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Competitive adsorption and desorption of tetracycline and sulfadiazine in crop soils

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ABSTRACT

In view of the environmental issues caused by antibiotics, this research studies competitive adsorption/desorption for tetracycline (TC) and sulfadiazine (SDZ) in agricultural soils. Competitive adsorption was studied in binary systems (adding equal concentrations of both antibiotics). In addition, it was compared with results from simple systems. In all cases, batch-type adsorption/desorption experiments were carried out. In the binary systems, for the highest antibiotic concentration added, adsorption percentages were always higher for TC (close to 100%) than for SDZ (10–90%). In these systems, TC desorption was lower than 5% for all soils, and generally <10% for SDZ. Comparing TC and SDZ adsorption for the different systems, SDZ was clearly affected by the presence of TC, with SDZ adsorption percentages being was much higher (with differences generally above 65%) in the binary than in the simple systems. On the contrary, comparing the results of TC adsorption in simple and binary systems, TC was not affected by the presence of SDZ, obtaining similar adsorption percentages in both systems. K_d and K_F values (in the Linear and Freundlich models), were higher in the simple systems in the case of TC, which could be due to competition with SDZ, while for SDZ K_d and K_F were higher in the binary systems, with a synergistic effect of TC favoring SDZ adsorption. Regarding desorption, it reached 100% for SDZ in some soils in simple systems, dropping to 10% in the presence of TC. TC desorption was <4%, not affected by SDZ. The results indicate that environmental risks would be higher for SDZ, showing differences when both antibiotics are present. This can be considered relevant as regards public health and environmental preservation, in view of direct toxicities and the promotion of resistance to antibiotics associated with the presence of these contaminants in the environment.

1. Introduction

Different antibiotics included in the groups of sulfonamides (SAs) and tetracyclines (TCs) are frequently used to treat or prevent diseases, and, sometimes, as growth promoters (Pikkemaat et al., 2016; Szymańska et al., 2019). It has been indicated that the annual use of antibiotics in the world is around 200,000 tons (Kümmerer, 2009). China is the country with the highest consumption (Van Boeckel et al., 2015; Zhang et al., 2015). This country used 150 times more antibiotics than UK and 10 times than the USA (Zhang et al., 2015). Spain is one of the EU countries with the highest consumption of these substances in animal production (about 3000 t/year) (Conde-Cid et al., 2018) and it is expected to continue growing.

Antibiotics are generally poorly metabolized and up to 90% are excreted in feces and urine, and can enter the environment through wastewater, sewage sludge and manures/slurries added to soils as fertilizers (Qiao and SingerZhu, 2018; Szymańska et al., 2019; Yufeng et al., 2020). The presence of these compounds has been reported for soil and water bodies, as well as for foods (Yufeng et al., 2020). In Galicia (NW Spain), the presence of TCs and SAs has been found in manure/slurry, soils and crops in areas with intensive farming (Conde-Cid et al., 2018).

On a global scale, a variety of issues have been reported when these antibiotics reach soils, such as those related to the increase in bacterial resistance and antibiotic-resistant genes, their passage into water bodies and the food chain, which poses a risk to human and animal health

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(Bengtsson-Palme and Larsson, 2016; Conde-Cid et al., 2018; Grenni et al., 2018; Kivits et al., 2018; Cycoń et al., 2019; Charuaud et al., 2019; Santás-Miguel et al., 2020).

It is essential to study the dynamics of antibiotics in the soil to determine their environmental fate. Adsorption onto soil components can be one of the main control factors to prevent the entry of these substances in the food chain. But this process depends on the characteristics of the soil and on those of the antibiotics. Regarding soils, organic matter quality and content, clay types, exchangeable cations, and pH values, are key factors (Parolo et al., 2008; Conde-Cid et al., 2020a), while, for antibiotics, the chemical characteristics with main relevance as regards their interactions with soils are water solubility, functional groups, and number and value of their acid dissociation constants (pK_a) (Wang and Wang, 2015). In addition, it should be taken into account that several antibiotics may reach simultaneously the soil as pollutants, which could modify their individual behavior in relation to interactions with soil components. In this regard, there are very few studies (and particularly in soils) focusing on the competitive adsorption of sulfonamides and tetracyclines (Cela-Dablanca et al., 2021; Yufeng et al., 2020).

In view of that background, the aim of the present research is to study, through adsorption/desorption experiments, the eventual competition between TC and SDZ for the adsorption sites of crop soils having different characteristics, also comparing the adsorption/desorption of each antibiotic for binary and simple (non-binary) systems. The results of this investigation could be relevant to unravel aspects corresponding to the environmental fate of these compounds when they reach soils and waters as pollutants, which could be a real hazard for public health and the whole environment.

2. Materials and methods

2.1. Soil samples

Six cultivation soils were used in this study, which were sampled at Sarria (Lugo province), denominated as S soils, and at A Limia (Ourense province), denominated as AL soils, both zones in Galicia (NW Spain), and characterized by intensive farming activities. In each plot, 10 subsamples of the topsoil (0–20 cm depth) were taken in a zigzag manner, by means of an Edelman probe, then mixing to obtain a single representative sample for each plot. Once in the laboratory, the samples were dried (exposed to the air), sieved by 2 mm, homogenized and stored.

The analyses carried out on these soil samples were performed as per standard methods (Tan, 1996). Specifically, C and N were determined by means of elemental analysis (CHNS Truspec, Leco, USA); pH in water (pH_{H2O}) and in 0.1 M KCl (pH_{KCl}) (with soil:solution ratio 1:2.5), by means of a pH-meter (pH-model 2001 Crison, Spain); available P, by means of the Olsen method; exchangeable cations were extracted with 1 M NH_4Cl and determined by means of atomic emission/absorption spectrometry; the effective cation exchange capacity (eCEC) was calculated as the sum of exchangeable Na, K, Ca, Mg, and Al; particle size fractions (clay, silt, sand) were determined by means of the pipette method; non-crystalline Al and Fe (Al_o, Fe_o) were quantified after extraction with ammonium oxalate acidified at pH 3. All determinations were carried out in triplicate.

Table 1 shows their main properties. In addition, these soils were previously described by Conde-Cid et al. (2018).

2.2. Adsorption and desorption experiments

To study adsorption, batch-type experiments were performed as follows. Binary experiments were carried out adding equal concentrations of TC and SDZ simultaneously to 1 g of each soil, the antibiotics being incorporated within 40 mL of a 0.005 M $CaCl_2$ solution (with this salt acting as background electrolyte, to equalize ionic strength). The individual concentrations of each antibiotic were 1, 3, 5, 25 and 50 μmol L^{-1}. The resulting suspensions were shaken for 24 h at 50 rpm in the dark, at 25 ± 2 °C, using a rotary shaker, and then they were centrifuged for 15 min at 2665×g, and finally filtered by means of 0.45 μm nylon syringe filters (Fisher Scientific, Madrid, Spain) before antibiotics quantification. Kinetic studies carried out previously had shown that 24 h was time enough to achieve the equilibrium. Adsorption experiments were performed without adjusting pH, working at "natural" (not modified) values. The concentrations of both antibiotics were quantified in the equilibrium solution by means of HPLC-UV, and, in addition, pH was determined using a glass electrode (Crison, Barcelona, Spain). The difference between the concentration of antibiotic added initially and the concentration remaining in the equilibrium solution allowed calculating the amount of antibiotic adsorbed. The following procedure was followed to study desorption of the antibiotics that were previously retained onto the soils: the soil materials remaining from the adsorption step were weighed with the aim of calculating the volume of the occluded solution; then, volumes of 40 mL of a 0.005 M $CaCl_2$ solution were added, followed by shaking, centrifuging, filtering, and finally analyzing, as indicated for adsorption. All the determinations were performed in triplicate.

Table 1

Physicochemical properties of the soils used. Mean values (n = 3) with coefficients of variation <5%.

Parameter	Units	Soil					
		3AL	19AL	50AL	6S	51S	71S
C	%	3.39	1.07	10.92	1.98	1.75	6.88
OM	%	5.84	1.84	18.83	3.41	3.02	11.86
N	%	0.31	0.09	0.84	0.23	0.19	0.48
C/N		10.94	11.89	13	8.44	9.05	14.21
pH_{H2O}		4.74	4.8	4.49	6.33	7.06	6.24
pH_{KCl}		4.3	4.25	4	5.86	6.39	5.44
P	mg kg^{-1}	117.9	225.43	135.9	71.42	120.03	96.77
Na_e	$cmol_c\ kg^{-1}$	0.35	0.25	0.42	0.36	0.28	0.41
K_e	$cmol_c\ kg^{-1}$	1	1.27	1.14	0.61	1.4	1.2
Ca_e	$cmol_c\ kg^{-1}$	2.24	1.53	5.94	12.86	9.89	12.79
Mg_e	$cmol_c\ kg^{-1}$	0.64	0.41	1.48	1.13	0.97	2.88
Al_e	$cmol_c\ kg^{-1}$	1.68	0.61	2.66	0	0.01	0.11
Al saturation	%	28.43	15	22.83	0	0.05	0.064
eCEC	$cmol_c\ kg^{-1}$	5.92	4.08	11.64	14.96	12.54	17.38
Clay	%	19.28	21.28	25.28	21.44	21.44	15.44
Silt	%	26	14	16	49.28	51.28	23.28
Sand	%	54.72	64.72	58.72	29.28	27.28	61.28
Al_o	mg kg^{-1}	5040	855	2995	18377.5	15755.7	50593.5
Fe_o	mg kg^{-1}	2585	1150	1430	56423.8	42377.4	73095.9

$Element_e$ = exchangeable concentration; $Element_o$ = concentration after extraction with ammonium oxalate.

Adsorption/desorption data from the binary systems (specifically including concentrations of 20 μmol L^{-1} SDZ and 20 μmol L^{-1} TC) were compared with those from single systems including concentrations of 20 μmol L^{-1} of TC or 20 μmol L^{-1} of SDZ.

2.3. *Quantification of the antibiotics TC and SDZ*

TC was determined as per Fernández-Calviño et al. (2015a, b) using a HPLC equipment (Dionex Corporation, Sunnyvale, USA), with UVD170U detector, paired to a TCC-100 thermostatized column compartment, a P680 quaternary pump, and an ASI-100 auto-sampler. As further details, a Luna C18 column (Phenomenex, Madrid, Spain), with 5 μm particle size, 150 mm long, 4.6 mm internal diameter) was used, combined with a guard column packed with the same material as the column, and with 5 μm particle size, 4 mm long, and 2 mm internal diameter. The flow rate 1.5 mL min^{-1} for an injection volume of 50 μL, with a mobile phase being 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, with the following details: a) from 5 to 32% of phase A and 95 to 68% of phase B within 10.5 min; b) the initial conditions were re-established in 2 min and held for 2.5 min. The retention time was 8.0 min, the time for the total analysis was 15 min, and the wavelength used for TC detection was 360 nm.

For SDZ, the injection volume was 50 μL and the flow rate was 1.5 mL min^{-1}. The mobile phase consisted of acetonitrile (phase A) and 0.01M phosphoric acid (phase B). A linear gradient ranging from 5% to 32% phase A (and 95%–68% phase B) was used. The initial conditions were then restored in 2 min and were maintained for 2.5 min. The total analysis time was 15 min, with a retention time of 5.2 min. The wavelength used for SDZ was 270 nm.

2.4. *Data treatment*

Adsorption data was assessed as regards their fitting to the following models: Lineal (Eq. (1)), Freundlich (Eq. (2)), Langmuir (Eq. (3)) and Temkin (Eq. (4)):

$$q_a = K_d\, Ceq \quad \text{(Eq. 1)}$$

$$q_a = K_F C_{eq}^{n} \quad \text{(Eq. 2)}$$

$$q_a = \frac{K_L C_{eq} q_m}{1 + K_L C_{eq}} \quad \text{(Eq. 3)}$$

$$q_a = \beta\, ln\, K_T + \beta\, ln\, C_{eq} \quad \text{(Eq. 4)}$$

where q_a (μmol kg^{-1}) is the amount of antibiotic adsorbed onto the soil in the equilibrium; C_{eq} (μmol L^{-1}) is the concentration of antibiotic in the equilibrium solution; K_F (L^n μmol^{1-n} kg^{-1}) is the Freundlich affinity coefficient; n (dimensionless) is the Freundlich linearity index; K_L (L μmol^{-1}) is a Langmuir constant related to the adsorption energy, and q_m (μmol kg^{-1}) is the Langmuir's maximum adsorption capacity of the soil. Regarding the Temkin model, *bt* is the Temkin isotherm constant, and $\beta = RT/bt$; K_T is the Temkin isotherm equilibrium binding constant (L g^{-1}); T is the Temperature (25 °C) (K = 298°), and R is the universal gas constant (8314 Pa m^3/mol K).

To evaluate situations of eventual competition for adsorption sites, the linear and Freundlich models can be adapted. For binary competitive systems, the first step would be the use of Equations (5) and (6) for the total amount of TC and SDZ adsorbed.

$$(Q_{aTC} + Q_{aSDZ}) = K_d\, (C_{eqTC} + C_{eqSDZ}) \quad \text{(Eq. 5)}$$

$$(Qa_{TC} + Q_{aSDZ}) = K_F\, (C_{eqTC} + C_{eqSDZ})^n \quad \text{(Eq. 6)}$$

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

Desorption percentages were calculated referred to the amounts previously adsorbed, which was carried out after calculating amounts of TC and SDZ desorbed expressed as μmol kg^{-1}.

The R statistical software, version 3.1.3 and the nlstools package for R were used for assessing the fitting of experimental data to the adsorption models, while the SPSS 21.0 software was used for any additional statistical treatment.

3. Results and discussion

3.1. *TC and SDZ adsorption/desorption in binary systems*

Fig. 1 shows the adsorption curves (adsorbed concentration versus equilibrium concentration in solution) for TC and SDZ when they were added simultaneously (binary system) at the same concentration (in a range that varies between 1 and 50 μmol L-1 of each antibiotic) in the six agricultural soils. These curves show a variety of shapes and indicate that TC adsorption is always higher than that of SDZ (especially in soils 3AL and 19AL), as well as that, overall, SDZ adsorption is higher in S soils.

Figs. 2 and 3 show the results regarding adsorbed quantities and percentages (respectively), depending on the added concentration.

Fig. 2 shows that TC and SDZ adsorption increases as the concentration of antibiotics added rises. For the maximum concentration added (50 μmol L^{-1}), TC adsorption values were similar for the various soils (with maximum of 1795 μmol kg^{-1}) (Fig. 2), and adsorption percentages were close to 100% for all of them (Fig. 3). Regarding SDZ, soils did show differences in adsorption, obtaining clearly lower values (for the highest concentration added) in soils 3AL and 19AL (200 and 800 μmol kg^{-1}, respectively), with maximum close to 1600 μmol kg^{-1} in the rest of the soils (Fig. 2). Expressed as percentage, the values obtained for the highest concentration added ranged between 10% (soil 3AL) and values close to 100% (soils 51S and 71S) (Fig. 3).

For high antibiotics concentrations added, adsorption was higher for TC than for SDZ, particularly in soils 3AL and 19AL (Figs. 2 and 3). To note that, in most soils, when low concentrations are added, adsorption is higher for SDZ than for TC, but by adding the above referred high concentrations (25 and 50 μmol L^{-1}), TC adsorption is higher in all soils. Different authors had previously reported higher adsorption for tetracycline antibiotics compared to sulfonamides, this being responsible for the greater persistence of tetracyclines in the environment (Carvalho and Santos, 2016; Jiang et al., 2020; Cela-Dablanca et al., 2021). Specifically, Laak et al. (2006) compared the adsorption of oxytetracycline with that of sulfochloropyridazine in 11 soils with different characteristics, obtaining the highest adsorption coefficients for oxytetracycline. Hamscher et al. (2005) also studied the behavior of TCs and SAs that were found simultaneously in soils fertilized with manure, verifying that the presence of TCs in the arable layer of the soil was much higher than that of SAs, due to the higher adsorption of TCs on soil components. Ding et al. (2017) concluded that SAs show a low adsorption capacity onto soil colloids, while TCs are more adsorbed, also reported by Song et al. (2016) when studying the adsorption of the two types of antibiotics on graphene. The differences in the adsorption of the two antibiotics included in the current study may also be related to their different physicochemical properties (hydrophobicity, solubility, structure, etc.) (Kemper, 2008).

Both SDZ and TC are amphoteric molecules that can be found as anion, zwitterion, or as cation, depending on the pH of the medium (Sarmah et al., 2006; Conde-Cid et al., 2018, 2019a, b, c, 2020b). TC has three dissociation constants (pK_a) related to three acid functional groups, which are dimethylammonium cation (pK_a 9.6), phenolic diketone (pK_a 7.8), and tricarbonyl methane (pK_a 3.3), and can exist in anionic form at pH > 7.8, in zwitterion form between pH 3.3 and 7.8, and in cationic form at pH < 3.3. Furthermore, this antibiotic can form complexes with chelating agents such as certain cations (Mg^{2+}, Ca^{2+}, Fe^{2+}, Zn^{2+}, Al^{3+} and Fe^{3+}) and β-diketones (Sarmah et al., 2006;

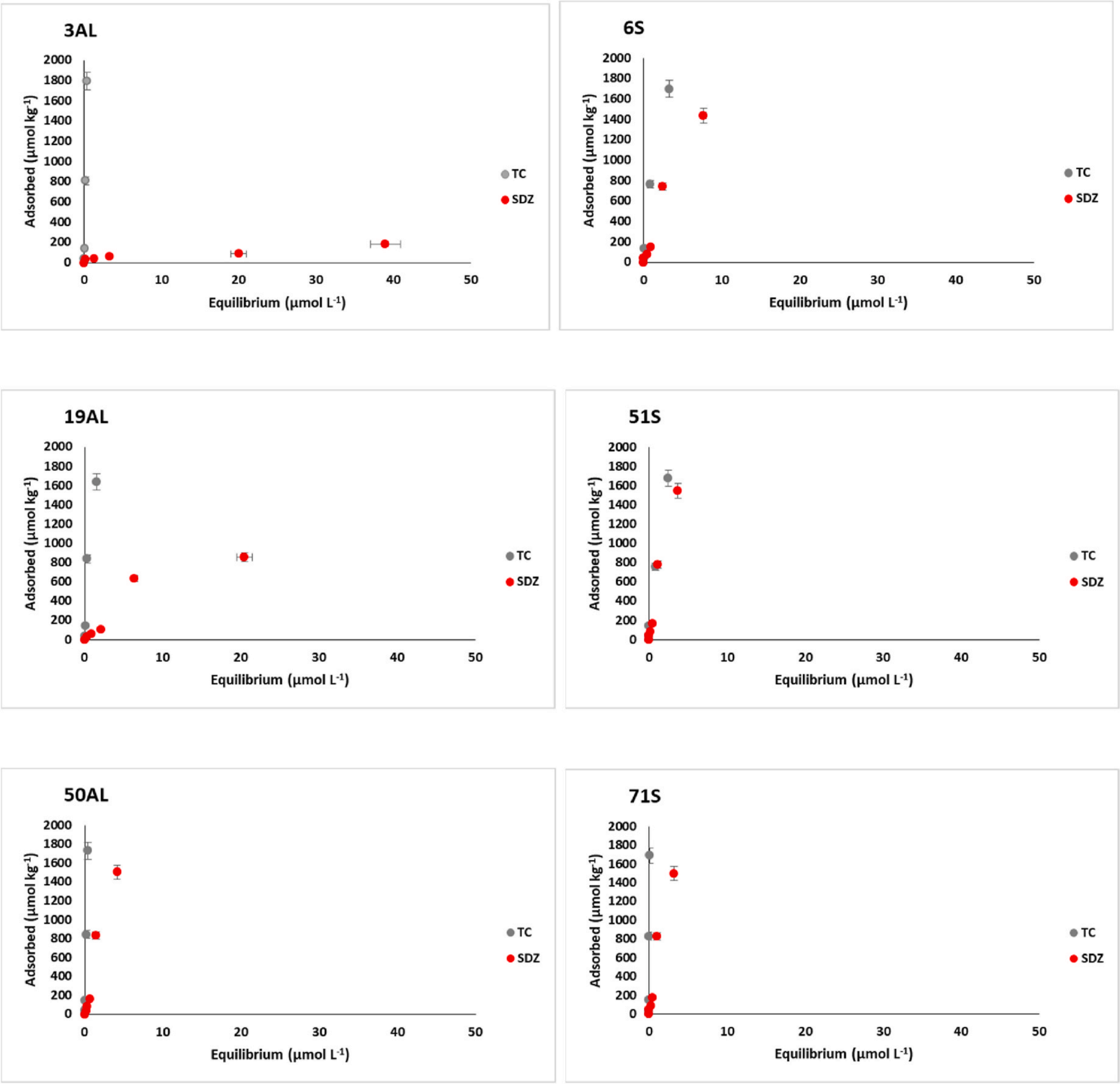

Fig. 1. Adsorption curves for the antibiotics TC and SDZ present simultaneously in competitive systems, corresponding to the six crop soils used.

Pikkemaat et al., 2016). SDZ has two pK_a values (2.1 and 6.28), and is positively charged at $pH < 2.1$, with no charge between 2.1 and 6.28, and negatively charged at pH above 6.28. This antibiotic has a low chelation tendency compared to TC (Ozumchelouei et al., 2020). The higher affinity for TC shown by the soils used in the current study could be related to the adsorption mechanisms affecting to each antibiotic. In SAs, adsorption occurs mainly through electrostatic interactions (Wang et al., 2015), while TCs have more mechanisms to interact with soil colloids: electrostatic interactions, cationic bridges, surface complexation or H bonds (Wegst-Uhrich et al., 2014), which would justify the greater adsorption of the TCs.

It should be noted the scarce difference obtained for the various soils in relation to TC adsorption, which would be related to the fact that all these soils have high adsorption capacity for this antibiotic. This may be due to the fact that relatively low concentrations (up to 50 µmol L^{-1}) were used in the binary systems of the present study, while in a previous study with simple systems it was shown that the difference among soils was observed at higher concentrations (greater than 100 µmol L^{-1}) due to the high affinity that soils have for TC (Conde-Cid et al., 2019c). In another study, it was also observed that the adsorption of three tetracyclines (tetracycline, oxytetracycline and chlortetracycline) was mainly influenced by the soil organic matter content, the process being dependent on pH, since this parameter affects both the charge of organic components (due to its variable nature), as well as the CT species present in the medium (Conde-Cid et al., 2020b). In fact, in the referred study, higher TCs adsorption was obtained for soils with more acidic pH, where the cationic and zwitterionic species of the antibiotic predominate and where the surfaces of the organic colloids have a predominantly negative charge due to deprotonation of the –COOH groups from pH 4.2 (Conde-Cid et al., 2020b).

Regarding the adsorption of SDZ (antibiotic with lower affinity for the adsorption sites compared to TC), it did present differences for the various soils, with clearly lower values for soils 3AL and 19AL, as mentioned above. Both soils have relatively low organic matter content (especially 19AL) and low pH (Table 1). The lower content in organic compounds may be one of the factors that influence this low adsorption. In a previous work in which SDZ adsorption was studied in a simple system (Conde-Cid et al., 2019a), a significant and positive correlation was obtained with the soil organic matter content, a fact that was also previously pointed out by other authors (Pereira-Leal et al., 2013; Srinivasan et al., 2014; Vieira et al., 2017). In relation to pH, other authors reported an increase in the adsorption of sulfonamides with increasing acidity, in simple systems (Białk-Bielińska et al., 2012), with the maximum adsorption taking place at pH between 4 and 4.25 (Ahmed

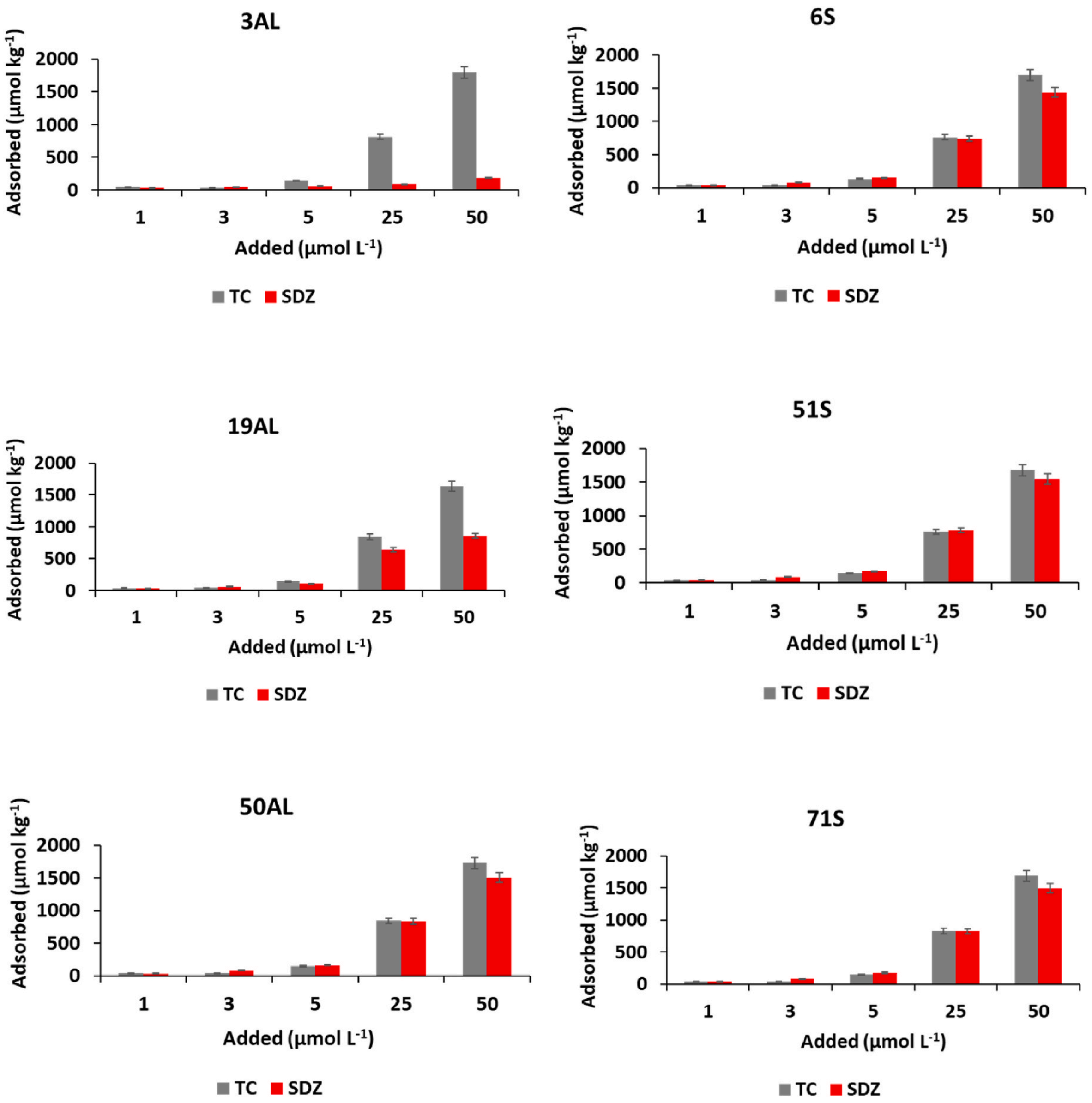

Fig. 2. TC and SDZ adsorption (in μmol kg^{-1}) onto the six crop soils studied in binary systems, expressed as a function of the concentrations of antibiotics added.

et al., 2017). This would be related to the amphoteric nature of these antibiotics, which at that pH value are in cationic form and bind to negatively charged soil components (mainly organic groups), through electrostatic interactions. This behavior was not observed in the present study, possibly due to the incorporation of TC to the system, which may represent a strong competition for SDZ.

3.2. *Fitting of experimental data to different adsorption models*

TC and SDZ adsorption of in the binary system were fitted to the Linear, Langmuir, Freundlich, and Temkin models, as well as for the Freundlich model modified for binary systems (Tables 2–5).

As regards the Linear model, Table 2 shows the parameters for SDZ and TC separately, as well as for both antibiotics in the binary systems. The fits to the linear model present R^2 values generally higher than 0.90. In these binary systems, the K_d coefficient was much higher for TC than for SDZ, which is consistent with the higher TC adsorption observed in these soils (Figs. 2 and 3). K_d is the soil–water partition coefficient, frequently used when describing the adsorption potential of pollutants and characteristics regarding their transport from soils to water bodies.

For the same soils of the present study, in previous investigations carried out with simple systems, much higher K_d values were also obtained for TC (between 53 and 30237 L kg^{-1}) than for SDZ (between 0.90 and 12.0 L kg^{-1}) (Conde-Cid et al., 2019a, c).

Other K_d values reported in the literature also show higher scores for TC (838–15278 L kg^{-1}, Bao et al., 2013) than for SDZ (0.1–24.3 L kg^{-1}, Sukul et al., 2008; 0.8–14.3 L kg^{-1}, Pereira-Leal et al., 2013), which suggests a greater affinity and adsorption capacity for TC on these soils.

Also for the same soils used in the present study, comparing the previously indicated K_d values obtained in simple systems for TC (53 and 30237 L kg^{-1}, Conde-Cid et al., 2019c) and SDZ (0.90 and 12.0 L kg^{-1} Conde-Cid et al., 2019a) with those obtained in the present work in binary systems (532 and 9554 L kg^{-1} for TC; 4.7 and 484.6 L kg^{-1} for SDZ), it is clear that in the binary systems the values are lower for TC and higher for SDZ, indicating that TC adsorption would decrease in the presence of SDZ, but SDZ adsorption would increase in the presence of TC. This may be due to interactions between TC and SDZ as regards adsorption sites, in which SDZ is favored by the presence of TC. Similar results were obtained by Li et al. (2018), in a study in which they found that TC adsorption decreased in a binary system also including

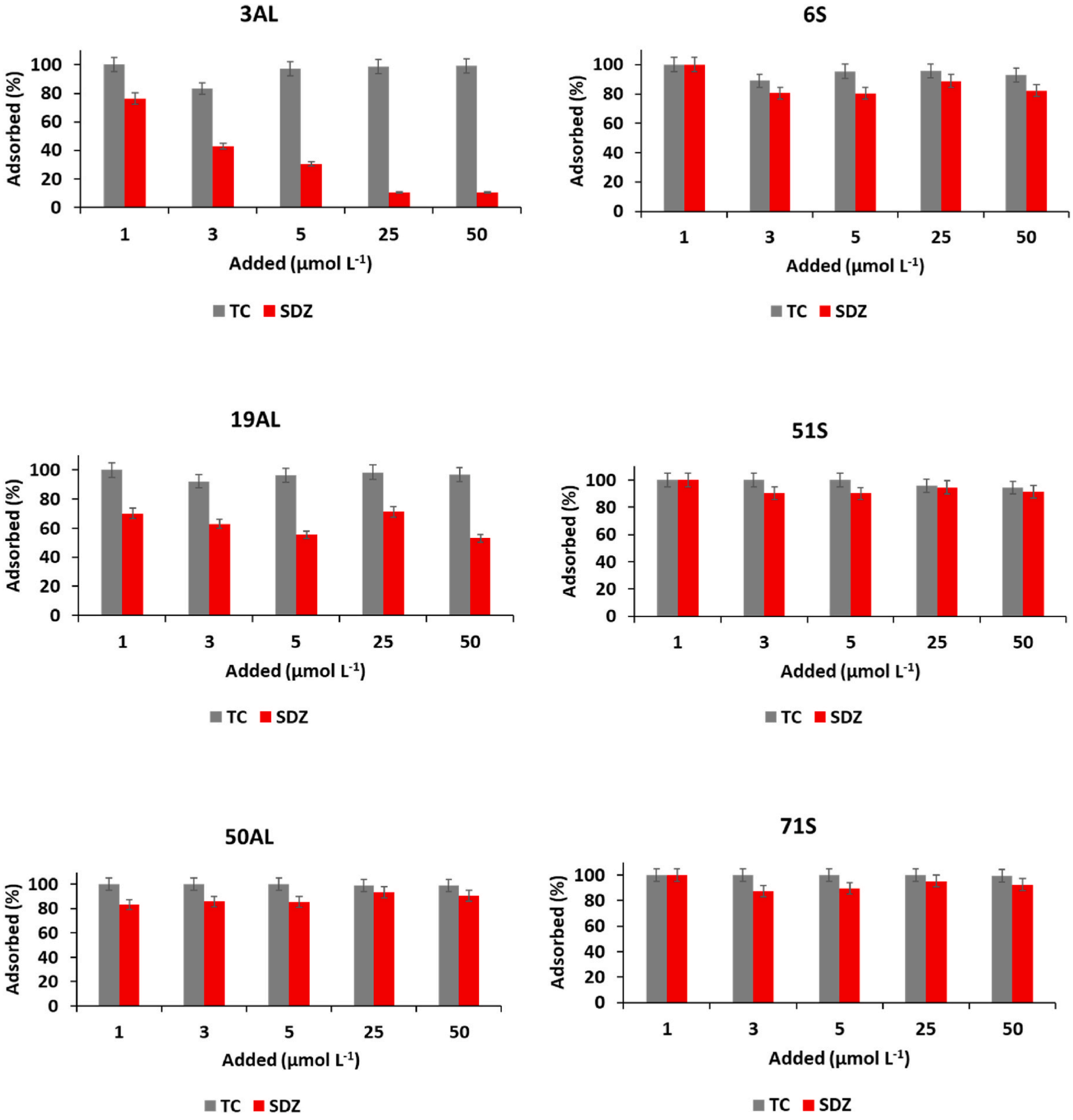

Fig. 3. TC and SDZ adsorption (as percentage) onto the six crop soils studied in binary systems, expressed as a function of the concentrations of antibiotics added.

ciprofloxacin, compared to the simple system.

The linear model was also applied to both antibiotics simultaneously present in the binary systems (TC + SDZ, Table 2), resulting in a good fit to this model, with R^2 values between 0.94 and 0.98. When the K_d values of TC + SDZ are compared with those obtained in a previous study for each antibiotic in simple systems (Conde-Cid et al., 2019a, c), it is observed that in the current study K_d scores are lower than those of TC found in simple systems, but they are higher than those of SDZ in these non-binary systems.

Considering the fittings to the Langmuir model, it was not the most appropriate to explain TC adsorption onto three of the six soils studied, while for SDZ R^2 was higher than 0.90 for all soils. The q_m parameter, related to the adsorption capacity, was higher for TC than for SDZ in two of the soils (Table 3). The K_L parameter, related to the adsorption energy (Khezami and Capart, 2005), was also higher for TC than for SDZ (Table 3), indicating that the retention of TC is stronger and therefore its mobility and risk of associated contamination will be lower than that of SDZ. In a previous study (Cela-Dablanca et al., 2021) we found that the Langmuir model was not appropriate for describing the adsorption of TC and SDZ onto oak ash and pine bark in binary systems. However, Wu et al. (2019) found a good adjustment to Langmuir for TC adsorption in binary systems with the presence of ciprofloxacin.

As regards the Freundlich model, Table 4 shows the model parameters for TC and SDZ separately (corresponding to non-binary systems) and for the set of the two antibiotics in binary systems. In this case, this equation does not satisfactorily explain TC adsorption in two of the soils, while for SDZ R^2 values > 0.95 were obtained in all soils.

In these binary systems, the values of the K_F parameter, related to the multilayers adsorption capacity (Bhaumik et al., 2012), are higher for TC (between 707.52 and 9172.90 L^n μmol^{1-n} kg^{-1}) than for SDZ (between 30.58 and 569.83 L^n μmol^{1-n} kg^{-1}), coinciding with what was detected in a previous research when studying the competitive adsorption of these antibiotics in bio-adsorbents (Cela-Dablanca et al., 2021) and between TC and sulfamethazine in soils (Song et al., 2016), which again indicates a higher affinity for TC in these soils.

In simple systems, Conde-Cid et al. (2019c) obtained for these same soils K_F values of between 901 and 9202 L^n μmol^{1-n} kg^{-1} for TC, which are of the same order as those obtained in the present study in binary

Table 2

Parameters of the Linear model for tetracycline (TC) and sulfonamide (SDZ) adsorption onto the six crop soils studied.

Soil	Antibiotic	Linear model parameter		
		K_d (L kg^{-1})	Error	R^2
3AL	TC	3425.879	576.080	0.901
	SDZ	4.755	0.646	0.896
	TC + SDZ*	49.065	1.251	0.995
19AL	TC	1124.686	133.12	0.947
	SDZ	47.061	7.331	0.903
	TC + SDZ*	122.232	13.229	0.911
50AL	TC	4119.729	189.84	0.991
	SDZ	380.265	31.625	0.972
	TC + SDZ*	735.241	47.434	0.983
6S	TC	532.934	37.58	0.981
	SDZ	195.894	14.827	0.977
	TC + SDZ*	296.653	20.210	0.982
51S	TC	685.032	37.95	0.988
	SDZ	434.015	30.830	0.960
	TC + SDZ*	537.136	30.531	0.975
71S	TC	9554.35	2134.52	0.831
	SDZ	484.693	43.567	0.936
	TC + SDZ*	971.341	84.606	0.942

K_d: parameter related to the adsorption capacity; *n*: parameter related to solid heterogeneity; R^2: coefficient of determination. * Obtained from Eq. (5).

Table 3

Parameters of the Langmuir model for tetracycline (TC) and sulfonamide (SDZ) adsorption onto the six crop soils studied.

Soil	Antibiotic	Langmuir parameter				
		q_m (μmol kg^{-1})	Error	K_L (L μmol^{-1})	Error	R^2
3AL	TC	–	–	–	–	–
	SDZ	306.40	233.55	0.03	0.05	0.904
19AL	TC	2846.24	772.27	0.90	0.49	0.981
	SDZ	1328.51	333.29	0.10	0.05	0.974
50AL	TC	–	–	–	–	–
	SDZ	–	–	–	–	–
6S	TC	3438.09	449.60	0.29	0.07	0.998
	SDZ	3647.82	1354.99	0.09	0.05	0.990
51S	TC	4730.72	1852.71	0.22	0.13	0.995
	SDZ	4122.11	1541.80	0.16	0.09	0.991
71S	TC	–	–	–	–	–
	SDZ	4274.62	2615.61	0.17	0.15	0.979

Q_m: maximum adsorption capacity; K_L: parameter related to the strength of interaction adsorbent/adsorbate; R^2: coefficient of determination; -: error too high for fitting.

Table 4

Parameters of the Freundlich model for tetracycline (TC) and sulfonamide (SDZ) adsorption onto the six crop soils studied.

Soil	Antibiotic	Freundlich parameter				
		K_F (L^n μmol^{1-n} kg^{-1})	Error	*n*	Error	R^2
3AL	TC	9172.90	3711.07	1.95	0.43	0.971
	SDZ	30.58	11.68	0.46	0.12	0.955
	TC + SDZ*	34.30	9.51	1.10	0.08	0.998
19AL	TC	–	–	–	–	–
	SDZ	140.11	60.56	0.62	0.16	0.954
	TC + SDZ*	282.61	109.52	0.72	0.13	0.976
50AL	TC	5470.06	1037.33	1.27	0.18	0.995
	SDZ	437.31	92.95	0.89	0.16	0.976
	TC + SDZ*	807.89	159.73	0.93	0.14	0.985
6S	TC	707.52	61.76	0.74	0.08	0.994
	SDZ	281.92	64.34	0.81	0.12	0.986
	TC + SDZ*	454.03	109.53	0.81	0.11	0.989
51S	TC	836.27	75.23	0.75	0.11	0.995
	SDZ	537.45	74.86	0.82	0.11	0.987
	TC + SDZ*	779.91	86.23	0.78	0.06	0.996
71S	TC	–	–	–	–	–
	SDZ	569.83	100.43	0.84	0.16	0.974
	TC + SDZ*	1130.45	212.47	0.86	0.16	0.975

K_F: parameter related to adsorption capacity; *n*: parameter related to solid heterogeneity; R^2: coefficient of determination. * Obtained from Eq. (6).

Table 5

Parameters of the Temkin model for tetracycline (TC) and sulfonamide (SDZ) adsorption onto the six crop soils studied.

Soil	Antibiotic	Temkin parameter				
		bt	Error	K_T (L/g)	Error	R^2
3AL	TC	2007.76	294.16	8.32	1.52	0.927
	SDZ	95978.99	8.00	–	–	0.892
19AL	TC	4326.07	28.76	11.57	0.94	0.996
	SDZ	11179.62	41.50	1.90	0.75	0.946
50AL	TC	1575.52	195.55	7.41	0.80	0.995
	SDZ	5003.07	83.83	3.75	0.97	0.954
6S	TC	5110.21	44.71	7.81	1.38	0.987
	SDZ	4869.13	53.32	1.90	0.32	0.985
51S	TC	2848.54	103.58	2.72	0.49	0.995
	SDZ	4531.24	60.87	3.89	0.69	0.983
71S	TC	–	–	–	–	–
	SDZ	3909.78	46.86	3.23	0.32	0.992

b_t: Temkin isotherm constant; K_T Temkin isotherm equilibrium binding constant (L/g); R^2: coefficient of determination; -: error too high for fitting.

systems, meaning that the presence of SDZ does not modify the affinity of these soils for TC. However, the K_F values obtained for SDZ in binary systems in the present study are much higher than those previously obtained for the same soils in simple systems by Conde-Cid et al. (2019a) (who reported levels between 1.0 and 9.2 L^n μmol^{1-n} kg^{-1}), indicating that the simultaneous presence of TC and SDZ in these soils could favor the adsorption of SDZ. The Freundlich *n* parameter, related to the reactivity and heterogeneity of the active sites of the sorbent, is generally lower than 1 for the two antibiotics, with the exception of TC in two soils (Table 4).

Values of $n < 1$ are related to the presence of heterogeneous adsorption sites and non-linear and concave curves, indicating that the number of available adsorption sites decreases when the concentration added increases, occupying firstly those sites with higher adsorption energy, followed by sites with lower adsorption energy (Foo and Hameed, 2010; Behnajady and Bimeghdar, 2014).

As for the Freundlich model adapted for binary systems (values for TC + SDZ in Table 4), it explains the joint adsorption of these two antibiotics, with R^2 values above 0.97 for all soils. To note that K_F values are higher for soils with high organic matter contents, demonstrating the importance of this soil component in TC and SDZ adsorption when the antibiotics are present simultaneously. The values corresponding to the *n* parameter are generally lower than 1, indicating the intervention of heterogeneous adsorption sites for these binary systems, with the exception of soil 3AL (where $n > 1$).

Temkin's model assumes that adsorption energy decreases linearly with the coverage of the adsorbent surface, due to adsorbent-adsorbate interactions (Ofomaja and Unuabonah, 2013). The Temkin isotherm explains the adsorption of TC and SDZ, with R^2 ranging between 0.892 and 0.996 (Table 5), and with much lower errors than those obtained for the Langmuir and Freundlich models (Tables 2 and 3). Temkin's model is considered appropriate to describe chemical adsorption based on strong electrostatic interaction (Gao et al., 2012; Rajapaksha et al., 2015).

3.3. TC and SDZ desorption from the six crop soils studied in binary systems

Fig. 4 shows desorption results corresponding to both antibiotics previously adsorbed in the binary systems. TC desorption is much lower than that observed for SDZ, indicating the low reversibility of TC retention for all soils, which coincides with the highest K_L value found

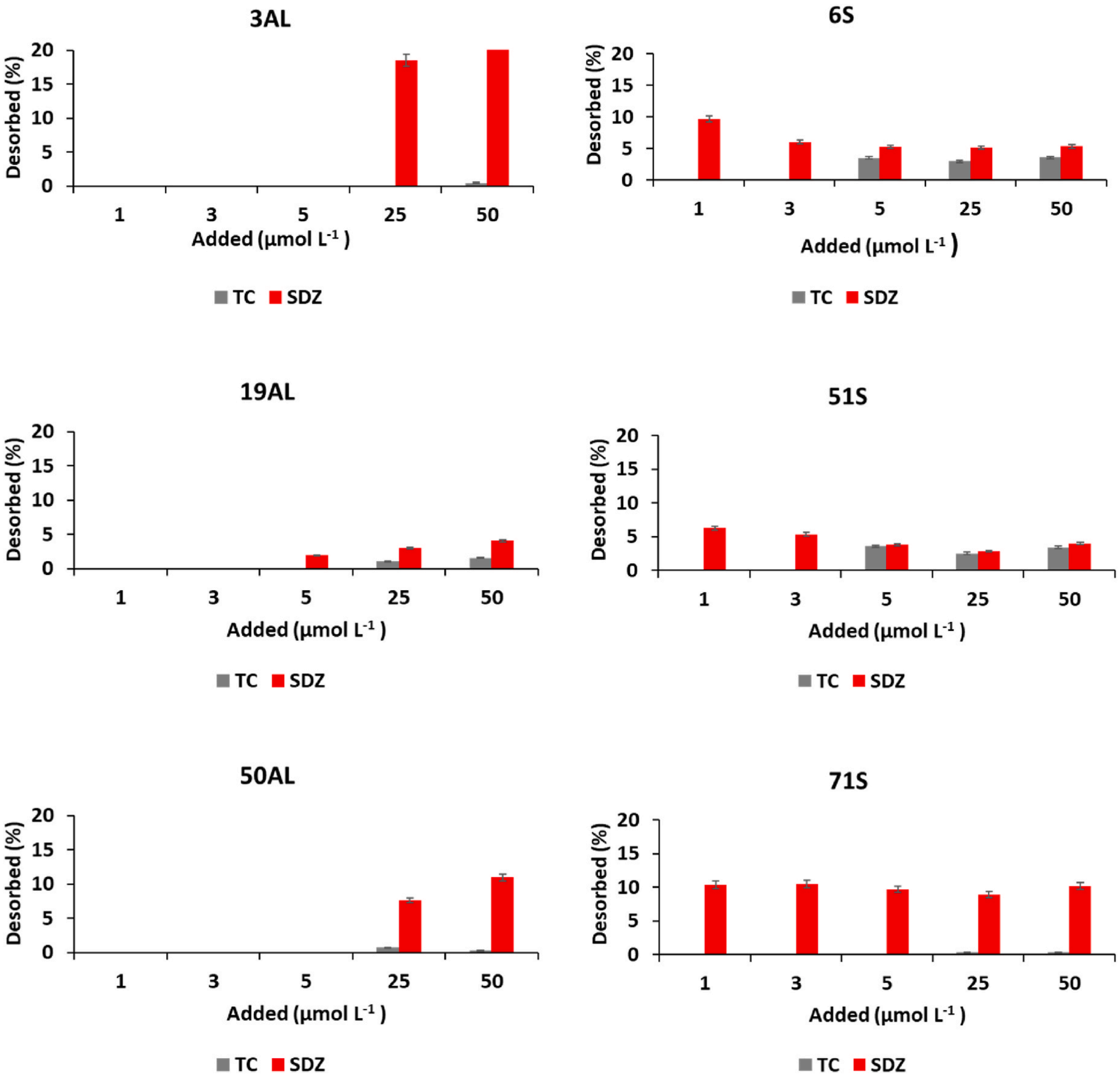

Fig. 4. TC and SDZ desorption (as percentage) from the soils in binary systems, expressed as a function of the concentrations of antibiotics added.

for TC, a parameter related to the adsorption intensity (Table 3). SDZ desorption does not exceed 5% in three of the soils (19AL, 51S and 6S), while it is 10% in those two soils with more organic matter, and reaches close to 20% in soil 3AL. The higher adsorption and retention energy for TCs compared to that for SAs was reported in previous studies and may be related to the different binding mechanisms onto soil colloids affecting to each antibiotic (Wegst-Uhrich et al., 2014; Hu et al., 2019). TC can bind to the soil by electrostatic attractions, or by ion exchange between the positively charged groups of the antibiotic and the cations present in the soil exchange complex in which organic matter is involved (Figueroa et al., 2004). Another possible adsorption mechanism is through H bonds, by interaction between the polar groups of the antibiotic and the soil (Gu et al., 2007). In addition, cations such as Ca^{2+} can act as a bridge between organic matter and the antibiotic, forming a ternary complex (MO-Ca-TC) (Zhang et al., 2010).

As for SDZ, this antibiotic can be adsorbed onto soil components through electrostatic attractions (which could be the predominant adsorption mechanism for sulfonamides), or by exchange with the cations present in the exchange complex, as indicated by Wegst-Uhrich et al. (2014).

3.4. TC and SDZ adsorption and desorption: comparison between simple and binary systems

Fig. 5 shows data corresponding to TC and SDZ adsorption in simple systems (with 25 µmol L^{-1} of TC or 25 µmol L^{-1} of SDZ, separately) and in a binary system (with 25 µmol L^{-1} of SDZ and 25 µmol L^{-1} of TC present simultaneously). With the concentrations used in the current study, TC adsorption was not affected by the presence of SDZ, neither positively nor negatively, obtaining similar adsorption percentages for simple and binary systems. This may be related to the fact that TC has a much higher affinity for soil colloids than SDZ, as it can be adsorbed by different mechanisms (those mentioned above: cationic bridges, surface complexation, electrostatic attractions), while SDZ is mainly adsorbed by electrostatic attractions (Wegst-Uhrich et al., 2014). However, as already indicated, K_d and K_F values of the Linear and Freundlich models indicate that the presence of SDZ would negatively affect TC adsorption, a fact that could occur at higher concentrations than those used in the present investigation. In the case of SDZ, the presence of TC would enhance SDZ adsorption, resulting in differences greater than 65% in most soils for SDZ retention when comparing binary and simple systems (Fig. 5). This coincides with what was observed in the Linear and Freundlich models, whose respective K_d and K_F values increase in binary

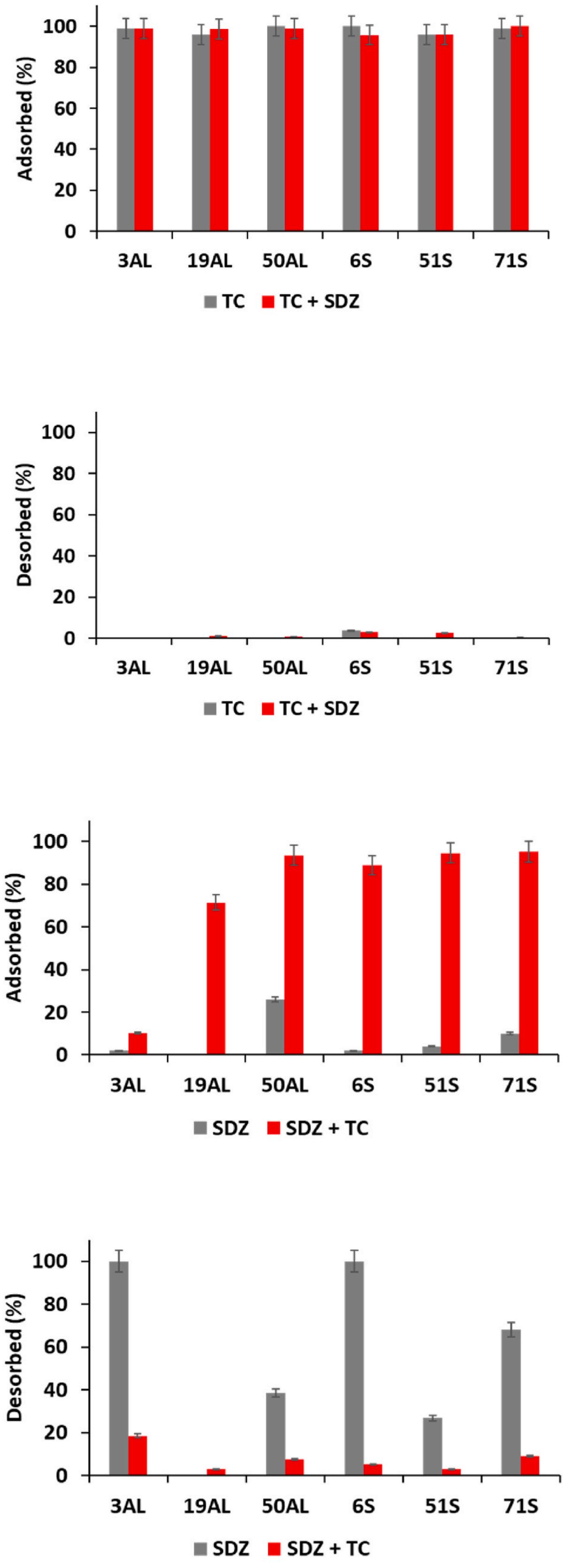

Fig. 5. TC and SDZ adsorption and desorption (as percentage) on/from the soils in single systems (25 μmol L^{-1} of each antibiotic added separately) and in binary systems (25 μmol L^{-1} of each antibiotic added simultaneously), expressed as a function of the concentrations of antibiotics added.

systems in compared to simple systems.

The increase in SDZ adsorption in the presence of TC can be interpreted taking into account the characteristics of these antibiotics and those of the soils. Both antibiotics are amphoteric, and at the pH values of the soils used in the present study they will be found mainly as zwitterions, with each antibiotic having positively charged groups and negatively charged groups, with the balance between charges being zero. It could happen that TC, with a high affinity for soil components (mainly organic matter), binds to these sorbent surfaces and provides charged groups, to which SDZ would bind electrostatically forming ternary complexes (soil-TC-SDZ), while SDZ would have more difficulty binding directly to soil sorbent surfaces to which TC does bind easily.

Regarding TC desorption, similarly to what happens with adsorption, it is not affected by the presence of SDZ, not exceeding 3.7% neither in the presence or absence of SDZ, which again may be related to the higher affinity of TC for soil colloids. In the case of SDZ desorption, it is very high in simple systems, reaching 100% in some soils. On the contrary, when SDZ is in a binary system with TC, its desorption decreases, being generally lower than 5% (Fig. 5). Therefore, TC does not compete with SDZ for the adsorption sites of soil colloids, but on the contrary, its presence favors the adsorption and binding energy of SDZ.

4. Conclusions

When TC and SDZ are simultaneously present in the six crop soils used in the present study, in binary systems, TC adsorption is almost total and irreversible, while SDZ adsorption is lower, and it is released more easily. The risk of SDZ entering the food chain is lower when it is present simultaneously with TC in soils, since it is more adsorbed and suffers lower desorption, indicating a synergistic effect of TC on SDZ adsorption. This effect is not reciprocal, since the comparison between simple and binary systems indicates that SDZ does not affect TC adsorption/desorption at the concentrations studied. The adsorption of both antibiotics fits well to the Linear and Freundlich models modified for binary systems, and to the Temkin model. These results can be considered relevant to determine the foreseeable evolution of TC and SDZ antibiotics when they reach soils as pollutants, and could be useful to design appropriate alternatives to reduce their risks for the environment and human health. In the future, it would be interesting to carry out additional studies with soils having different characteristics compared to those used in the current research, and it could also be of interest to combine soils with low-cost bio-adsorbent materials, which could increase the retention of these antibiotics. In the same way, it would be advisable to perform complementary studies that would allow shed light on the specific mechanisms involved in the retention/release of each antibiotic, as well as extending the study to other antibiotics.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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