics when bound to these non-crystalline minerals.[54] On the other hand, Conde-Cid *et al.*[55] found that soils with higher organic matter content adsorbed all the added antibiotic, whereas soils with low organic matter did not perform equally. This may be because soils with less organic matter have fewer adsorption sites, which become saturated. Considering the Freundlich n parameter, two of the soils (VP3 and F) had $n < 1$, indicating a heterogeneous adsorption surface, where the highest energy sites are occupied first, while the rest exhibited $n > 1$. When n values are higher than 1, adsorption would be promoted as the concentration of added antibiotics increases.[56]

Regarding the linear model, in the ternary system the K_d value oscillated between 2.99 and 9.554 L kg^{-1}. These values are lower than those obtained for these antibiotics in simple systems, and similarly to what was observed for the K_F parameter, with this difference being more evident in the case of CFX.

Fig. S1 (SI) shows the adsorption curves for the three antibiotics added simultaneously and their adjustments to the Freundlich and linear models.

3.3 Bio-adsorbents adsorption

Fig. 4 shows adsorption curves for AMX, CFX and AZM, both in simple and ternary systems, corresponding to oak ash, pine bark and mussel shell, while Fig. 5 shows the adsorption data expressed in percentages.

Oak ash was the bio-adsorbent that presented the highest adsorption for all the antibiotics in both systems, more

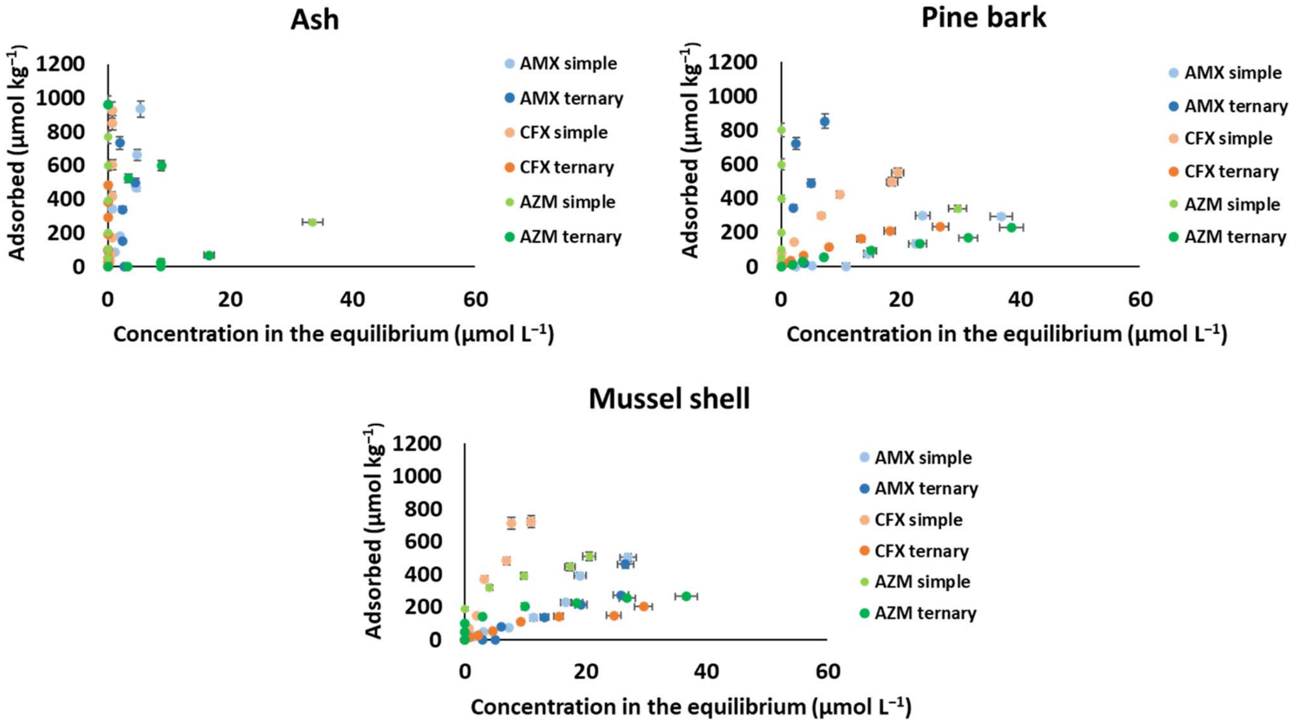

Fig. 4 Adsorption curves for each antibiotic obtained from simple and ternary systems. AMX: amoxicillin; CFX: cefuroxime; AZM: azithromycin.

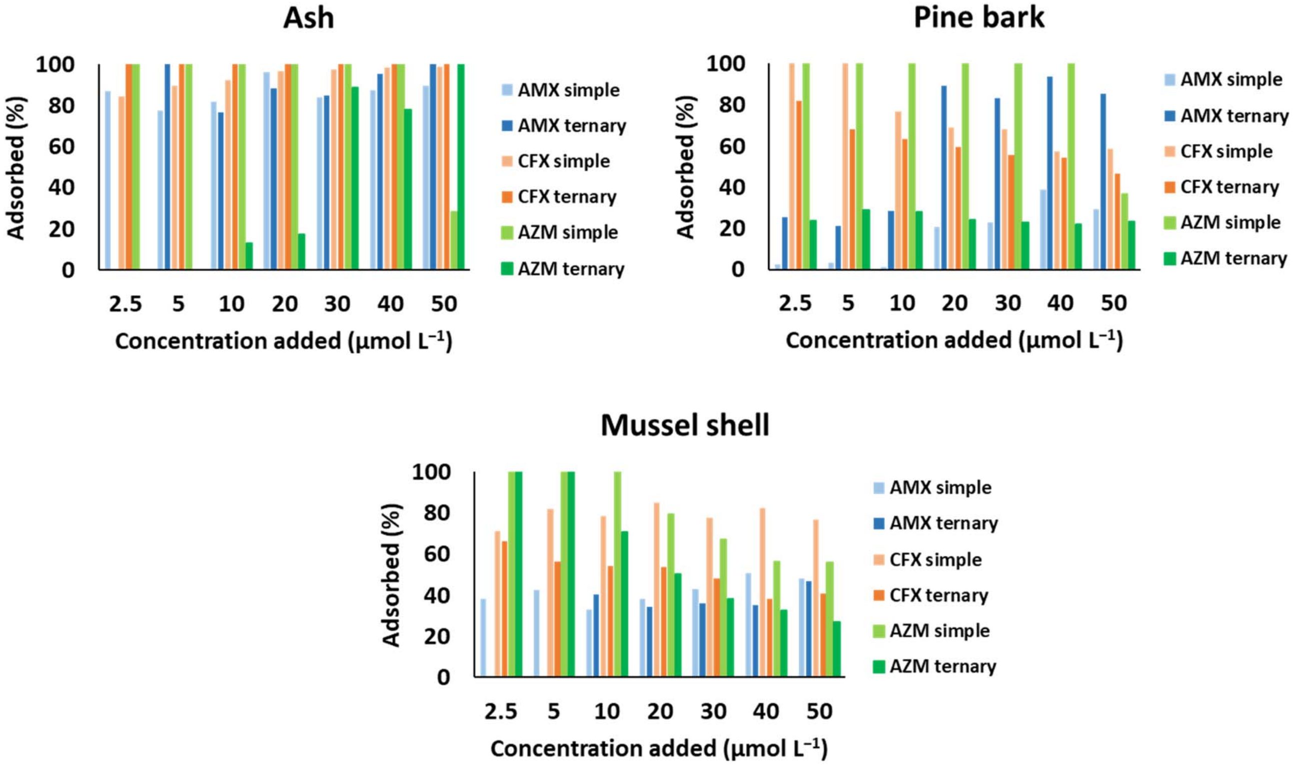

Fig. 5 Adsorption by the bio-adsorbents (in percentages) for each antibiotic (amoxicillin = AMX, cefuroxime = CFX, azithromycin = AZM) obtained from simple and ternary systems, as a function of the antibiotic concentrations added.

pronounced in the case of CFX and AMX. For pine bark and mussel shell, the results are very variable, with a tendency towards higher adsorption using pine bark, especially at higher doses of antibiotic. In a previous study for three tetracyclines in a ternary system, pine bark and oak ash showed high adsorption scores, while mussel shell presented lower adsorption, suggesting that, for the first two materials, the adsorption surfaces were not saturated at the antibiotic concentrations used, and no competition among antibiotics was observed.[54]

Comparing both systems, although oak ash adsorbs generally high percentages in both systems, reaching 100% in many cases, there is a tendency for higher adsorption in the ternary system, especially at higher doses added. These results indicate that there is a synergistic effect between all antibiotics, that can be related to the cooperative adsorption model described by several authors.[57,58] The alkaline nature of this material and its abundance of variable charge components, specifically non-crystalline Fe and Al (Fe_{ox}, Al_{ox}) would not favor the retention of antibiotics, as this alkaline pH would result in a high negative charge density for both the antibiotics and the variable charge components present in the adsorbent, preventing binding through electrostatic attractions.[54] However, other mechanisms, such as adsorption through cation bridging, may still play a role,[9] probably using Ca as a binding element.

Nevertheless, in the case of pine bark (except for AMX) and mussel shell, the opposite effect occurs, with adsorption being lower when the three antibiotics were added together, indicating competition for adsorption sites. The lower adsorption of AZM and CFX by pine bark is attributed to its acidic pH, as these antibiotics generally exhibit higher adsorption at higher pH levels. Under strongly acidic conditions, pine bark shows low negative surface charge for the adsorption of positively charged AZM and the cationic groups of CFX. As a result, when present in a single-solute system at low concentrations, the adsorption percentage of these antibiotics is high. However, in a multicomponent system, the adsorbent surface becomes saturated, and the antibiotics compete for the available adsorption sites. In contrast, AMX shows the opposite behavior, with greater adsorption occurring under more acidic conditions and a synergistic effect of the other antibiotics on its adsorption onto pine bark. Mussel shell exhibits an alkaline pH, as oak ash; however, its non-crystalline elements and Ca contents are significantly lower than that of oak ash. Therefore, the adsorption capacity is lower for mussel shell, especially at higher doses of antibiotic, where adsorption values generally do not exceed 47% in the ternary system.

In a previous study investigating the competition between AMX and CIP for the same bio-adsorbents, it was also found that CIP had a synergistic effect on AMX adsorption in both pine bark and mussel shell. However, CIP was affected by the presence of AMX, decreasing its adsorption, and, again, this competition was more evident for mussel shell.[45]

Table 2 Parameters of the linear and Freundlich models for amoxicillin, cefuroxime and azithromycin adsorption by different bio-adsorbents in simple and ternary systems. K_F expressed in $L^n\ kg^{-1}\ \mu mol^{1-n}$; n = dimensionless; K_d expressed in $L\ kg^{-1}$; — = error value too high for fitting. AMX: amoxicillin; CFX: cefuroxime; AZM: azithromycin

		Freundlich					Linear		
Adsorbent	Antibiotic	K_F	Error	n	Error	R^2	K_d	Error	R^2
Oak ash	AMX	100.826	77.588	1.213	0.49	0.816	139.604	16.152	0.812
	CFX	1177.352	772.661	2.170	1.896	0.562	766.994	157.816	0.496
	AZM	11.79	0	0.885	0.476	—	—	—	—
	AMX + CFX + AZM	—	—	—	—	—	—	—	—
Pine bark	AMX	—	—	1.370	0.434	0.822	7.919	1.131	0.789
	CFX	110.851	27.973	0.535	0.094	0.965	30.413	2.701	0.867
	AZM	11.452	0	1.002	0.390	—	—	—	—
	AMX + CFX + AZM	—	—	**0.517**	**0.507**	**0.317**	**14.887**	**5.236**	**0.214**
Mussel shell	AMX	5.300	2.995	1.391	0.183	0.966	17.251	1.213	0.933
	CFX	119.306	33.638	0.782	0.134	0.948	75.246	5.209	0.927
	AZM	208.193	106.681	0.282	0.194	0.820	27.826	4.256	0.592
	AMX + CFX + AZM	**37.496**	**11.458**	**0.691**	**0.072**	**0.978**	**10.015**	**0.613**	**0.934**

3.4 Adjustment of AMX, CFX and AZM adsorption by bio-adsorbents to adsorption models

The obtained adsorption data were fitted to the linear and Freundlich models. Table 2 shows the results of parameters obtained in the adjustments.

The data in Table 2 show that the fittings are worse in the ternary than in simple systems. Only mussel shell presented a rather good adjustment to the Freundlich and linear models, with $R^2 > 0.9$, while oak ash and pine bark did not fit well to any model. Fig. S2 (SI) shows adsorption curves, both real and according to the linear and Freundlich models.

The Freundlich affinity coefficient (K_F), related to the adsorbent adsorption capacity, in the ternary system reached 111.004 $L^n\ kg^{-1}\ \mu mol^{1-n}$ for pine bark and 37.496 $L^n\ kg^{-1}\ \mu mol^{1-n}$ for mussel shell. This value was higher than that obtained in the simple systems of the three antibiotics for pine bark (Table 2). In the case of mussel shell, the score was significantly lower than that obtained in the simple system for CFX and AZM; however, it was much higher than that obtained for AMX in the simple system (Table 2). The K_F values obtained in the ternary system were lower than those previously found for three tetracyclines in a ternary system using the same bio-adsorbents,[54] and similar to the obtained for CIP and AMX in a binary system by the same bio-adsorbents.[45] The n parameter reached a value of 0.517 for pine bark and 0.691 for mussel shell, indicating a heterogeneous adsorption surface. Different results were obtained by Cela-Dablanca *et al.*[45] for a binary system of AMX and CIP, where n was higher than 1 for oak ash and mussel shell. Conde-Cid *et al.*,[54] in a study dealing with the simultaneous adsorption of three tetracyclines, reported a value of $n < 1$ for pine bark; however, in the case of mussel shell it was $n > 1$.

Regarding the linear model, the distribution constant (K_d) reached 14.887 L kg^{-1} for pine bark and 10.015 L kg^{-1} for mussel shell. These values were generally lower than the obtained for simple system (Table 2), indicating lower adsorption capacities when the three antibiotics were added together.

3.5 Soil desorption

Fig. 6 shows the desorption percentages of AMX, CFX and AZM in simple and ternary systems by the six soils studied.

Fig. 6 shows that AMX was the antibiotic with the highest desorption both in simple and ternary systems. AMX desorption was higher in the ternary system, ranging from 0% to 37%, compared to the range 0% to 14% in the simple system. AZM desorption was null in all cases, except for soil F in the ternary system, where it reached a maximum desorption of 10%. This coincides with what was obtained by other authors for three tetracyclines[52] and three sulfonamides,[53] showing higher desorption from soils when the antibiotics were added simultaneously. However, for CFX the opposite occurs, with desorption being slightly higher in the simple system, although the desorbed values were very low (always lower than 8%). Comparing soils, the one with the lowest pH (F soil) presented higher desorption percentages for CFX and AZM, while the soil with highest pH (C) presented the lowest desorption values. This behavior is opposite to that observed in the adsorption process, where the highest retention occurred in soils with the highest pH, suggesting that the bindings are highly stable and rather irreversible. These results also indicate that adsorption was stronger for CFX and AZM than for AMX. It would be because AMX in presence of the other two antibiotics occupies low-energy sites, while AZM and CFX bind to the higher-energy sites, this also agrees with the generally higher values of the Freundlich K_F parameter obtained for AZM and CFX compared to AMX (Table 1). Chen *et al.*[59] found that two sulfonamides (sulfamethizole and sulfamethazine) occupied adsorption sites with different energy, and they concluded that adsorption energy is a decisive factor determining the competition strength.

3.6 Bio-adsorbents desorption

Fig. 7 shows the desorption in percentage for the three antibiotics studied both in simple and ternary systems, from mussel shell, pine bark and oak ash.

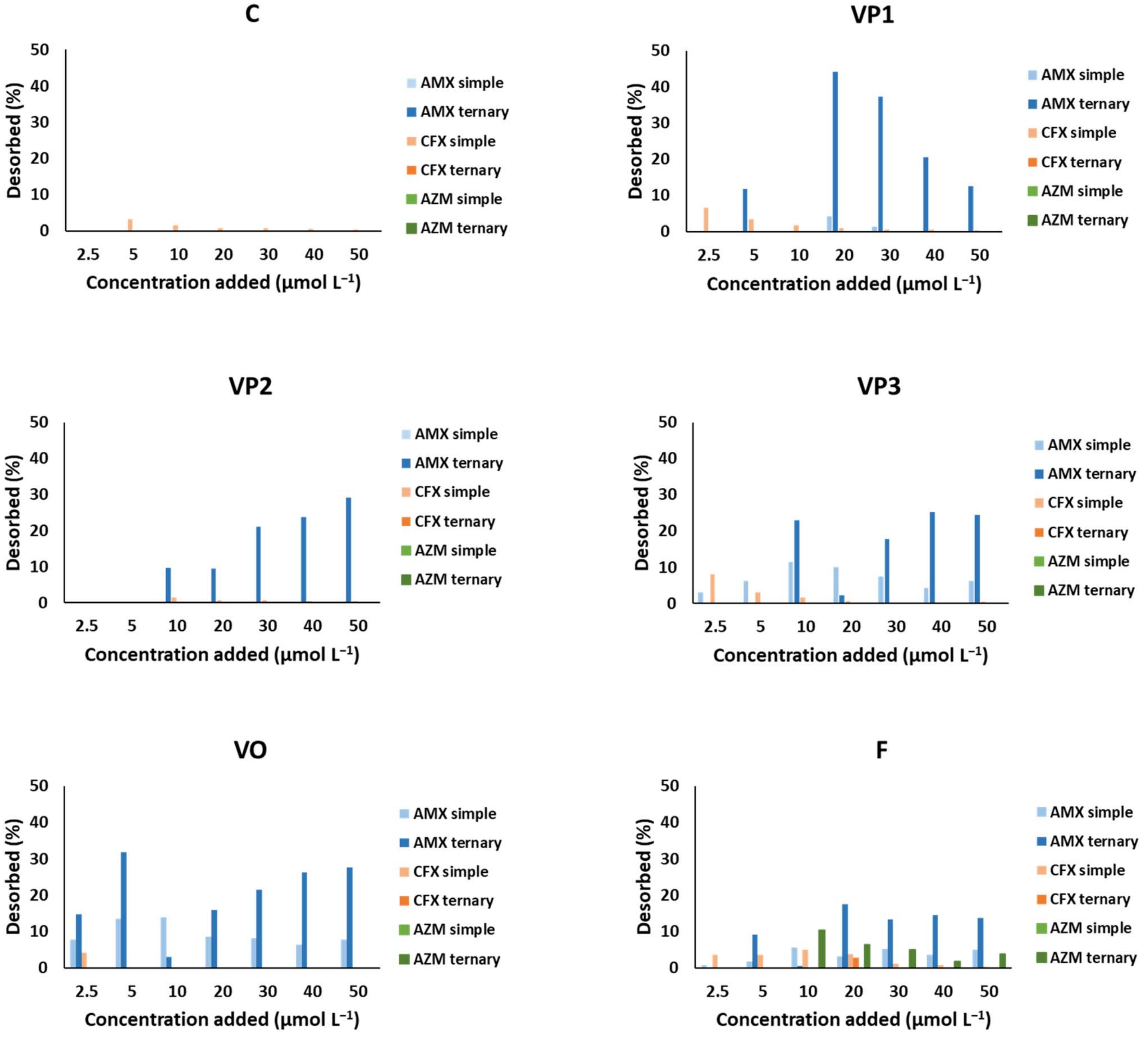

Fig. 6 Soil desorption percentages for each antibiotic (amoxicillin, azithromycin and cefuroxime) obtained from simple and ternary systems. AMX: amoxicillin; CFX: cefuroxime; AZM: azithromycin; C: corn soil; VP: vineyard soil (Pontevedra province); VO: vineyard soil (Ourense province); F: forest soil.

Mussel shell was the bio-adsorbent with the lowest desorption values, showing null desorption for all antibiotics in both systems, except for CFX in the simple system, where it reached values of 12%. Regarding pine bark, AZM desorption was null for all concentrations and in both systems, while for AMX the desorption values reached 4% in the simple system and 33% in the ternary system. CFX was the antibiotic which presented the highest desorption percentages for pine bark in the simple system, with values ranging from 59% to 27%, whereas in the ternary system desorption is always null. Oak ash was the bio-adsorbent that presented the highest desorption values for AZM, reaching 91% and 53% in simple and ternary systems, respectively, when 10 μmol L^{-1} were added, whereas, as the antibiotic concentration increased, the desorption percentage decreased to below 2% for both systems. As for CFX and AMX, desorption levels are practically null for both systems, except for CFX in the simple system, with values not exceeding 8% at low doses.

These findings indicate that oak ash emerged as the most effective bio-adsorbent for AMX and CFX, both in simple and combined (ternary) systems, demonstrating the highest adsorption efficiencies and low desorption. However, it is not suitable for AZM, as although adsorption was high (particularly in the single system and at the highest doses), desorption percentages were significantly elevated at intermediate concentrations, limiting its practical applicability. Pine bark showed good retention capacity for AZM in the single system (up to 40 μmol L^{-1}), but its efficiency declined in the ternary

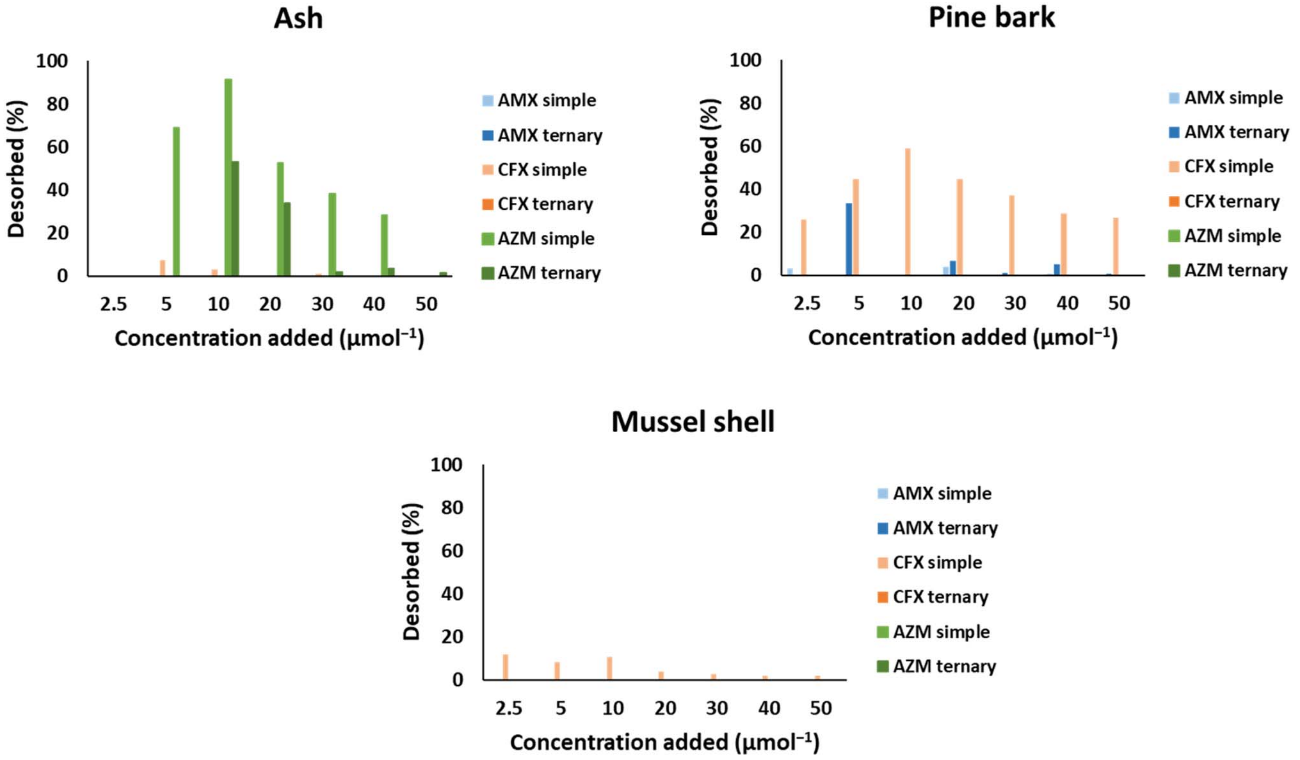

Fig. 7 Desorption percentages from the bio-adsorbents for each antibiotic (amoxicillin, azithromycin and cefuroxime), considering both simple and ternary systems. AMX: amoxicillin; CFX: cefuroxime; AZM: azithromycin.

system. It was also ineffective for CFX at higher doses, with adsorption values below 60% and desorption rates reaching approximately 20%. Nevertheless, pine bark displayed its best adsorption capacity for AMX in the ternary system, where high and stable adsorption was observed. Mussel shell, on the other hand, consistently showed poor adsorption capacity for all three antibiotics, particularly at elevated concentrations, with efficiencies generally below 60%, indicating limited suitability as a bio-adsorbent under the tested conditions.

4 Conclusions

The adsorption of AMX by soils was enhanced in the presence of AZM and CFX, whereas the adsorption of AZM and CFX was reduced when all three antibiotics co-occurred. Despite its increased adsorption, AMX exhibited significantly higher desorption percentages compared to CFX and AZM, suggesting that AMX preferentially binds to lower-energy adsorption sites. The retention of antibiotics by these soils is primarily governed by factors such as pH, organic matter content, non-crystalline minerals and the pK_a values of the compounds. Among the tested bio-adsorbents, oak ash demonstrated the highest efficacy for retaining all three antibiotics in the ternary system. Its high pH, abundance of non-crystalline minerals, and high levels of exchangeable calcium contribute to achieve strong and stable adsorption of the pollutants, resulting in minimal desorption. In contrast, mussel shell and pine bark generally exhibited poor efficiency in retaining the antibiotics under the same conditions. These findings highlight that the presence of multiple antibiotics in soil can increase the risk of environmental contamination. Therefore, the use of oak ash may enhance the soil's retention capacity and serve as a potential barrier to antibiotic mobility, offering a promising strategy for mitigating contamination risks in both terrestrial and aquatic environments.

Author contributions

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analysis: Raquel Cela-Dablanca; resources: Esperanza Álvarez-Rodríguez, María J. Fernández-Sanjurjo, Avelino Núñez-Delgado; funding acquisition: Esperanza Álvarez-Rodríguez, Avelino Núñez-Delgado; project administration: Esperanza Álvarez-Rodríguez, María J. Fernández-Sanjurjo, Manuel Arias-Estévez.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: **https://doi.org/10.1039/d5va00245a**.

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