Adsorption of Tetracycline and Sulfadiazine onto Three Different Bioadsorbents in Binary Competitive Systems

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Date Submitted: 2021-09-21

Keywords: sorbents, retention/release, competitive sorption, antibiotics

Abstract:

Different antibiotics contained in manure, slurry, wastewater or sewage sludge are spread into the environment. The harmful effects of these antibiotics could be minimized by means of immobilization onto bioadsorbent materials. This work investigates the competitive adsorption/desorption of tetracycline (TC) and sulfadiazine (SDZ) onto pine bark, oak ash and mussel shell. The study was carried out using batch-type experiments in binary systems (with both antibiotics present simultaneously), adding 5 equal concentrations of the antibiotics (between 1 and 50 µmol L?1). The adsorption percentages were higher for TC (close to 100% onto pine bark and oak ash, and between 40 and 85% onto mussel shell) than for SDZ (75?100% onto pine bark, and generally less than 10% on oak ash and mussel shell). Pine bark performed as the best adsorbent since TC adsorption remained close to 100% throughout the entire concentration range tested, while it was between 75 and 100% for SDZ. Desorption was always higher for SDZ than for TC. The results of this study could be useful to design practices to protected environmental compartments receiving discharges that simultaneously contain the two antibiotics here evaluated, and therefore could be relevant in terms of protection of the environment and public health.

Record Type: Published Article

Submitted To: LAPSE (Living Archive for Process Systems Engineering)

Citation (overall record, always the latest version): LAPSE:2021.0723
Citation (this specific file, latest version): LAPSE:2021.0723-1
Citation (this specific file, this version): LAPSE:2021.0723-1v1

DOI of Published Version: https://doi.org/10.3390/pr9010028

processes

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Abstract: Different antibiotics contained in manure, slurry, wastewater or sewage sludge are spread into the environment. The harmful effects of these antibiotics could be minimized by means of immobilization onto bioadsorbent materials. This work investigates the competitive adsorption/desorption of tetracycline (TC) and sulfadiazine (SDZ) onto pine bark, oak ash and mussel shell. The study was carried out using batch-type experiments in binary systems (with both antibiotics present simultaneously), adding 5 equal concentrations of the antibiotics (between 1 and 50 μmol L^{-1}). The adsorption percentages were higher for TC (close to 100% onto pine bark and oak ash, and between 40 and 85% onto mussel shell) than for SDZ (75–100% onto pine bark, and generally less than 10% on oak ash and mussel shell). Pine bark performed as the best adsorbent since TC adsorption remained close to 100% throughout the entire concentration range tested, while it was between 75 and 100% for SDZ. Desorption was always higher for SDZ than for TC. The results of this study could be useful to design practices to protected environmental compartments receiving discharges that simultaneously contain the two antibiotics here evaluated, and therefore could be relevant in terms of protection of the environment and public health.

Keywords: antibiotics; competitive sorption; retention/release; sorbents

Citation: Cela-Dablanca, R.; Conde-Cid, M.; Ferreira-Coelho, G.; Arias-Estévez, M.; Fernández-Calviño, D.; Núñez-Delgado, A.; Fernández-Sanjurjo, M.J.; Álvarez-Rodríguez, E. Adsorption of Tetracycline and Sulfadiazine onto Three Different Bioadsorbents in Binary Competitive Systems. *Processes* **2021**, *9*, 28. https://dx.doi.org/10.3390/pr9010028

Received: 30 November 2020
Accepted: 22 December 2020
Published: 24 December 2020

1. Introduction

Antibiotics are widely used for the treatment of infectious diseases, both in humans and animals, but in addition, these drugs are administered in intensive livestock production systems to prevent infections, and in some countries, they are also used as promoters of animal growth [1–5]. Cycon et al. [2], analyzing the situation in 75 countries, indicated that between the years 2000 and 2015, the consumption of antibiotics increased by 65%, and predictions indicate that, on a global scale, in 2030, the consumption of antibiotics will be 200% higher than that in 2015.

The fact that antibiotics are discharged into the environment has led to their presence being detected in soils, waters and crops [4–7]. The reason is that antibiotics are not completely metabolized by humans and animals, and a high percentage of the administered drug is released as the parent compound through feces and urine, discharging into domestic wastewater and into the pits where slurries/manures are deposited [2]. The use of sewage sludge and animal slurries as fertilizers, as well as the irrigation of farmland with wastewater, has traditionally generated risks of chemical and microbiological contamination [8,9] and can lead to the introduction of antibiotics into the soil, and subsequently could be transferred to surface and groundwater, as well as to crops [5,10]. These pollutants can also

reach waterbodies from aquaculture facilities and through wastewater effluents because many conventional treatments do not effectively remove these compounds [1]. All this implies serious environmental problems, one of the most worrying being the proliferation of bacteria resistant to antibiotics and the spread of genes resistant to antibiotics, which reduce the effectiveness of these drugs to effectively fight against pathogenic bacteria causing diseases in humans and animals [5,10]. To prevent environmental contamination due to these emerging pollutants, different procedures have been used, trying to get their degradation or removal, including techniques such as filtration, coagulation, flocculation, advanced oxidation processes, membrane processes, and combined methods [11]. Many of these methods are effective but expensive, and some of them generate products that lead to secondary contamination [11]. Therefore, it is necessary to further investigate low-cost strategies that are effective in minimizing environmental pollution due to antibiotics.

In this line, bioadsorbent materials have been used in recent years, investigating their ability to retain these compounds. In previous studies, our team studied three abundant and low-cost byproducts (pine bark, oak ash, and mussel shell) regarding their ability to adsorb tetracyclines (TCs) and sulfonamides (SAs), working in individual systems (with a single antibiotic added in each experiment). The results indicated that pine bark could be used to effectively immobilize these pollutants due to its high adsorption and low desorption capacities [12].

Despite the fact that antibiotics of these two groups (tetracyclines and sulfonamides) are widely used in veterinary medicine [6,13] and can be present simultaneously in discharges that reach soils and water bodies, there is a lack of studies on the characteristics of their eventual competition for adsorption sites in different soils and bioadsorbents [13].

In view of this, the objective of this work is to shed light on the eventual competition for adsorption sites of the bioadsorbents pine bark, oak ash and mussel shell, taking place between tetracycline (TC) and sulfadiazine (SDZ). To do this, batch-type adsorption/desorption experiments were carried out in binary systems (with both antibiotics present simultaneously). The results of the research could be useful to design systems or management strategies/alternatives for the treatment of pollution affecting environmental compartments where both antibiotics are spread simultaneously, which can also be considered relevant at the public health level.

2. Materials and Methods

2.1. Bioadsorbent Materials

Three different low-cost and abundant byproducts were used in this study. Specifically, two of them were from the forestry industry (pine bark and oak ash), and one from the food industry (mussel shell). A complete characterization of these materials is detailed in Quintáns-Fondo et al. [14], and the Supplementary Material (Tables S1 and S2) includes methodological details regarding the analyses carried out.

2.2. Chemicals

Both antibiotics were supplied by Sigma-Aldrich (Barcelona, Spain), TC with a purity of 95%, and SDZ with a purity of 99.7%. The reagents used were of analytical grade, with a high degree of purity, and were supplied by Panreac (Barcelona, Spain), except for acetonitrile (HPLC grade), which was supplied by Fisher Scientific (Madrid, Spain). All solutions were prepared using Milli-Q water (Millipore, Madrid, Spain).

2.3. Adsorption/Desorption Experiments

2.3.1. Adsorption

Batch-type binary experiments (with TC and SDZ present simultaneously) were carried out, putting in contact, for each of the bioadsorbents, 1 g of sorbent material with 40 mL of a solution containing 0.005 M $CaCl_2$ (added as background electrolyte to keep constant the ionic strength) together with both antibiotics, containing the same concentration for both, specifically 1, 3, 5, 25 and 50 μmol L^{-1} for each of them. The suspensions

were shaken for 24 h (which was enough time to reach equilibrium, as demonstrated in previous kinetic studies), in the dark and at room temperature (25 ± 2 °C) on a rotary shaker, at 50 rpm, and then centrifuged (2665× *g*, 15 min) and filtered (using 0.45 µm nylon syringe filters, Fisher Scientific, Madrid, Spain). All the adsorption tests were done in natural (not adjusted) pH. HPLC-UV equipment was used to quantify the concentration of the antibiotics in the equilibrium solution (see details below), while pH was measured by means of a combined glass electrode (Crison, Barcelona, Spain). The amount of antibiotic adsorbed was calculated as the difference between that initially added and that present in the solution at equilibrium.

2.3.2. Desorption

To quantify desorption of the previously adsorbed antibiotics, the solids remaining from the adsorption experiments were first weighed to calculate the volume of the occluded solution. Next, 40 mL of 0.005 M $CaCl_2$ were added, and the suspensions were shaken, centrifuged, filtered and analyzed in the same way as described for adsorption. In parallel, blanks without byproducts (containing just antibiotic) were performed to quantify the possible loss of antibiotic due to degradation and/or adsorption to the tubes or filters, obtaining in all cases that the loss of antibiotic was very low (<3%). In addition, the biodegradation of both antibiotics has been ruled out in previous research [15,16]. All experiments were carried out in triplicate.

2.4. Quantification of the Antibiotics

Tetracycline (TC) was determined as indicated in Fernández-Calviño et al. [17,18] using HPLC equipment (Dionex Corporation, Sunnyvale, CA, USA) with a P680 quaternary pump, an ASI-100 autosampler, a TCC-100 thermostated column compartment and a UVD170U detector. Chromatographic separations were carried out by means of a Luna C18 column (5 µm particle size; 4.6 mm internal diameter; 150 mm long) and a guard column (5 µm particle size; 2 mm i.d.; 4 mm long) packed with the same material, both from Phenomenex (Madrid, Spain). The flow rate was 1.5 mL min^{-1}, for an injection volume of 50 µL, with a mobile phase constituted by acetonitrile (phase A) and 0.02 mol L^{-1} oxalic acid/0.01 mol L^{-1} triethylamine (phase B). A linear gradient elution program was run within 10.5 min, from 5% to 32% of phase A (and the rest to 100% of phase B). After 2 min, the initial conditions were reestablished and then held for 2.5 min. The total time for analysis was 15 min, using 8.0 min as the retention time. The wavelength for detection of TC was 360 nm.

Regarding the quantification of sulfadiazine (SDZ), it was carried out after passing the suspensions through 0.45 µm nylon filters (Panreac, Spain), using the same HPLC equipment as above, as well as the same flow rate and volume of injection. In this case, the mobile phase A was also acetonitrile, and phase B was 0.01 M phosphoric acid. The linear gradient was also run in 10.5 min, from 5% to 32% of phase A. Furthermore, coincident, the total time for analysis was 15 min, but the retention time was 5.2 min, and the wavelength for detection was 270 nm.

2.5. Data Analysis and Statistical Treatment

To describe the experimental adsorption data, the fitting to the following models were tested: linear Equation (1), Freundlich Equation (2) and Langmuir Equation (3):

$$Q_a = K_d Ceq, \quad (1)$$

$$Q_a = K_F C_{eq}^n, \quad (2)$$

$$Q_a = \frac{K_L C_{eq} q_m}{1 + K_L C_{eq}}, \quad (3)$$

In these equations, Q_a (expressed in μmol kg^{-1}) is the amount of antibiotic adsorbed once the equilibrium is reached; C_{eq} (μmol L^{-1}) is the concentration of antibiotic remaining in solution in the situation of equilibrium; K_d (L kg^{-1}) is the distribution coefficient; K_F (L^n μmol^{1-n} kg^{-1}) is the Freundlich's affinity coefficient; n (dimensionless) is the Freundlich's linearity index; K_L (L μmol^{-1}) is a Langmuir parameter related to the adsorption energy; q_m (μmol kg^{-1}) is the Langmuir's maximum adsorption capacity.

In addition, considering the possibility of eventual competition for adsorption sites, the linear and Freundlich models could be adapted to be used in binary competitive systems [19]. In this regard, the first step is to use Equations (4) and (5) to focus on the total amount of adsorbed of both antibiotics (TC and SDZ).

$$(Q_{aTC} + Q_{aSDZ}) = K_d\ (C_{eqTC} + C_{eqSDZ}), \quad (4)$$

$$(Q_{aTC} + Q_{aSDZ}) = K_F\ (C_{eqTC} + C_{eqSDZ})^n, \quad (5)$$

where Q_a is the individual amount adsorbed of each of both antibiotics; C_{eq} is the concentration of each of both antibiotics in the equilibrium solution; K_d is the distribution coefficient, and K_F and n are the Freundlich parameters indicated above.

As the second step, the model developed by Murali and Aylmore [20] was also used to deepen the study of TC and SDZ competitive adsorption in the binary system Equations (6) and (7).

$$Q_{a1} = (K_{F1} {C_{eq1}}^{n1+1})/(C_{eq1} + a_{12} C_{eq2}), \quad (6)$$

$$Q_{a2} = (K_{F2} {C_{eq2}}^{n2+1})/(C_{eq2} + a_{21} C_{eq1}), \quad (7)$$

In these equations, Q_a is the amount adsorbed of each of both antibiotics; C_{eq} is the concentration in the equilibrium solution for TC (1) and SDZ (2); K_F and n are the Freundlich parameters obtained from the individual (not binary) experiments, and a_{12} and a_{21} are parameters related to the competition between TC and SDZ for adsorption sites. Taking into account that a_{12} and a_{21} are placed in the denominator of the quotients, higher a_{12} and a_{21} values will give lower Q_a results, indicating lower adsorption for the antibiotics.

Desorption was presented as percentages, which were calculated in relation to the amounts previously adsorbed after determination of values for desorbed TC and SDZ expressed as μmol kg^{-1}.

The fitting of experimental data to the adsorption models was performed by using R statistical software, version 3.1.3 and the nlstools package for R. In addition, any further statistical treatments were carried out by means of the SPSS 21.0 software.

3. Results and Discussion

3.1. Adsorption of TC and SDZ onto the Bioadsorbents in Binary Systems

Figure 1 shows TC and SDZ adsorption when both are added simultaneously and at the same concentration (with added concentration values between 1 and 50 μmol L^{-1} for each antibiotic) to each of the three bioadsorbents (oak ash, pine bark and mussel shell).

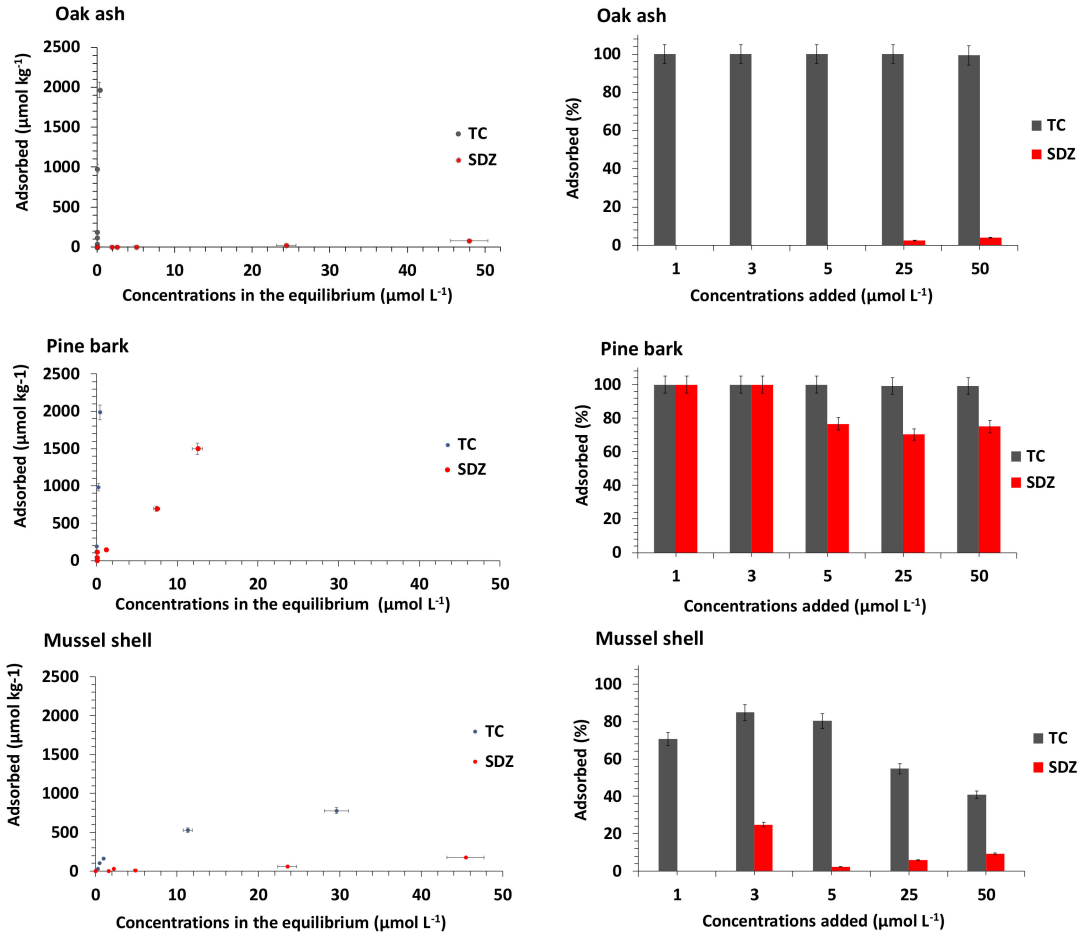

Figure 1. Tetracycline (TC) and sulfadiazine (SDZ) adsorption onto the three bioadsorbents studied (oak ash, pine bark and mussel shell) in binary competitive systems. Adsorption curves on the left, and percentage adsorption on the right. Average values (n = 3) with error bars indicating that coefficients of variation were <5%.

As shown in Figure 1, TC adsorption reached really high scores on the three bioadsorbents in these binary systems. Oak ash and pine bark have similar adsorption values (maxima of 1966 and 1983 µmol kg^{-1}, respectively), while mussel shell adsorbed much less (maximum of 777 µmol kg^{-1} of TC). Regarding SDZ adsorption, the most effective bioadsorbent was pine bark, reaching a maximum value of 1499 µmol kg^{-1}, while the other two bioadsorbents adsorbed less than 175 µmol kg^{-1} when the maximum concentration of antibiotics (50 µmol L^{-1}) was added.

When the results are expressed in percentage values, it is shown that pine bark adsorbed 100% of both antibiotics when they were added at the two lowest doses (1 and 3 µmol L^{-1}), while this sorbent was able of adsorbing 100% of added TC and about 75% of added SDZ when the highest doses of antibiotics (25 and 50 µmol L^{-1}) were applied. Regarding oak ash, this sorbent was able of retaining 100% of the TC added, but the retention percentages were poor for SDZ (always lower than 5%), causing that it could not be considered as an effective bioadsorbent for simultaneous retention of the antibiotics evaluated in the competitive binary systems. Finally, mussel shell adsorbed about 80% of the added TC when the doses of antibiotic were low, but adsorption decreased to 40% when the highest doses of TC were added, while SDZ adsorption onto mussel shell was always less than 20%.

In a previous study, Conde-Cid et al. [21] worked with binary systems that included different tetracyclines (not sulfonamides), finding that pine bark was able to adsorb most of the antibiotics added, with low desorption in most cases. Oak ash showed high adsorption for each antibiotic individually, but retention clearly decreased in the binary systems, and

finally, the mussel shell showed poor adsorption in most cases. In addition, in another research, Conde-Cid et al. [22] studied the adsorption of sulfonamides (including SDZ) onto agricultural soils after being amended with the same byproducts here used, but in individual (not competitive) experiments. These authors found that the pine bark amendment caused an increase in the adsorption (and also decreased desorption) for the three sulfonamide antibiotics they studied. However, mussel shell and oak ash did not increase adsorption. These authors postulated that the positive effect of pine bark could be due to its high organic carbon content and to its acidic pH value. In fact, as previously found by Conde-Cid et al. [21], pine bark has the highest organic matter content (48.7%) among all three bioadsorbents, while oak ash and mussel shell showed values clearly lower (13.23 and 11.43%, respectively). These authors also indicate that oak ash showed an alkaline value for pH in water (11.31), as mussel shell (9.39), while it was acidic for pine bark (3.99), with differences between pH in KCl and pH in water indicating that oak ash had more positive charges, while negative charges dominate in pine bark and mussel shell. Conde-Cid et al. [21] also reported that oak ash showed an exchangeable Ca value (95 $cmol_c$ kg^{-1}) that was higher than those found for mussel shell (24.75 $cmol_c$ kg^{-1}) and pine bark (5.38 $cmol_c$ kg^{-1}), and BET surface area was higher for oak ash, followed by mussel shell and by pine bark.

In the current work, when analyzing the results and making a comparison focused on the antibiotics, it can be observed that TC is generally more adsorbed than SDZ. Similarly, other authors [13,23,24] found higher adsorption of tetracyclines in relation to sulfonamides, this fact being responsible for the higher persistence of TCs in the environment, and specifically in solid media.

It is noteworthy that both antibiotics (TC and SDZ) are amphoteric and can be present as cations, zwitterions or as anions, depending on the pH of the medium [6,12,21,22]. However, the higher affinity for TC shown by the three bioadsorbents here assessed could be related to the adsorption mechanisms of each antibiotic. Thus, while TC can be adsorbed by various mechanisms, such as electrostatic interactions, complexation, cationic bridges, H bonds [25], SDZ has electrostatic attractions as the predominant and almost exclusive mechanism for adsorption [26], which reduces the possibility of interacting with the functional groups of sorbents.

For example, at neutral pH, SDZ is mainly in its neutral form (SDZ^0), and the adsorption mechanism would imply the intervention of weak hydrophobic forces [13,27], while TC molecules can be present as different chemical species, which is of great relevance since they can be adsorbed by different mechanisms [13,17,28], also affected by their Log K_{OW} [29] and pK_a values [30].

Focusing on the differences regarding adsorption onto the three bioadsorbents, the most remarkable is the higher adsorption of SDZ taking place in pine bark, which could be explained based on the pH and organic matter content of this sorbent, as previously indicated by Conde-Cid et al. [22].

In fact, pH influences the speciation of both antibiotic molecules and the charge on the surface of adsorbent materials, which can undergo protonation/deprotonation reactions depending on the pH value [31], thus affecting the interaction between sorbate and sorbent. In this regard, Białk-Bielińska et al. [32] indicate that as the pH decreases, the adsorption capacity of sulfonamides increases, with maximum adsorption taking place at pH 4–4.25, with these antibiotics being in the cationic form [33].

In view of this, it must be taken into account that pine bark has a pH of 3.99, and the cationic species of SDZ will be adsorbed on the deprotonated carboxylic groups of the organic matter of this bioadsorbent through electrostatic interactions [26]. On the contrary, at the alkaline pH values characterizing oak ash and mussel shell, anionic species will predominate for SDZ, which will be repelled by the negative charges of the organic matter of these two bioadsorbents, causing that the SDZ/adsorbent bond would have to occur through a cationic bridge, which is a rare mechanism for sulfonamides [26].

However, TC is fully adsorbed both when the sorbent is acidic (pine bark) or strongly alkaline (oak ash). As previously noted, TC has several mechanisms for binding to sorbents. Thus, at an acidic pH, such as that found in pine bark (3.99), there are cationic species of TC that will interact electrostatically with the carboxylic groups of the organic matter of the bark, which begins to deprotonate from pH 3 [34,35]. At a strongly alkaline pH, like that of oak ash (11.31), TC will be in anionic form, and the organic matter (13.23% carbon) and non-crystalline components (8323.0 and 4233.0 mg kg^{-1} Al and Fe extracted with ammonium oxalate) present in the ash will also be negatively charged, causing that adsorption will occur through a cationic bridge, in which cations such as Ca^{2+} can intervene [13,25,35], facilitated by its abundance in this sorbent (95 $cmol_C$ kg^{-1} of exchangeable Ca, clearly higher than 24.75 and 5.38 $cmol_C$ kg^{-1} in mussel shell and pine bark, respectively). The lower adsorption of TC in mussel shell can be related to the lower content of organic matter (11.43% carbon) and non-crystalline components (178.33 and 171.0 mg kg^{-1} Al and Fe extracted with ammonium oxalate) characterizing this sorbent.

Based on the adsorption data obtained under the conditions of this study, it can be stated that pine bark could be used as an effective bioadsorbent for TC and SDZ in a binary system (with both antibiotics present), while oak ash could be used to effectively remove TC (but not SDZ) from solution, and finally, mussel shell would not be recommended as a bioadsorbent for these two antibiotics, due to its limited efficacy.

3.2. Fitting of TC and SDZ Adsorption Data to Different Models

Tables 1–3 show results on the fitting of TC and SDZ adsorption onto the three bioadsorbents, in binary systems, to three different models.

Table 1. Parameters of the linear model for tetracycline (TC) and sulfonamide (SDZ) adsorption onto the three biosorbents studied.

Bioadsorbent	Antibiotic	K_d (L kg^{-1})	*Error*	R^2
Oak ash	TC	-	-	-
	SDZ	1.51	0.16	0.939
	TC + SDZ	42.06	0.46	0.999
Pine bark	TC	4805.01	275.58	0.979
	SDZ	113.09	7.17	0.975
	TC + SDZ	256.45	12.42	0.982
Mussel shell	TC	29.04	4.18	0.858
	SDZ	3.50	0.37	0.934
	TC + SDZ	13.49	0.96	0.955

Table 2. Parameters of the Langmuir model for tetracycline (TC) adsorption onto mussel shells. All other values for both antibiotics and the three biosorbents studied had too high error values for fitting.

Bioadsorbent	Antibiotic	Langmuir Parameter				
		Q_m (μmol kg^{-1})	*Error*	K_L (L μmol^{-1})	*Error*	R^2
Mussel shell	TC	934.35	97.63	0.14	0.05	0.986

Q_m: maximum adsorption capacity; K_L: constant related to the strength of interaction adsorbent/adsorbate; R^2: coefficient of determination.

Table 3. Parameters of the Freundlich model for tetracycline (TC) and sulfonamide (SDZ) adsorption onto the three biosorbents studied.

Sorbent	Antibiotic	Freundlich Parameter				
		K_F (L^n μmol^{1-n} kg^{-1})	*Error*	*n*	*Error*	R^2
Oak ash	TC	-	-	-	-	-
	SDZ	0.07	0.01	1.82	0.05	1
	TC + SDZ *	35.16	3.12	1.05	0.02	1
Pine bark	TC	6036.53	1411.70	1.22	0.22	0.985
	SDZ	46.07	23.98	1.37	0.21	0.988
	TC + SDZ *	123.29	54.40	1.30	0.6	0.991
Mussel shell	TC	148.88	18.95	0.50	0.04	0.992
	SDZ	-	-	1.67	0.37	0.997
	TC + SDZ *	50.18	9.16	0.70	0.04	0.997

K_F: parameter related to the adsorption capacity; *n*: parameter related to the heterogeneity of the sorbent; R^2: coefficient of determination.
* Obtained from Equation (5); -: error values too high for fitting.

Table 1 shows that the adjustments to the linear model are generally good, with high R^2 values. However, in the case of TC adsorption onto oak ash, the fitting was not possible to the linear or any other model due to the high adsorption capacity of the sorbent for TC (100% in most cases), causing that no TC was detected in the equilibrium solution, making not possible to apply adsorption models. The best fit to the linear model corresponded to pine bark for both antibiotics. In addition, it is noteworthy that K_d values were much higher for TC (between 29.04 and 4805.01 L kg^{-1}) than for SDZ (between 1.51 and 113.09 L kg^{-1}), which indicates that the bioadsorbents studied have a higher affinity for TC [13]. Furthermore, relevant, pine bark showed higher affinity for both antibiotics, compared to oak ash and mussel shell (Table 1), which is in agreement with the experimental results (Figure 1).

Just for comparison, we could take into account that Conde-Cid et al. [36] obtained K_d values between 0.40 and 9.43 L kg^{-1} for SDZ in soils of Galicia, which are of the same order as those obtained for other soils by Sukul et al. [37] (between 0.1 and 24.3 L kg^{-1}), and by Leal et al. [38] (from 0.8 to 14.3 L kg^{-1}), while Hu et al. [39] found lower values (1.54 and 3.41 L kg^{-1}) in other agricultural soils. Compared to these results, the K_d values obtained in the present study for SDZ in oak ash and mussel shell (1.51 and 3.50 L kg^{-1}) are of the order of those reported in the soils above, while K_d was clearly higher in pine bark (113.09 L kg^{-1}), which indicates a high affinity of this material for SDZ, and its potential feasibility to be used to retain this antibiotic in soils, slowing its passage into water bodies and the food chain.

Regarding TC, K_d values obtained in previous studies for Galician soils ranged between 53 and 30,237 L kg^{-1} [40], while Bao et al. [41] reported values between 838 and 15,278 L kg^{-1} for other soils. In the present study, K_d values for TC in mussel shell were lower than those obtained in the lower range of the soils reported above, while K_d was high in pine bark (4805 L kg^{-1}), suggesting that this biosorbent could be used to increase the retention of TC in soils with low adsorption capacity.

Table 1 also shows that when the linear model is applied to the set of the two antibiotics in the binary system (TC + SDZ), R^2 improves slightly compared to when considering the antibiotics separately, and it is also observed that K_d values for TC + SDZ are lower than those obtained for TC alone but higher than those for SDZ alone (Table 1).

Regarding the Langmuir model, Table 2 shows that it is not satisfactory to explain the adsorption of TC and SDZ onto oak ash and pine bark in binary systems, just fitting for TC adsorption onto mussel shell. In all other cases, error values were too high for fitting.

As regards the Freundlich model, Table 3 shows the model parameters for TC and SDZ separately and for the set of the two antibiotics in the binary system. In fact, as previously commented, the Freundlich model can be adapted to be used in binary competitive systems,

as shown in Equation (5). The fits to this model are generally good, with R^2 values between 0.985 and 1 (Table 3).

The values of the Freundlich K_F parameter (related to the adsorption capacity of a certain adsorbent, [42]) were higher for TC than for SDZ (Table 3). These results also indicate a higher affinity of the bioadsorbents used in this study (specifically of pine bark) for TC than for SDZ, and also a higher adsorption capacity of pine bark for both antibiotics, compared to oak ash and mussel shell, which coincides with the experimental results (Figure 1).

Using the Freundlich model adapted for the binary systems (Equation (5)), the resulting K_F values for the set of the two antibiotics (TC + SDZ) were lower than those obtained for TC and higher than those obtained for SDZ (Table 3), so that the sequence for the three bioadsorbents, considering both the antibiotics individually and in binary systems, was: TC> TC + SDZ> SDZ.

Regarding possible comparisons between the K_F values of the present study and those from previous research, it is hard to perform it properly due to the differences affecting the experimental conditions, including the initial concentrations added. Therefore, at the level of data comparison among different publications and adsorbent materials, it is preferable to use the partition coefficient (K_d) discussed above for the linear model, which is less sensitive to variations in the initial concentration than the adsorption capacity [43–45].

As regards the n parameter, it is related to the reactivity and heterogeneity of the active sites of the adsorbents. Specifically, when $n = 1$ the adsorption is linear, when $n > 1$ the adsorption process is mainly chemical, and when $n < 1$ physical adsorption is dominant, with heterogeneous high-energy sites present, strong interactions taking place between adsorbent and sorbate, and with high-energy sites being the first to be occupied [46–48]. In the present study, n values were generally > 1 (denoting dominance of chemisorption), with the exception of TC and the sum of TC + SDZ in mussel shell (Table 3). Other authors also obtained values of $n > 1$ in chlortetracycline + SDZ binary systems, which suggest a strong interaction between these two antibiotics and the high-energy sites of the bioadsorbents [13]. On the contrary, in studies dealing with soils in individual (non-binary) systems, values of $n < 1$ were obtained for both TC [40] and SDZ [36], which suggests that the simultaneous presence of both antibiotics in binary systems could cause modifications in the mechanisms of interaction of these compounds with adsorbent surfaces.

Table 4 shows the results of the adsorption adjustments of TC and SDZ to the model of Murali and Aylmore [20], with R^2 values ranging between 0.725 and 0.991. This model is used to study the competition between different sorbates for adsorption sites, which is expressed by the competitiveness index a. The lower the value of a, the lower is the competition between sorbates for the adsorption sites of the sorbents. Comparing the index a_{12} (index of competition of SDZ to eventually occupy adsorption sites before TC) and a_{21} (index of competition of TC to eventually occupy adsorption sites before SDZ), it is observed that the former are always lower than the latter (Table 4); therefore TC would be more likely to displace SDZ and occupy first the adsorption sites for which they compete.

Table 4. Fitting of adsorption results to the Murali and Aylmore equation, using TC and SDZ solutions in relation 1:1, with concentrations of the antibiotic adsorbed expressed in μmol kg^{-1} and concentrations of antibiotic present in the equilibrium solution in μmol L^{-1}.

Bioadsorbent	a_{12}	R^2	a_{21}	R^2
Oak ash	−0.956	0.907	0	-
Pine bark	−0.555	0.991	−0.013	0.975
Mussel shell	−0.501	0.725	−0.045	0.98

a: parameter related to competition between antibiotics; a_{12}: index of competition of SDZ with TC; a_{21}: index of competition of TC with SDZ.

3.3. Desorption of TC and SDZ from the Three Bioadsorbents in Binary Systems

Figure 2 represents the percentage of desorption for SDZ and TC, calculated taking into account the amounts previously adsorbed in the binary systems in each of the three bioadsorbents studied (oak ash, pine bark and mussel shell).

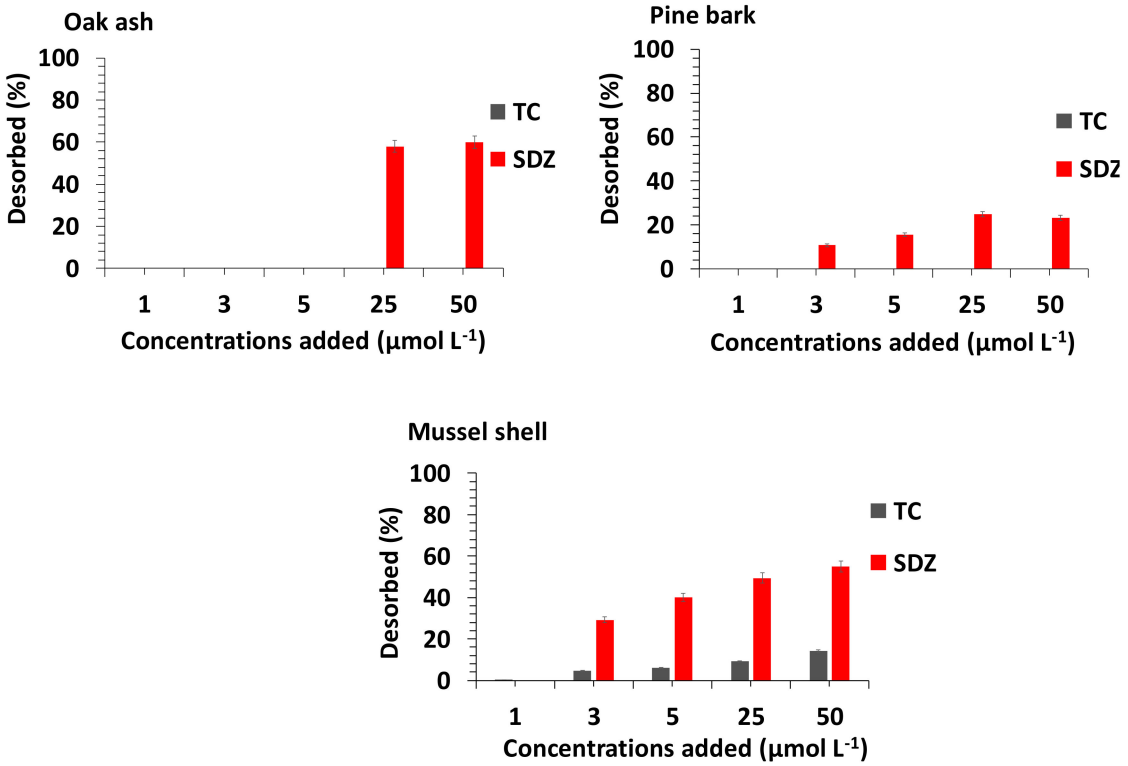

Figure 2. Desorption of TC and SDZ from the three different bioadsorbents studied (oak ash, pine bark and mussel shell) in binary systems. Average values (n = 3), with error bars indicating that coefficients of variation were <5%.

Figure 2 shows that TC was irreversibly adsorbed (no desorption taking place) onto pine bark and oak ash and intensely adsorbed onto mussel shell (desorption <10%). Regarding desorption of SDZ, it was always higher than that of TC, and pine bark was the material desorbing the least, with percentages always lower than 20%. In oak ash, the adsorption of SDZ was irreversible up to a concentration of antibiotic added of 5 μmol L^{-1}, but for the two highest concentrations added, the desorption values exceeded 50% (Figure 2). Finally, mussel shell desorbed up to 60% of SDZ for the three highest concentrations added. A sim-

ilar behavior, with higher desorption of different sulfonamides in relation to tetracyclines, was found in previous studies using individual (non-binary) systems in soils [12,49].

Taking into consideration adsorption and desorption data commented above, it is clear that, in those cases where TC and SDZ are present simultaneously in a binary system, pine bark is promising as bioadsorbent. However, it must be taken into account that from concentrations of antibiotic added reaching values of 3 μmol L^{-1}, SDZ adsorption drops to 75% and its desorption increases to 20%. In any case, pine bark is the adsorbent material performing best among the three evaluated in the binary systems since oak ash and mussel shell show very low adsorption capacity for SDZ, also desorbing practically half of the previously retained amount.

In the present work, the good performance of pine bark to retain the antibiotics studied in binary systems can be due to its high organic matter content, with an abundance of adsorption sites, with a high affinity for these compounds, as previously shown for tetracyclines [21]. To be noted that pine bark has a markedly acidic pH (<4) at which these antibiotics have a positive or neutral charge, favoring binding to the negatively charged carboxylic groups contained in the organic matter of the bark, that dissociate at pH between 3 and 6 [21].

4. Conclusions

The results of this study indicate that the three bioadsorbents evaluated (oak ash, pine bark and mussel shell) have a higher affinity for tetracycline (TC) than for sulfadiazine (SDZ). When TC and SDZ were incorporated together in a binary system, pine bark was the most suitable sorbent for the retention of both antibiotics, but the efficacy against SDZ decreased when the antibiotics were added in high concentrations due to lower adsorption and higher desorption values. Oak ash and mussel shells were not efficient enough to be recommended for adsorption of TC and SDZ in binary systems, as they have limited affinity for SDZ. In the binary systems, adsorption data corresponding to each individual antibiotic and to both present simultaneously showed the highest K_d and K_F values (after fitting to the linear and Freundlich models) for pine bark, which indicates that this material has highly reactive adsorption sites for TC and SDZ, that hardly could be saturated. It was also shown that competition for adsorption sites between TC and SDZ was favorable to TC, with the highest competition taking place in mussel shells. Specifically, adsorption percentages for TC were close to 100% onto pine bark and oak ash and between 40 and 85% onto mussel shell, thus being higher than for SDZ (75–100% onto pine bark, and generally less than 10% on oak ash and mussel shell). TC adsorption onto pine bark remained close to 100% throughout the entire concentration range tested, while it was between 75 and 100% for SDZ. In addition, desorption was always higher for SDZ than for TC. The results of this study could be useful when evaluating management strategies related to situations with risks of simultaneous contamination by TC and SDZ, which may have environmental and public health relevance. Future studies could consider other tetracycline and sulfonamide antibiotics in competition, as well as other concentrations than that used here, and even more than two antibiotics present simultaneously. In addition, studying additional low-cost adsorbents, as well as modified sorbents, would give a broader view regarding alternatives to retain/remove antibiotics from environmental compartments.

Supplementary Materials: The following are available online at https://www.mdpi.com/2227-9717/9/1/28/s1, Table S1. Main characteristics of the three bioadsorbents studied. Average values (n = 3), with coefficients of variation always <5%. Table S2. Data corresponding to the BET surface area results for the three bioadsorbent materials studied. Mean values (n = 3) with coefficients of variation always <5%.

Author Contributions: Conceptualization, E.Á.-R., M.A.-E., M.J.F.-S. and A.N.-D.; methodology, E.Á.-R., M.A.-E., D.F.-C. and M.C.-C.; software, G.F.-C., R.C.-D. and M.C.-C.; validation, E.Á.-R., M.A.-E., M.J.F.-S. and A.N.-D.; formal analysis, G.F.-C., R.C.-D., D.F.-C. and M.C.-C.; investigation, R.C.-D., D.F.-C. and M.C.-C.; resources, E.Á.-R., M.A.-E., M.J.F.-S., D.F.-C. and A.N.-D.; data curation, E.Á.-R., M.A.-E., M.J.F.-S., D.F.-C. and A.N.-D.; writing—original draft preparation, G.F.-C., R.C.-D.,

M.J.F.-S. and E.Á.-R.; writing—review and editing, A.N.-D.; visualization, E.Á.-R., M.A.-E., M.J.F.-S. and A.N.-D.; supervision, E.Á.-R., M.A.-E., M.J.F.-S., D.F.-C. and A.N.-D.; project administration, E.Á.-R., M.A.-E.; funding acquisition, E.Á.-R., M.A.-E. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Spanish Ministry of Science, Innovation and Universities, grant numbers RTI2018-099574-B-C21 and RTI2018-099574-B-C22. It also received funds from the European Regional Development Fund (ERDF) (FEDER in Spain), being a complement to the previous grants, without additional grant number. M. Conde-Cid holds a pre-doctoral contract (FPU15/0280, Spanish Government). The research of Dr. Gustavo F. Coelho was also supported by the Improving Coordination of Senior Staff (CAPES), Post-Doctoral Program Abroad (PDE) Process number {88881.172297/2018-01} of the Brazilian Government.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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