Influence of pH on the adsorption-desorption of doxycycline, enrofloxacin, and sulfamethoxypyridazine in soils with variable surface charge

Cristina Álvarez-Esmorís [a], Lucia Rodríguez-López [a], Avelino Núñez-Delgado [b], Esperanza Álvarez-Rodríguez [b], David Fernández-Calviño [a], Manuel Arias-Estévez [a,*]

[a] *Soil Science and Agricultural Chemistry, Fac. Sciences, Univ. Vigo, 32004, Ourense, Spain*
[b] *Dept. Soil Science and Agricultural Chemistry, Engineering Polytechnic School, Univ. Santiago de Compostela, 27002, Lugo, Spain*

A B S T R A C T

In this research, the adsorption/desorption of the antibiotics doxycycline (DC), enrofloxacin (ENR), and sulfamethoxypyradazine (SMP) was studied in 6 agricultural soils with predominance of variable charge, both before and after removing organic matter by calcination. DC adsorption was high at acidic pH, and decreased at pH values above 8. Removal of organic matter with calcination caused just a slight decrease in adsorption, and even in some soils adsorption was similar to that in non-calcined samples. The adsorption coefficients (K_d) were higher for the DC^- species compared to DC^+, DC^0 and DC^{2-}. Regarding DC desorption, the values were very low throughout the pH range covered in the study (2–12), both in the calcined samples and in those not subjected to calcination. ENR showed a similar behavior to DC regarding the effect of pH, since ENR adsorption also decreased at basic pH, but the effect of removing organic matter was different, as it caused a clear decrease in ENR adsorption. The species with the highest K_d was in this case ENR^0, although ENR^+ is also quantitatively important as regards K_d value in calcined samples. For this antibiotic, no differences in desorption were observed between calcined and non-calcined samples. Finally, SMP adsorption also decreased as pH increased, and, in addition, similarly to what happened with ENR, in general, there was a strong decrease in SMP adsorption when organic matter was removed. The species with the highest K_d in this case was SMP^+ in non-calcined samples, but SMP^0 and SMP^- become more relevant in calcined samples. The percentages of SMP desorption were higher than those for the other two antibiotics, and an increase occurs at intermediate pH values, being higher for calcined samples. These results can be considered relevant in terms of increasing the knowledge as regards the possible evolution and fate of the three antibiotics studied. Specifically, for different pH conditions and with different organic matter contents, when they reach soils and other environmental compartments after being discharged as contaminants. This could have important repercussions on public health and the overall environment.

1. Introduction

Agricultural soils are increasingly receiving the spreading of emerging contaminants, such as antibiotics, which can generate environmental or public health problems (Du and Liu, 2012; Santás-Miguel et al., 2020). Veterinary antibiotics enter the soil through the application of manure and other organic fertilizers (Kuppusamy et al., 2018; Conde-Cid et al., 2020), whereas those used in human medicine reach soils mainly through wastewater and sewage sludge (Verlicchi and Zambello, 2015; Yang et al., 2016). In fact, increasing concentrations of antibiotics have been detected in the last two decades both in sewage sludge and water (Batt and Aga, 2005; Carballa et al., 2008) and in

manures/slurries (Martínez-Carballo et al., 2007; Conde-Cid et al., 2018). As a consequence, these antibiotics are also increasingly detected in soils that receive this kind of residues or amendments (Martínez-Carballo et al., 2007; Kemper, 2008).

Once the spread antibiotics reach soils, the interaction with soil components will determine their fate, in the sense of promoting their retention in soil colloids or, on the contrary, facilitating their transport to surface, sub-surface or groundwater if the retention/removal after interacting with soil components is scarce (López-Periago et al., 2002; Núñez-Delgado et al., 2002; Xie et al., 2018). The purifying/buffer capacity of soils depends not only on physical aspects (such as the size and distribution of pores), but also on the physicochemical characteristics of

Table 1

Main physicochemical properties of the three antibiotics used in the study. DC: doxycycline; ENR: enrofloxacin; SMP: sulfamethoxypyridazine; MW: molecular weight; WS: water solubility; K_{ow}: octanol/water partition coefficient.

Antibiotic	Family	Chemical formula	MW (g mol^{-1})	WS (mg L^{-1})	Log K_{ow}	pK$_a$
DC	Tetracyclines	$C_{22}H_{24}N_2O_8$	444.44[a]	630[a]	−0.02[a]	3.0–7.97–9.15[b]
ENR	Fluoroquinolones	$C_{19}H_{22}FN_3O_3$	359.5[d]	63[e]	1.1[d]	6.3–8.3[d]
SMP	Sulfonamides	$C_{11}H_{12}N_4O_3S$	280.3[c]	147[c]	0.32[c]	2.2–7.2[c]

[a] Chen et al. (2015).
[b] Babić et al. (2007).
[c] Gao et al. (2019).
[d] Riaz et al. (2018).
[e] Martínez-Mejía et al. (2017).

its components, both inorganic and organic, in particular, on its surface charge properties (Gathuka et al., 2021; Kim et al., 2018). In soils with a predominance of variable charge, which are those that present 1:1 clays, such as kaolinite, as well as Fe and Al oxides, or those containing significant amounts of organic matter, their attenuation/buffer capacity is conditioned by management aspects. These are especially those related to management of pH through liming, or due to the use of fertilizers with the ability to modify soil acidity (He et al., 2021; Oliver et al., 2019). It should be noted that in surface horizons with abundant organic matter, as is the case of most soils in NW of Spain, an important part of their surface charge is due to organic matter. This is a result of the dissociation of some of the functional groups present in organic compounds, with negative charges increasing as the pH rises (Carstens et al., 2021; Choppala et al., 2018). Furthermore, pH also affects the speciation of antibiotic molecules (protonation or deprotonation of ionizable compounds) and these different antibiotic species may have different adsorption characteristics (Laak et al., 2006; Anskjær et al., 2014).

The influence of organic matter on the retention/release of antibiotics reaching soils as pollutants can be studied by establishing relations with the antibiotic adsorption capacity (Zhang et al., 2010; Conde-Cid et al., 2019a). But, also, through the addition of humic substances to soils or clays, or by focusing on the humic substances themselves (Zhao et al., 2011b; Yang et al., 2012). Another final option could be by removing organic matter (which can be done by calcination, Alvarez-Esmorís et al., 2021a, 2021b), the method that has been less studied.

On the other hand, the characteristics of the antibiotics themselves also have a great influence on the possible interactions with soil components, making necessary to carry out specific studies for antibiotics of different classes (Cela-Dablanca et al., 2022; Franklin et al., 2022).

In view of the above background, this research was designed to study the adsorption capacity of three antibiotics in 6 soils with different organic matter contents (calcined or not), depending on the pH. These three antibiotics belong to different families, and specifically they are doxycycline (DC) which belongs to the tetracycline group and shows high adsorption and low desorption by soils (Zhu et al., 2015; Alvarez-Esmorís et al., 2020), enrofloxacin (ENR), which belongs to the fluoroquinolone group and which has a medium-high adsorption capacity by soils (Riaz et al., 2018; Alvarez-Esmorís et al., 2020), and sulfamethoxypyridazine (SMP) which belongs to the sulfonamide group and that presents a lower adsorption capacity by soils compared to the previous ones (Pereira-Leal et al., 2013; Alvarez-Esmorís et al., 2020). The influence of pH and organic matter on desorption is also taken into account, which is a less studied process but no less important from an environmental point of view.

2. Material and methods

2.1. Soil sampling and soil characteristics

To carry out this study, 6 agricultural surface (0–20 cm depth) soil samples (numbered from 1 to 6) were used, four of them being cultivated with potatoes (soils 1 to 4) and two dedicated to vineyard (soils 5

and 6). The parent material was granite in all cases except for soil 1, in which it was a mixture of granite and schist. These same 6 soils were used in a previous study (Alvarez-Esmorís et al., 2021a, 2021b), in which the characteristics related to sampling, the pretreatment of the samples and the analysis methods to which they were subjected were presented. These soil samples (not subject to calcination) will be referred to throughout the text as untreated soils.

The results of the analyzed parameters (Table S1, Supplementary Material) indicate that the values of pH in water of these untreated soils range between 4.2 and 7.0, decreasing to 3.4–6.7 for pH in KCl; the C contents range between 0.3 and 10.9%, and the effective cation exchange capacity varies between 3.31 and 27.70 cmol(c) kg^{-1}. Three of the soils are sandy loam (soils 3, 5 and 6) and the other 3 are sandy clay loam (soils 1, 2 and 4).

Samples of the 6 soils were subjected to calcination at 450 °C for 2 h, resulting in organic matter contents ≤0.1% in all cases. In addition, some other modifications took place affecting to the rest of the parameters analyzed in these soil samples. It has been evidenced that calcining at 450 °C causes small changes in the mineralogy of the phyllosilicates, resulting in the disappearance of illite-vermiculite, as well as illite-vermiculite interlayers (Table S1, Supplementary Material; Alvarez-Esmorís et al., 2021a, 2021b).

2.2. Electro-kinetic determinations

Electro-kinetic measurements were carried out using an electrophoretic apparatus (Zetasizer Nanoseries 3600 micro-electrophoresis Malvern Instruments, Malvern, UK), with results expressed as Z-potential values. The clay fraction was extracted by sedimentation applying Stokes' law (Tan, 1996) without removal of organic matter in non-calcined samples. Subsequently, the clay fraction was dried at 40 °C and stored in plastic tubs until later use. To do this, aliquots of 100 mg of the clay fraction of the samples were individually (for each soil sample) suspended in 30 mL 0.01 M NaNO$_3$, prepared at the desired pH in the range 2–12 by adding HNO$_3$ or NaOH. The samples were shaken for 1 h and subsequently a 10 mL sample was pipetted out, diluted and the determination procedure was run. Ten replicate runs were performed for each sample of clay fraction.

2.3. Chemical reagents

The antibiotics used were from Sigma-Aldrich (Buchs, Switzerland): Doxycycline (DC), with purity ≥95.0%, Enrofloxacin (ENR), with purity ≥98.0%, and sulfamethoxypyradazine (SMP), with purity ≥98.0%. Table 1 shows the main chemical characteristics of the three antibiotics. All the reagents used for the quantification of the antibiotics by HPLC (acetonitrile, phosphoric acid, oxalic acid and triethanolamine) were of high purity analytical grade, supplied by Panreac (Barcelona, Spain) and by Fisher Scientific (Madrid, Spain). All solutions were prepared with Milli-Q water (Millipore, Madrid, Spain).
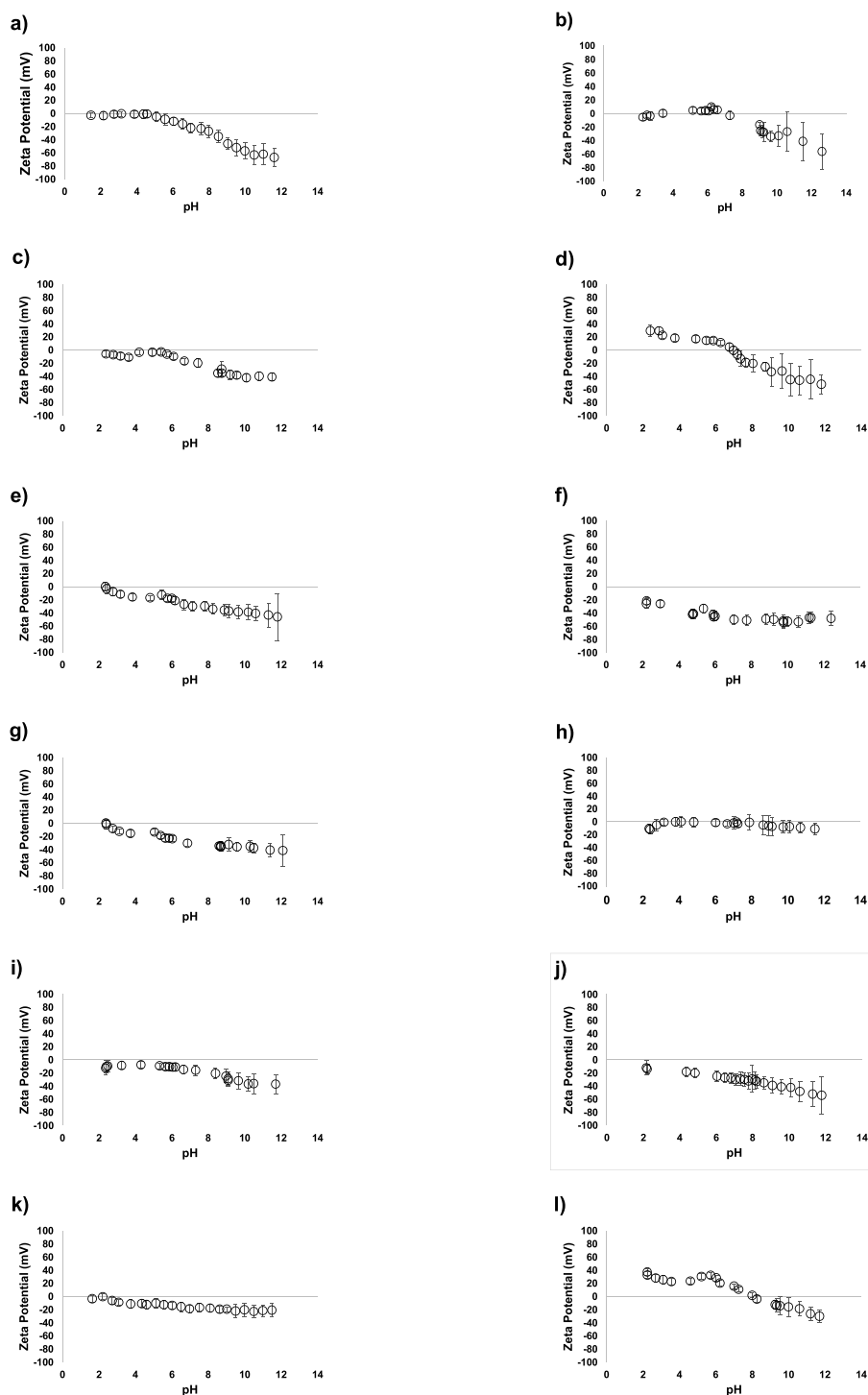
Fig. 1. Graphs showing Zeta-potential values versus pH for the clay materials extracted from the various untreated and calcined soil samples. a) Soil 1 untreated; b) Soil 1 calcined; c) Soil 2 untreated; d) Soil 2 calcined; e) Soil 3 untreated; f) Soil 3 calcined; g) Soil 4 untreated; h) Soil 4 Calcined; i) Soil 5 untreated; j) Soil 5 calcined; k) Soil 6 untreated; l) Soil 6 calcined. Average values (n = 10). Error bars: 2 standard deviations.

2.4. Adsorption-desorption studies: influence of pH

Batch-type experiments were carried out at different pH values (between 2 and 12), adjusted by adding different amounts of 0.5 M HCl and 0.5 M NaOH. The concentrations of antibiotic added were 200 μM for DC and ENR, and 50 μM for SMP. The soil:solution ratios were 1:40 for DC and ENR, and 1:2.5 for SMP. In all cases, 0.005 M $CaCl_2$ was used as background electrolyte.

The suspensions were shaken at 50 rpm for 24 h (time previously determined to be sufficient to reach equilibrium), and they were centrifuged at 4000 rpm for 15 min. The resulting supernatants were passed through nylon syringe filters (0.45 μm pore size), and the antibiotic concentration was determined by HPLC (see details below). The amount of antibiotic adsorbed to the soil was calculated by the difference between the initial concentration and the equilibrium concentration (measured in the supernatant).
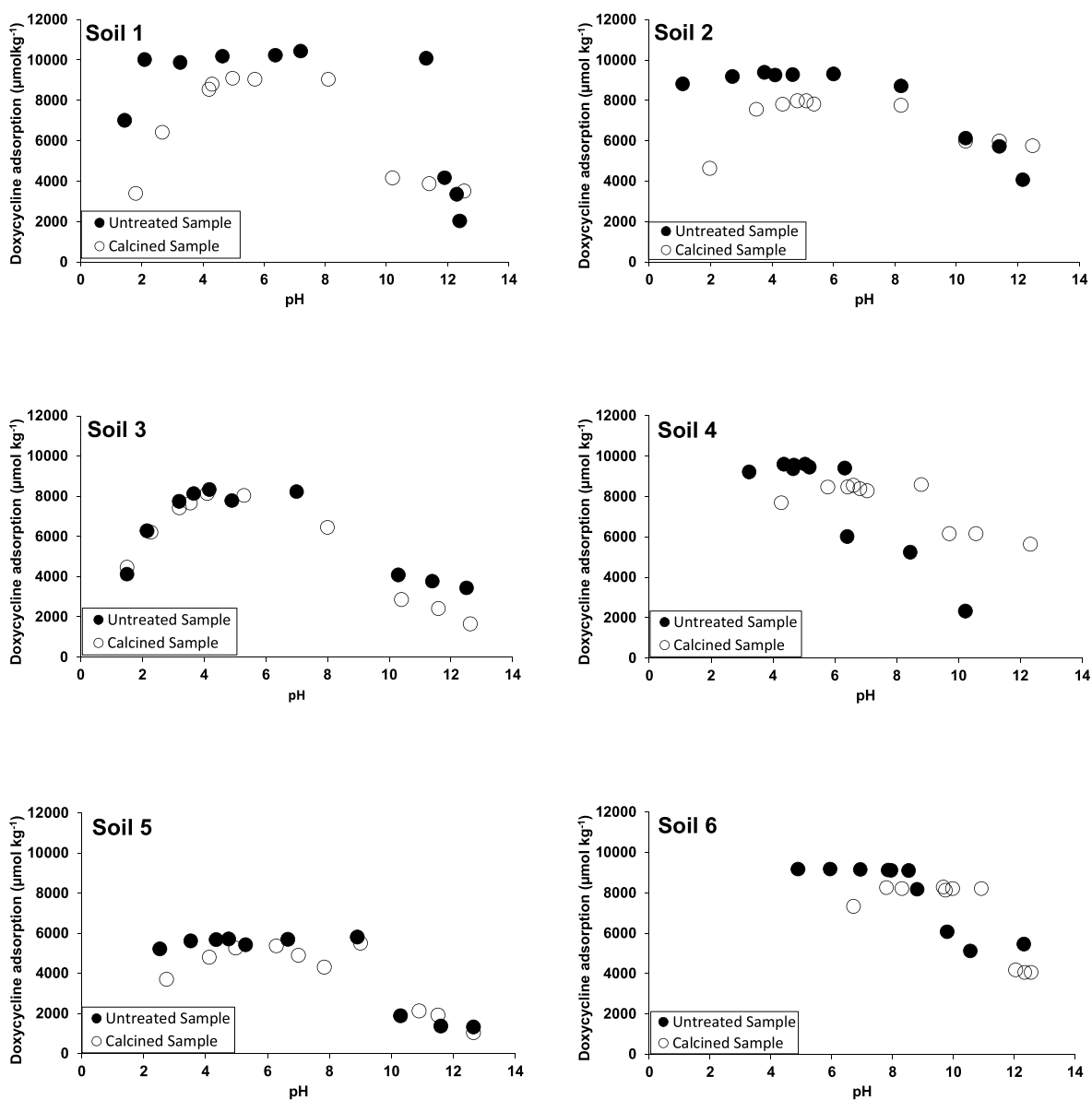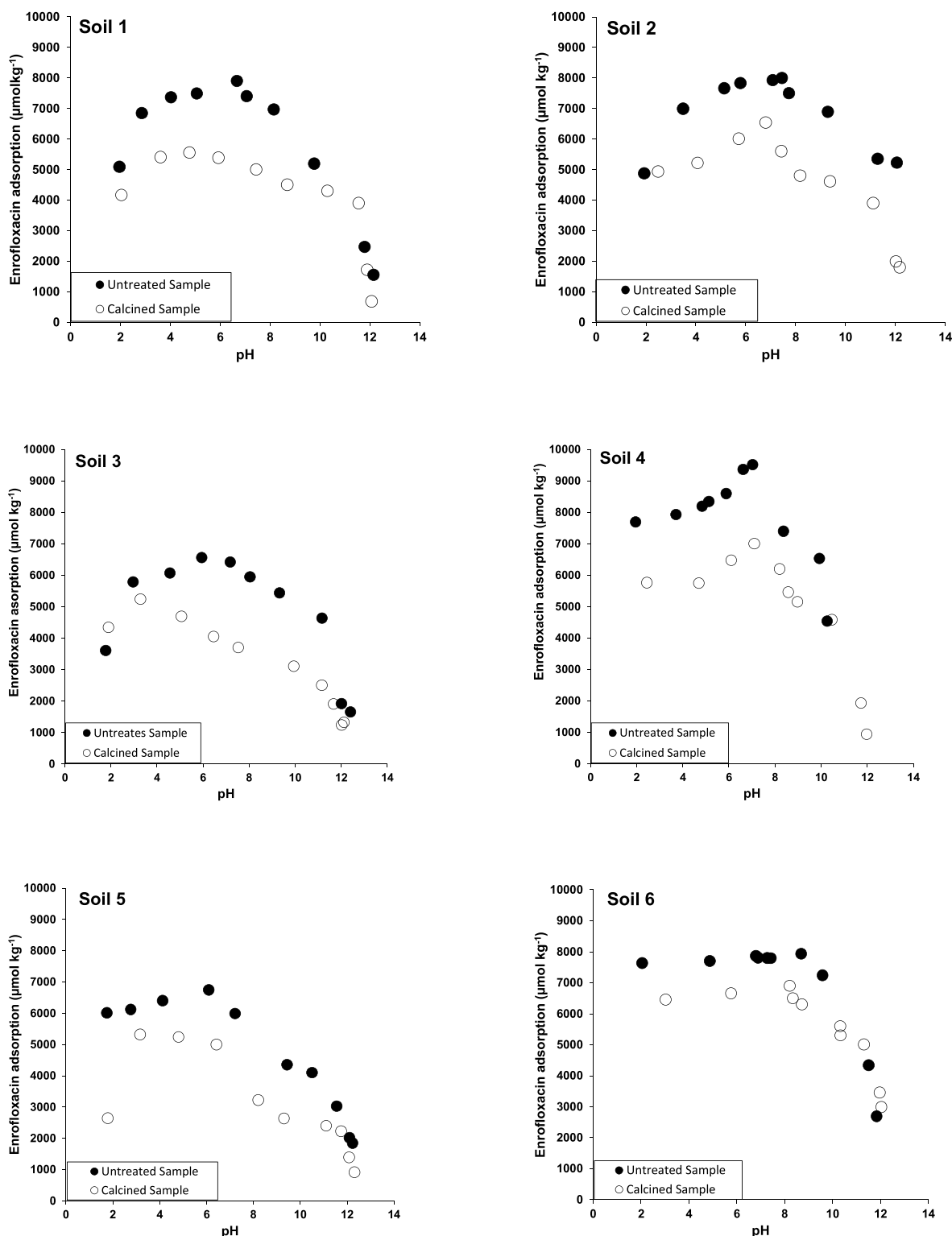
Fig. 2. Doxycycline adsorption onto the different soil samples (both untreated and calcined) as a function of pH. Average values. The coefficients of variation were in all cases less than 10%.

Table 2
K_d values (L kg^{-1}) for the different forms of doxycycline. K_dDC^+ (L kg^{-1}): adsorption coefficient for the positively charged form; K_dDC^0 (L kg^{-1}): adsorption coefficient for the zwitterionic form; K_dDC^- (L kg^{-1}): adsorption coefficient for the negatively charged form; K_dDC^{2-} (L kg^{-1}): adsorption coefficient for the form with two negative charges calculated using equation (1). R^2 indicates the goodness of the fit.

Soil		K_dDC^+	K_dDC^0	K_dDC^-	K_dDC^{2-}	R^2	R^2 significance
1	Untreated	nd	853 ± 201	18,723 ± 2366	nd	0.946	P < 0.005
	Calcined	nd	1614 ± 483	4944 ± 1740	nd	0.625	P < 0.05
2	Untreated	nd	5886 ± 692	6738 ± 2233	nd	0.825	P < 0.005
	Calcined	nd	2511 ± 388	6520 ± 1384	nd	0.800	P < 0.005
3	Untreated	nd	607 ± 177	nd	nd	0.591	P < 0.05
	Calcined	nd	632 ± 98	nd	nd	0.776	P < 0.005
4	Untreated	nd	10,430 ± 501	nd	nd	0.953	P < 0.005
	Calcined	nd	1968 ± 482	nd	nd	0.501	P < 0.05
5	Untreated		2380 ± 434	nd	nd	0.735	P < 0.005
	Calcined	nd	845 ± 238	3878 ± 694	nd	0.825	P < 0.005
6	Untreated	nd	3147 ± 190	2692 ± 259	3406 ± 206	0.474	P < 0.1
	Calcined	nd	nd	2012 ± 447	635 ± 90	0.724	P < 0.005

nd: not different from 0.

Fig. 3. Enrofloxacin adsorption onto the different soil samples, both untreated and calcined, as a function of pH. Average values. The coefficients of variation were in all cases less than 12%.

For the desorption study, the centrifuged residues of the soil samples previously subjected to the adsorption process were weighed to determine the amount of occluded solution (to be able to take the antibiotic dissolved in this solution into account when calculating desorption). Then they were re-suspended in 5 mL of 0.005 M CaCl₂ and shaken, centrifuged, filtered and analyzed under the same conditions as in the adsorption experiment. All experiments were performed in triplicate.

Empirical models were used to calculate adsorption coefficients (K_d) corresponding to the different forms of antibiotics (K_d^+ is the adsorption coefficient for the positively charged form of the antibiotic; K_d^0 is the coefficient for the zwitterion form; K_d^- is the coefficient for the negatively charged form, and K_d^{2-} is the form with the highest negative charge). For this, both Equation (1) and Equation (2) were used. Specifically, Eq. (1) was used to fit experimental data for DC:

Table 3

K_d values (L kg^{-1}) for the different forms of Enrofloxacin. K$_d$ENR$^+$(L kg^{-1}): adsorption coefficient for the positively charged form; K$_d$ENR^0(L kg^{-1}): adsorption coefficient for the zwitterionic form; K$_d$ENR$^-$(L kg^{-1}): adsorption coefficient for the negatively charged form calculated using equation (2). R^2 indicates the goodness of the fit.

Soil		K$_d$ENR$^+$	K$_d$ENR^0	K$_d$ENR$^-$	R^2	R^2 significance
1	Untreated	260 ± 56	372 ± 93	nd	0.655	P < 0.05
	Calcined	69 ± 9	66 ± 19	21 ± 8	0.701	P < 0.05
2	Untreated	401 ± 121	1096 ± 161	nd	0.765	P < 0.005
	Calcined	96 ± 18	nd	nd	0.601	P < 0.05
3	Untreated	94 ± 22	143 ± 38	nd	0.587	P < 0.05
	Calcined	56 ± 5	34 ± 9	14 ± 4	0.857	P < 0.005
4	Untreated	1443 ± 212	2588 ± 391	nd	0.770	P < 0.005
	Calcined	100 ± 38	307 ± 44	nd	0.817	P < 0.005
5	Untreated	146 ± 5	48 ± 9	21 ± 4	0.985	P < 0.005
	Calcined	58 ± 11	nd	nd	0.655	P < 0.05
6	Untreated	572 ± 150	967 ± 134	nd	0.799	P < 0.005
	Calcined	64 ± 5	62 ± 8	25 ± 3	0.885	P < 0.005

nd: not different from 0.

$$K_d = (K_d^+ \ \alpha^+) + (K_d^0 \ \alpha^0) + (K_d^- \ \alpha^-) + (K_d^{2-} \ \alpha^{2-}) \tag{1}$$

While Eq. (2) was used in the case of ENR and SMP, since they have only two pK$_a$ values (Table 1):

$$K_d = (K_d^+ \ \alpha^+) + (K_d^0 \ \alpha^0) + (K_d^- \ \alpha^-) \tag{2}$$

In these equations K_d is the total adsorption coefficient (L kg^{-1}), which is calculated at different pH values. In addition, α is the fraction of each antibiotic species as a function of pH. Specifically, α^+, α^0, α^- and α^{2-} represent the proportions of the different chemical species of antibiotics obtained from their pK$_a$ values (De-Levie, 1999; Enke, 2001). K_d^+ is the adsorption coefficient for the positively charged form of the antibiotic under consideration; K_d^0 is the coefficient for the zwitterion form. K_d^- is the coefficient for the negatively charged form, and K_d^{2-} is the form with the highest negative charge in the case of DC and are obtained empirically using equations (1) and (2). The different adjustments were obtained using the statistical program SPSS v 20.

2.5. Antibiotics quantification

The quantification of each antibiotic was carried out by means of a HPLC equipment (Dionex Corporation, USA) connected to an ultraviolet–visible detector (UVD170U). A Luna C18 column from Phenomenex (Madrid, Spain) was used for the chromatographic separation. An injection volume of 50 μL and a flow rate of 1.5 mL min^{-1} were used. The mobile phase consisted of acetonitrile and 0.02 M oxalic acid/0.01 M triethanolamine in the case of DC, and acetonitrile and 0.01 M phosphoric acid for ENR and SMP. The total analysis time was 15 min. For the detection of DC a wavelength of 360 nm was used, and for SMP and ENR a wavelength of 270 nm was used.

3. Results and discussion

3.1. Electro-kinetic determinations

Fig. 1 shows the Z-potential values for all the analyzed samples. The untreated soil samples (Fig. 1a, 1c, 1e, 1g, 1i and 1k) present, in general, negative potentials in the entire range of pH studied (between 2 and 12), which is indicative of a predominance of negative charge in these samples. In addition, this negative potential rises as the pH increases, which indicates a predominance of components with variable charge in these samples. This is due to organic matter and to the presence of 1:1

phyllosilicates (such as kaolinite and halloysite) that also have a predominance of variable charge.

The calcination of the samples resulted in different behaviors in relation to the Z potential (Fig. 1b; 1d, 1f, 1h, 1j and 1l). On the one hand, there are samples showing few changes in relation to the untreated ones, such as Soil 1 (Fig. 1a and b), Soil 3 (Fig. 1e and f) and Soil 5 (Fig. 1i and j). Other soils, when calcined show positive Z potentials, fundamentally at acidic pHs, as is the case of Soil 2 (Fig. 1c and d), and Soil 6 (Fig. 1k and l). Finally, Soil 4, which had high organic matter content before calcination, behaves differently from the others, in the sense that when the organic matter is eliminated, the Z potentials remain close to 0 mV throughout the whole pH range considered (Fig. 1g and h). This indicates that in this soil organic matter is the main responsible of the surface charge.

3.2. Influence of pH on adsorption

Fig. 2 shows the results of DC adsorption as a function of pH. These results indicate that the adsorption maximum for non-calcined soils reaches 8000–10,000 μmol kg^{-1} for most of the samples, except for Soil 5 whose adsorption maximum is around 6000 μmol kg^{-1}. These data are of the same order as those provided by Alvarez-Esmorís et al. (2020) for a group of 20 agricultural soils from the same geographic area. Comparing with other antibiotics, the results from the current study are higher than those provided for different tetracycline antibiotics (Teixidó et al., 2012; Conde-Cid et al., 2019a). Another aspect to note is that adsorption maxima take place at a pH around 6, from which adsorption decreases. These results coincide with those obtained by other authors who indicate that DC adsorption is greater at acidic pHs compared to basic pH values (Zhu et al., 2015). It also takes place for other tetracycline antibiotics in soils (Sassman and Lee, 2005; Zhang et al., 2011) and in individual soil components, such as kaolinite (Zhao et al., 2011a), montmorillonite (Parolo et al., 2008; Wang et al., 2008) and goethite (Zhao et al., 2011b).

In the calcined samples there is a slight decrease in adsorption, especially at acid pHs (Fig. 2, Soils 1 and 2) and in other samples there are hardly any significant changes (Fig. 2, Soils 3, 4, 5 and 6). These data coincide with those provided by Alvarez-Esmorís et al. (2021a, 2021b), in the sense that DC is adsorbed in significant amounts even in samples where organic matter was removed. This important adsorption even in samples where the organic matter was removed (calcined samples) is due to the fact that DC, like other tetracycline antibiotics, strongly adsorbs both on organic surfaces and on clays. In fact, the clay fraction has been mentioned as an important adsorbent for DC (Alvarez-Esmorís et al., 2020; Xu et al., 2021), as well as for other tetracyclines (Jones et al., 2005; Conde-Cid et al., 2019a).

Since DC has three pK$_a$ values (Table 1) and, therefore, its speciation is a function of pH, the K_d values for the different DC species were calculated using Eq. (1). The results obtained are presented in Table 2. In general, the adjustments were significant judging by the values of R^2, which ranged between 0.474 and 0.946. The DC$^+$ species presents K_d values not different from 0 in all cases, both in the untreated samples and in the calcined ones. For the DC^{2-} species, values not different from 0 were also obtained, except for Soil 6, which is the one with the highest pH in water (7.0). The behavior for the other two DC species was dependent on the specific soil: in Soil 1 there was an increase in the K_d of DC^0 when the sample was calcined (going from 853 to 1614 L kg^{-1}), as well as a decrease in the K_d of DC$^-$ when the sample was calcined (going from 18,723 to 4944 L kg^{-1}). In Soil 2, there was a decrease in the K_d value of DC^0 when calcining the sample (going from 5886 to 2511 L kg^{-1}), while the K_d values of DC$^-$ remained non-different, comparing the untreated and calcined samples. Soils 3 and 4 only present a K_d different from 0 for the DC^0 fraction, with values remaining in the same proportion when the samples were calcined (Soil 3) or with values decreasing (from 10,430 to 1968 L kg^{-1}, Soil 4). Soil 5 behaves similarly to Soils 3 and 4, but, when calcining the sample, there was a decrease in
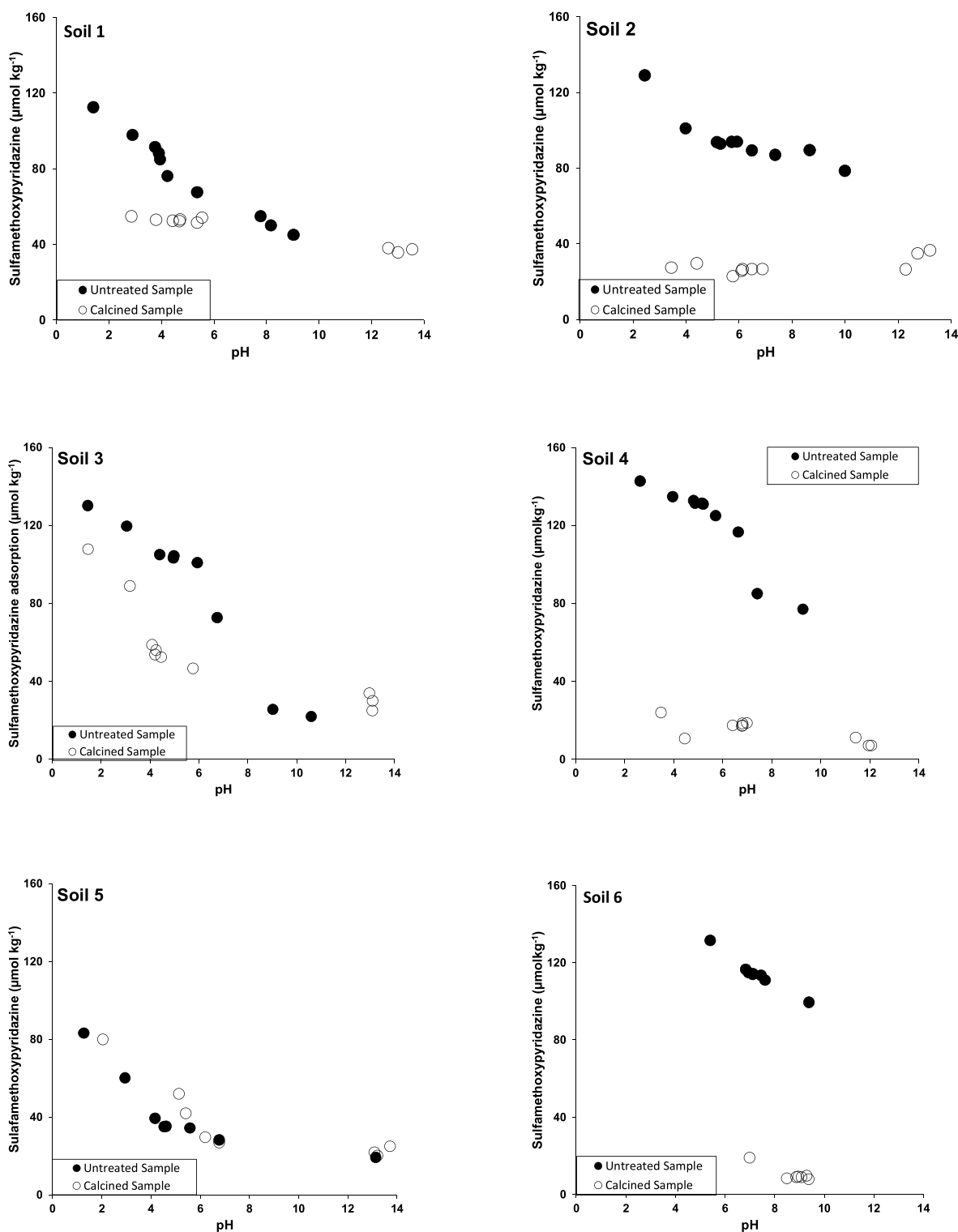
Fig. 4. Adsorption of Sulfamethoxypyridazine onto the different soil samples, both untreated and calcined, depending on the pH. Average values. The coefficients of variation were in all cases less than 6%.

the K_d value of DC^0 (going from 2380 to 845 L kg^{-1}) and K_d of DC^- reached a value of 3878 L kg^{-1} (Table 2).

Finally, Soil 6 showed very similar K_d values for the three species (DC^0, DC^- and DC^{2-}), ranging between 2692 and 3406 L kg^{-1}, decreasing to a range between 635 and 2012 L kg^{-1} when the samples were calcined (Table 2).

Adsorption data corresponding to ENR are presented in Fig. 3. Non-calcined samples show adsorption maxima between pH 6 and 8 (ranging

between 6500 μmol kg^{-1} for Soil 3 and 9500 μmol kg^{-1} for Soil 4), with a drastic decrease when pH is increased above 8. The behavior of the calcined samples is very similar, but with lower adsorption values (between 5200 μmol kg^{-1} for Soil 3 and 7000 μmol kg^{-1} for Soils 4 and 6). The decrease in the adsorption of ENR as the pH increases has been described previously for soil components such as smectite, illite and kaolinite (Wang et al., 2013), humic acids (Martínez-Mejía et al., 2017) and for whole soils (Graouer-Bacart et al., 2015). This behavior has also

Table 4
K_d values (L kg^{-1}) for the different species of sulfamethoxypyridazine. K$_d$SMP$^+$ (L kg^{-1}): adsorption coefficient for the positively charged form; K$_d$SMP^0 (L kg^{-1}): adsorption coefficient for the zwitterionic form; K$_d$SMP$^-$ (L kg^{-1}): adsorption coefficient for the negatively charged form calculated using equation (2). R^2 indicates the goodness of the fit.

Soil		K$_d$SMP$^+$	K$_d$SMP^0	K$_d$SMP$^-$	R^2	R^2 significance
1	Untreated	9.8 ± 0.8	3.4 ± 0.3	1.7 ± 0.4	0.918	P < 0.005
	Calcined	nd	1.5 ± 0.1	0.9 ± 0.1	0.727	P < 0.005
2	Untreated	20.5 ± 1.7	4.6 ± 0.3	5.1 ± 0.4	0.918	P < 0.005
	Calcined	nd	0.5 ± 0.0	0.9 ± 0.1	0.678	P < 0.05
3	Untreated	27.9 ± 1.7	6.6 ± 0.6	nd	0.968	P < 0.005
	Calcined	8.7 ± 0.8	1.7 ± 0.3	1.1 ± 0.4	0.914	P < 0.005
4	Untreated	128.7 ± 8.0	28.9 ± 0.9	27.7 ± 1.9	0.956	P < 0.005
	Calcined	nd	0.003 ± 0.000	0.002 ± 0.000	0.537	P < 0.05
5	Untreated	3.8 ± 0.2	0.9 ± 0.1	nd	0.965	P < 0.005
	Calcined	4.1 ± 0.5	1.1 ± 0.2	nd	0.898	P < 0.005
6	Untreated	18,632 ± 5048	17 ± 2	nd	0.955	P < 0.005
	Calcined	nd	nd	nd	0.704	P < 0.05

nd: not different from 0.

been reported for other materials, such as biochar (Wang et al., 2019), and activated carbon, showing an adsorption maximum around pH 5–6 (Chowdhury et al., 2019; DasSharma et al., 2020). Other fluoroquinolones, such as ciprofloxacin, also show a similar behavior in their adsorption on soils, reaching maximum adsorption values for pH values above 5–6 (Vasudevan et al., 2009).

Since ENR has two pK$_a$ values (6.3 and 8.3, Table 1), it presents three different species depending on the pH (ENR$^+$ at acidic pH, ENR^0 at intermediate pH values, and ENR$^-$ at basic pH). The K_d values of the different species were calculated using equation (1) and the results obtained are presented in Table 3.

Table 3 shows that, for the 6 soils studied, the highest K_d values correspond to the cationic species (ENR$^+$), ranging between 94 and 1443 L kg^{-1}, and to the zwitterionic species (ENR^0), ranging between 48 and 2588 L kg^{-1}. These K_d values of the different species decrease in all cases when the samples are calcined (Table 3), ranging between 56 and 100 L kg^{-1} for ENR$^+$ and between 0 and 307 L kg^{-1} for ENR^0. The ENR$^-$ species only presented values different from 0 for Soil 5 without calcination (21 L kg^{-1}) and for Soils 1 and 6 after calcination (21 and 25 L kg^{-1} respectively).

The data corresponding to SMP adsorption as a function of pH are presented in Fig. 4, both for the untreated and calcined samples. In the untreated soil samples, there is a decrease in adsorption as the pH increases, also noting that SMP adsorption is much lower than that observed for both DC and ENR. When the samples are calcined, there is a decrease in adsorption, but pH has lesser effect, with adsorption remaining practically constant as pH increases. The exceptions are found in Soils 3 and 5, where the tendency to decrease with increasing pH also occurs in calcined samples (Fig. 4). Although SMP has not been extensively studied previously, the behavior of other sulfonamides has been shown to be similar, in the sense of decreasing its adsorption onto soils as pH increases, as is the case of sulfadimethoxine, sulfamethoxazole and sulfamethazine (Park and Huwe, 2016), sulfachloropyridazine (Laak et al., 2006), sulfadiazine, sulfadoxine, and sulfacetamide (Anskjær et al., 2014). SMP also has two pK$_a$ values (2.2 and 7.2, Table 1) but they are lower than those of ENR, resulting in higher adsorption at acidic pH values.

The K_d values of the different SMP species were calculated using Eq.

(2), and the results are presented in Table 4. In this case, the highest K_d values of the untreated samples were obtained for the SMP$^+$ fraction, ranging from 3.8 L kg^{-1} (for Soil 5) to 1832 L kg^{-1} (for Soil 6), being very high scores compared to the other soils, but it is noteworthy that Soil 6 is the one with the highest pH value. The K_d values of the other two fractions are very similar in all the samples studied, highlighting that for some Soils (3, 5 and 6) the K_d values of SMP$^-$ are not different from 0. When calcining the samples, a drastic decrease takes place in the K_d values of the different SMP species, even with values not different from 0 in some cases (Table 4). This indicates that, in this case, organic matter has a decisive role in the adsorption of SMP, as previously highlighted for different sulfonamides (Laak et al., 2006; Alvarez-Esmorís et al., 2020; Conde-Cid et al., 2019b, 2020).

Although the K_d data of the different species is obtained from empirical equations (Eqs. (1) and (2)), it can be interpreted that changes in the species also mean changes in the adsorption mechanisms, which will be different depending on the pH. Therefore, adsorption could take place through hydrophobic interactions in acid soils, and yet could occur through the cation exchange mechanism for alkaline soils, as previously indicated by Chen et al. (2020) for the adsorption of tetracycline in different soils.

3.3. Influence of pH on desorption

Fig. 5 shows DC desorption percentages, which were less than 10% for the untreated soil samples (unless Soil 3 at very acidic pH values, reaching between 14% and 37%). In addition, desorption percentages tend to be lower as the pH increases, both in the treated (calcined) and untreated soil samples. These low percentages of desorption coincide with those obtained previously in similar soils, which in all cases were less than 1% (Alvarez-Esmorís et al., 2020), as well as with those obtained for various tetracyclines (Pils and Laird, 2007; Munira and Farenhorst, 2017; Conde-Cid et al., 2019a). Finally, it should be noted that these desorption percentages do not increase significantly when the organic matter is removed (calcined samples), except in some cases and at very acidic pH values (Soils 4, 5 and 6). This indicates a strong irreversibility in the DC adsorption process, and subsequent low mobility in soils even at very extreme pH values.

As shown in Fig. 6, ENR desorption percentages were also low, and in general also less than 10%, which coincides with that reported in previous publications, where desorption percentages for fluoroquinolones (including enrofloxacin) were even less than 0.22% (Pereira-Leal et al., 2012). But desorption data provided for other fluoroquinolones were very high, such as for ciprofloxacin (Vasudevan et al., 2009), indicating that in this case the process is fully reversible. In the present study the percentages increased significantly at basic pHs, only for soil 1, soil 5 and the calcined soil 6. In all the other cases the desorption value was around 5% for the whole alkaline range (Fig. 6). Also, to be noted, the untreated and calcined samples behaved in a similar way, indicating that the desorption percentages did not increase significantly in the soil samples where organic matter had been removed (Fig. 6).

Fig. 7 shows that SMP desorption percentages were higher than those of the other two antibiotics, exceeding 30% in many cases. Although there are no previous desorption data available for SMP, desorption percentages previously reported for other sulfonamides are also quite high, as is the case of sulfadimethoxine (ranging between 13 and 97%) and sulfaguanidine (ranging 14–72%) (Bialk-Bielińska et al., 2012) and for sulfadiazine (ranging 30–52%) and sulfamethoxazole (ranging 44–48%) (Hu et al., 2019). Although it should also be noted that the desorption results depend on the type of soil and the sulfonamide in question. In this way, Conde-Cid et al. (2019b) found desorption percentages that were higher in soils with less organic matter, with desorption following the sequence: sulfamethazine < sulfachloropyridazine ≈ sulfadiazine. In the present study, the behavior of the SMP desorption percentages is very different from that of DC and ENR, with a maximum appearing at pH between 5.5 and 7.0 in most of
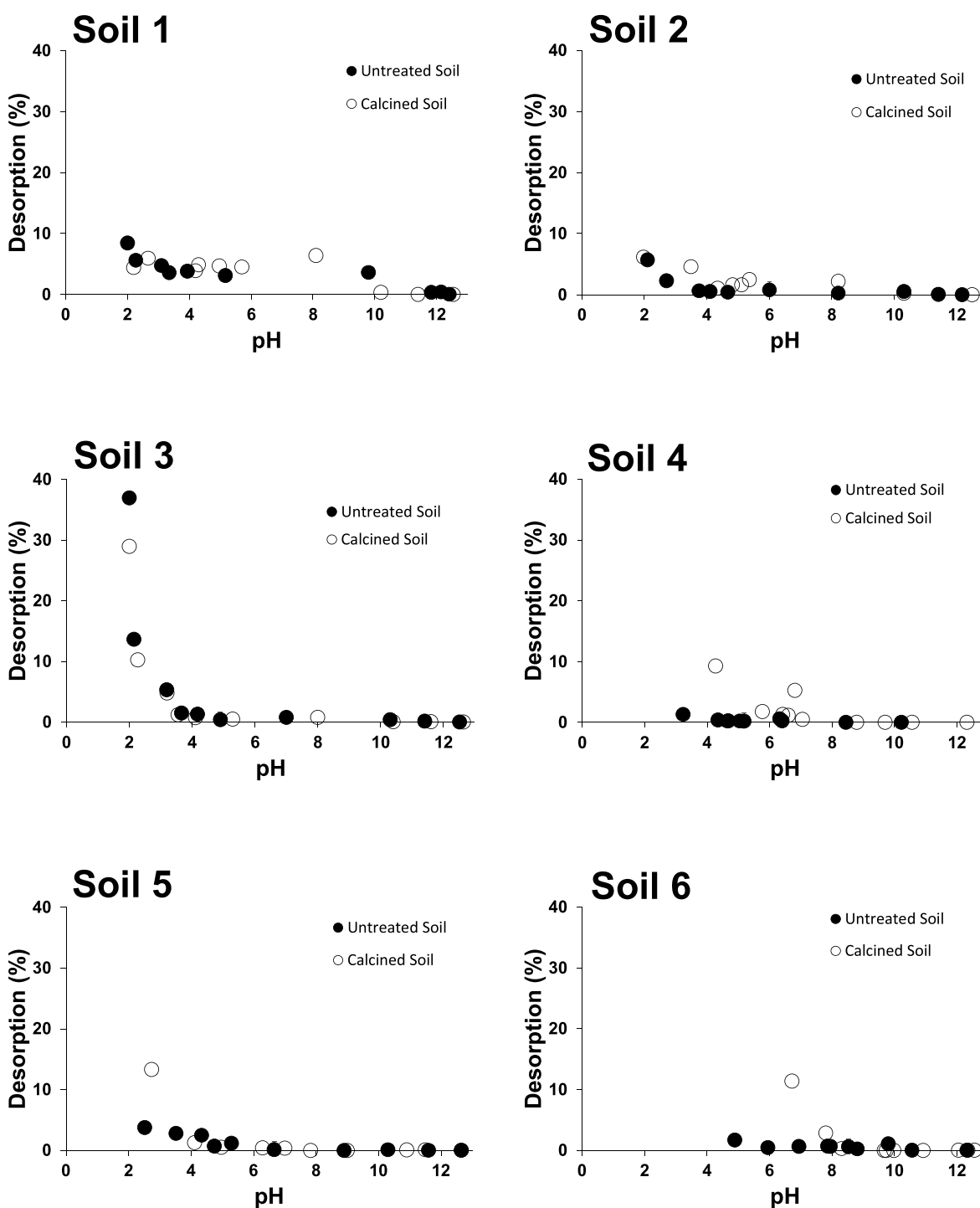
Fig. 5. Doxycycline desorption percentages as a function of pH in the different soil samples, both untreated and calcined. Average values. The coefficients of variation were in all cases less than 15%.

the samples, and with desorption percentages being in general higher in the calcined soil samples (Fig. 7). These results indicate that this antibiotic is much more mobile than DC and ENR in soils, and that changes in pH, for example due to certain agricultural practices, can mobilize an important part of the antibiotic previously adsorbed to soil colloids, generating pollution problems and eventual toxicity.

4. Conclusions

This study shows that the removal of soil organic matter by

calcination causes important modifications in the surface charge characteristics of the soils, losing part of the variable charge provided by the organic matter, judging by Z-potential values obtained as a function of pH. For the antibiotic doxycycline (DC) the adsorption coefficients (K_d) were higher for the chemical species DC^- compared to DC^+, DC^0 and DC^{2-}, if we exclude soil 6, which is the one with the highest pH and where the species DC^0, DC^-, and DC^{2-} have a similar weight. There is only a slight decrease in the adsorption of DC due to the removal of the soil organic matter by calcination, indicating that inorganic components are also involved in the adsorption of this antibiotic. In addition,
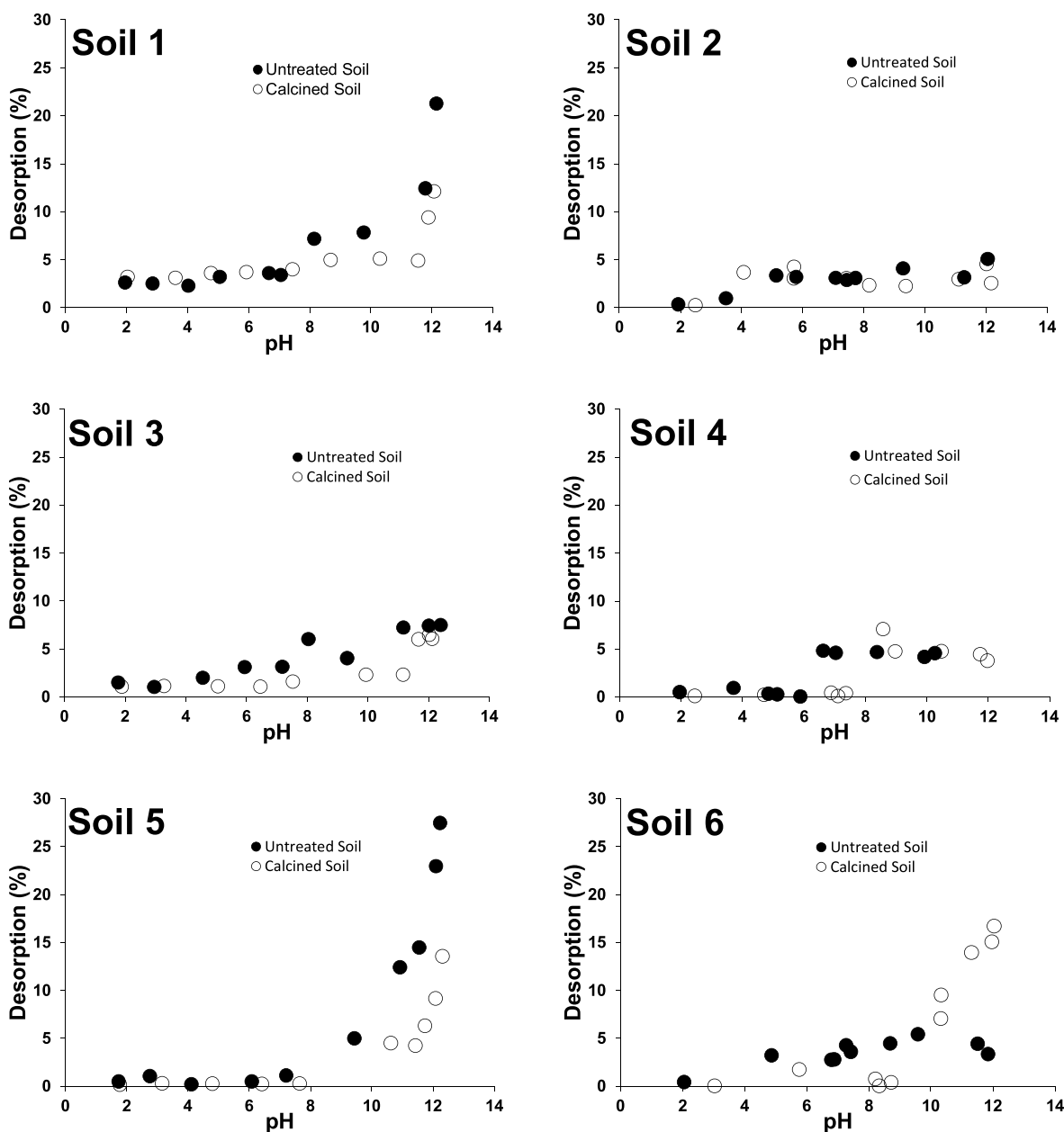
Fig. 6. Enrofloxacin desorption percentages as a function of pH in the different soil samples, both untreated and calcined. Average values. The coefficients of variation were in all cases less than 12%.

desorption percentages were very low throughout the pH range studied, which is indicative of a strong hysteresis considering the adsorption/desorption processes. Regarding enrofloxacin (ENR), its adsorption decreases at high pHs (from approximately pH 6–8). The behavior of the calcined samples was similar, but with lower adsorption values. The species with the highest K_d in this case was ENR^0, although the ENR^+ species also acquires a certain weight when the organic matter is removed. The adsorption of sulfamethoxypyridazine (SMP) is much lower than that of the other two antibiotics, and is clearly higher at acidic pHs. When calcining the samples, there is a decrease in the adsorption of SMP and also a lower effect of pH on adsorption, so that in this case the role of organic matter in adsorption is more decisive. The species with the highest K_d in this case was SMP^+, while SMP^0 and SMP^- acquire much more weight when the samples are calcined. The desorption percentages were very low for both DC and ENR in the entire range of pH studied (2–12) and higher for SMP. DC and ENR did not show important changes in desorption when calcining the samples, but

for SMP a maximum of desorption is observed at pH between 5.5 and 7.0, and desorption increased when calcining the samples. Calcination produces important changes in the K_d values of the different chemical species of the three antibiotics studied, which may be related to different adsorption mechanisms depending on the pH, probably taking place through hydrophobic interactions in acid soils, and by cation exchange mechanisms for alkaline soils. Finally, it can be concluded that eventual changes in pH caused by certain agricultural practices, such as liming or the application of different fertilizers, can affect the evolution and environmental fate of antibiotics such as the three studied in this research, an aspect that in the future should be considered in order to carry out a more sustainable agriculture with lower risks of environmental pollution.

CRediT author statement
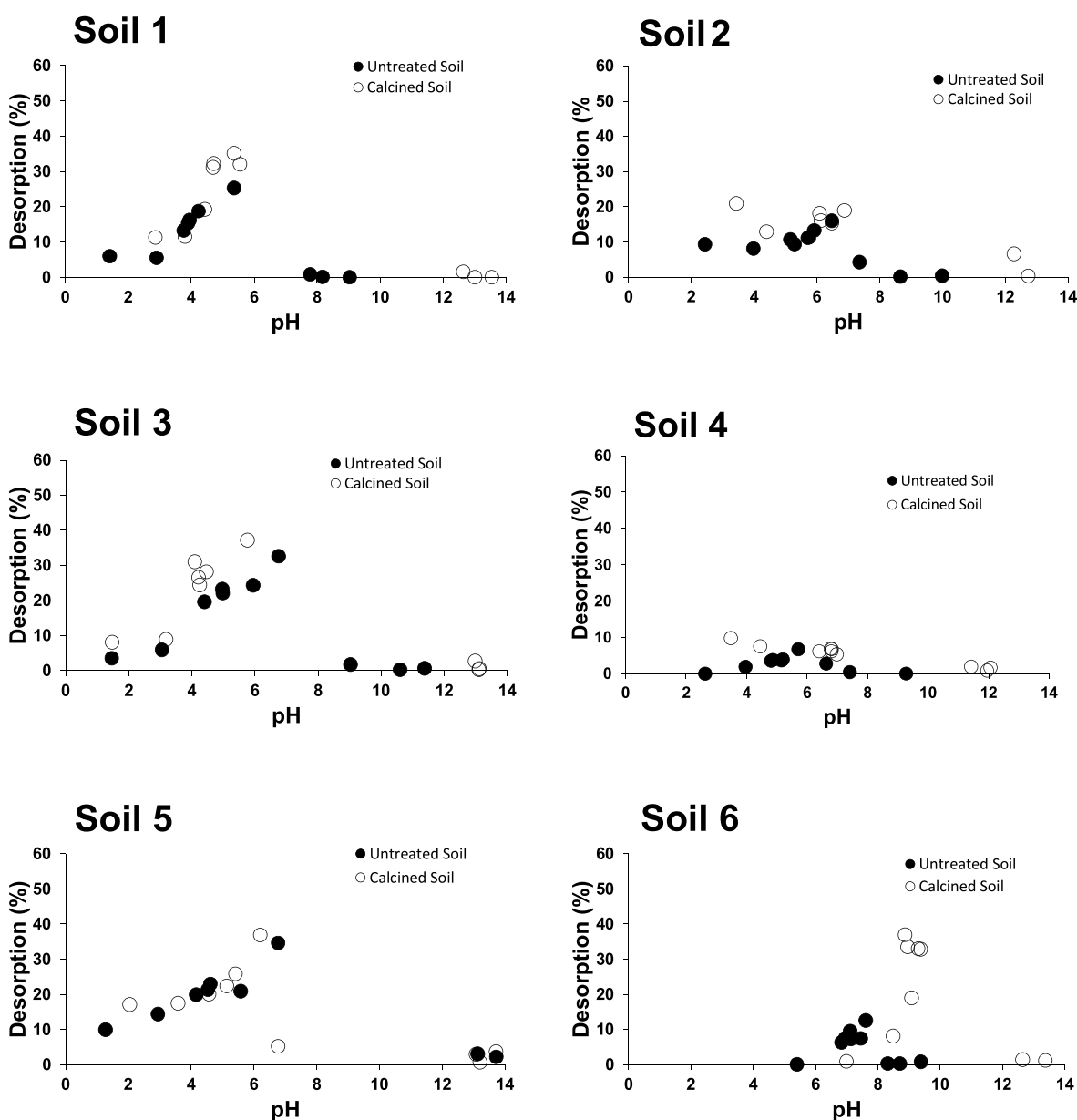
Manuel Arias-Estévez, Esperanza Álvarez-Rodríguez, David

Soil 1

Soil 2

Soil 3

Soil 4

Soil 5

Soil 6

Fig. 7. Sulfamethoxypiridazine desorption percentages as a function of pH in the different soil samples, both untreated and calcined. Average values. The coefficients of variation were in all cases less than 5%.

Fernández-Calviño, Avelino Núñez-Delgado: Conceptualization. Manuel Arias-Estévez, Esperanza Álvarez-Rodríguez, David Fernández-Calviño, Avelino Núñez-Delgado: Methodology. Cristina Álvarez-Esmorís, Lucia Rodríguez López: Software. Manuel Arias-Estévez, Esperanza Álvarez-Rodríguez, David Fernández-Calviño: Data curation. Cristina Álvarez-Esmorís, Lucia Rodríguez López, Manuel Arias-Estévez, David Fernández-Calviño: Writing- Original draft preparation. Cristina Álvarez-Esmorís, Lucia Rodríguez López, Manuel Arias-Estévez, David Fernández-Calviño, Esperanza Álvarez-Rodríguez, Avelino Núñez-Delgado: Visualization. Cristina Álvarez-Esmorís, Lucia Rodríguez López: Investigation. Manuel Arias-Estévez, Esperanza Álvarez-Rodríguez, David Fernández-Calviño, Avelino Núñez-Delgado: Supervision. Manuel Arias-Estévez, Esperanza Álvarez-Rodríguez, David Fernández-Calviño, Avelino Núñez-Delgado: Validation. Avelino Núñez-Delgado: Writing-Reviewing and Editing.

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.

Data availability

No data was used for the research described in the article.

Acknowledgements

and Competitiveness).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2022.114071.

References

Alvarez-Esmorís, C., Conde-Cid, M., Fernández-Calviño, D., Fernández-Sanjurjo, M.J., Núñez-Delgado, A., Álvarez-Rodríguez, E., Arias-Estévez, M., 2020. Adsorption-desorption of doxycycline in agricultural soils: batch and stirred-flow-chamber experiments. Environ. Res. 186, 109565 https://doi.org/10.1016/j.envres.2020.109565.

Alvarez-Esmorís, C., Conde-Cid, M., Ferreira-Coelho, G., Fernández-Sanjurjo, M.J., Núñez-Delgado, A., Álvarez-Rodríguez, E., Arias-Estévez, M., 2021a. Adsorption/desorption of sulfamethoxypyridazine and enrofloxacin in agricultural soils. Sci. Total Environ. 706, 136015 https://doi.org/10.1016/j.scitotenv.2019.136015.

Alvarez-Esmorís, C., Conde-Cid, M., Fernández-Sanjurjo, M.J., Núñez-Delgado, A., Álvarez-Rodríguez, E., Arias-Estévez, M., 2021b. Environmental relevance of adsorption of doxycycline, enrofloxacin, and sulfamethoxyprridazine before and after the removal of organic matter. J. Environ. Manag. 287, 112354 https://doi.org/10.1016/j.envman.2021.112354.

Anskjær, G.G., Krogh, K.A., Halling-Sørensen, B., 2014. Dialysis experiments for assessing the pH-dependent sorption of sulphonamides to silt clay fractions. Chemosphere 95, 116–123.

Babić, S., Horvat, A.J.M., Mutavdžić-Pavlović, D., Kaštelan-Macan, M., 2007. Determination of pKa values of active pharmaceutical ingredients. Trends Anal. Chem. 26, 1043–1061. https://doi.org/10.1016/j.trac.2007.09.004.

Batt, A.L., Aga, D.S., 2005. Simultaneous analysis of multiple classes of antibiotics by ion trap LC/MS/MS for assessing surface water and groundwater contamination. Anal. Chem. 77, 2940–2947.

Bialk-Bielińska, A., Maszkowska, J., Mrozik, W., Bielawska, A., Kolodziejska, M., Palavinskas, R., Stepnowski, P., Kumirska, J., 2012. Sulfadimethoxine and Sulfaguanidine: their sorption potential on natural soils. Chemosphere 86, 1059–1065. https://doi.org/10.1016/j.chemosphere.2011.11.058.

Carballa, M., Fink, G., Omil, F., Lerma, J.M., Ternes, T., 2008. Determination of the solid–water distribution coefficient (Kd) for pharmaceuticals, estrogens and musk fragrances in digested sludge. Water Res. 42, 287–295.

Carstens, J.F., Bachmann, J., Guggenberger, G., 2021. Aggregation and transport behavior of goethite colloids as affected by dissolved organic matter and pH: electrostatic vs. hydrophilic interactions. Colloids Surf. A Physicochem. Eng. Asp. 609, 125639 https://doi.org/10.1016/j.colsurfa.2020.125639.

Cela-Dablanca, R., Barreiro, A., Rodríguez López, L., Santás-Miguel, V., Arias-Estévez, M., Núñez-Delgado, A., Álvarez-Rodríguez, E., Fernández-Sanjurjo, M.J., 2022. Relevance of sorption in bio-reduction of amoxicillin taking place in forest and crop soils. Environ. Res. 208, 112753 https://doi.org/10.1016/j.envres.2022.112753.

Chen, M., Yi, Q., Hong, J., Zhang, L., Lin, K., Yuan, D., 2015. Simultaneous determination of 32 antibiotics and 12 pesticides in sediment using ultrasonic-assisted extraction and high performance liquid chromatography-tandem mass spectrometry. Anal. Methods 7, 1896–1905. https://doi.org/10.1039/C4AY02895C.

Chen, Y., Hu, C., Deng, D., Li, Y., Luo, L., 2020. Factors affecting sorption behaviors of tetracycline to soils: importance of soil organic carbon, pH and Cd contamination. Ecotoxicol. Environ. Saf. 197, 110572 https://doi.org/10.1016/j.ecoenv.2020.110572.

Choppala, G., Kunhikrishnan, A., Seshadri, B., Park, J.H., Bush, R., Bolan, N., 2018. Comparative sorption of chromium species as influenced by pH, surface charge and organic matter content in contaminated soils. J. Geochem. Explor. 184 (B), 255–260. https://doi.org/10.1016/j.gexplo.2016.07.012.

Chowdhury, S., Sikder, J., Mandal, T., Halder, G., 2019. Comprehensive analysis on sorptive uptake of enrofloxacin by activated carbon derived from industrial paper sludge. Sci. Total Environ. 665, 438–452. https://doi.org/10.1016/j.scitotenv.2019.02.081.

Conde-Cid, M., Álvarez-Esmorís, C., Paradelo-Núñez, R., Nóvoa-Muñoz, J.C., Arias-Estévez, M., Álvarez-Rodríguez, E., Fernández-Sanjurjo, M.J., Núñez-Delgado, A., 2018. Occurrence of tetracyclines and sulfonamides in manures, agricultural soils and crops from different areas in Galicia (NW Spain). J. Clean. Prod. 197, 491–500. https://doi.org/10.1016/j.jclepro.2018.06.217.

Conde-Cid, M., Fernández-Calviño, D., Nóvoa-Muñoz, J.C., Núñez-Delgado, A., Fernández-Sanjurjo, M.J., Arias-Estévez, M., Álvarez-Rodríguez, E., 2019a. Experimental data and model prediction of tetracycline adsorption and desorption in agricultural soils. Environ. Res. 177, 108607 https://doi.org/10.1016/j.envres.2019.108607.

Conde-Cid, M., Fernández-Calviño, D., Fernández-Sanjurjo, M.J., Núñez-Delgado, A., Arias-Estévez, M., Álvarez-Rodríguez, E., 2019b. Adsorption/desorption and transport of sulfadiazine, sulfachloropyridazine, and sulfamethazine, in acid agricultural soils. Chemosphere 234, 978–986. https://doi.org/10.1016/j.chemosphere.2019.06.121.

Conde-Cid, M., Núñez-Delgado, A., Fernández-Sanjurjo, M.J., Álvarez-Rodríguez, E., Fernández-Calviño, D., Arias-Estévez, M., 2020. Tetracycline and sulfonamide antibiotics in soils: presence, fate and environmental risks. Processes 8, 1479. https://doi.org/10.3390/pr8111479.

DasSharma, D., Samanta, S., Kumar, D.N., Halder, G., 2020. A mechanistic insight into enrofloxacin sorptive affinity of chemically activated carbon engineered from Green coconut shell. J. Environ. Chem. Eng. 8, 104140 https://doi.org/10.1016/j.jece.2020.104140.

De-Levie, R., 1999. Aqueous Acid-Base Equilibria and Titration. Oxford, New York, USA.

Du, L., Liu, W., 2012. Occurrence, fate, and ecotoxicity of antibiotics in agro-ecosystems. A review. Agron. Sustain. Dev. 32, 309–327.

Enke, C.G., 2001. The Art and Science of Chemical Analysis. Wiley, New York, USA.

Franklin, A.M., Williams, C., Andrews, D.M., Watson, J.E., 2022. Sorption and desorption behavior of four antibiotics at concentrations simulating wastewater reuse in agricultural and forested soils. Chemosphere 289, 133038. https://doi.org/10.1016/j.chemosphere.2021.133038.

Gathuka, L.W., Kato, T., Takai, A., Flores, G., Inui, T., Katsumi, T., 2021. Effect of acidity on attenuation performance of sandy soil amended with granular calcium-magnesium composite. Soils Found. 61 (4), 1099–1111. https://doi.org/10.1016/j.sandf.2021.05.007.

Gao, Y., Kang, R., Xia, J., Yu, G., Deng, S., 2019. Understanding the adsorption of sulfonamide antibiotics on MIL-53s: metal dependence of breathing effect and adsorptive performance in aqueous solution. J. Colloid Interface Sci. 535, 159–168. https://doi.org/10.1016/j.jcis.2018.09.090.

Graouer-Bacart, M., Sayen, S., Guillon, E., 2015. Adsorption of enrofloxacin in presence of Zn(II) on a calcareous soil. Ecotoxicol. Environ. Saf. 122, 470–476. https://doi.org/10.1016/j.ecoenv.2015.09.019.

He, L.L., Huang, D.Y., Zhang, Q., Zhu, H.H., Xu, C., Li, B., Zhu, Q.H., 2021. Meta-analysis of the effects of liming on soil pH and cadmium accumulation in crops. Ecotoxicol. Environ. Saf. 223, 112621 https://doi.org/10.1016/j.ecoenv.2021.112621.

Hu, S., Zhang, Y., Shen, G., Zhang, H., Yuan, Z., Zhang, W., 2019. Adsorption/desorption behaviour and mechanisms of sulfadiazine and sulfamethoxazole in agricultural soils systems. Soil Till. Res. 186, 233–241. https://doi.org/10.1016/j.still.2018.10.026.

Jones, A.D., Bruland, G.L., Agrawal, S.G., Vasudevan, D., 2005. Factors influencing the sorption of oxytetracycline to soils. Environ. Toxicol. Chem. 24, 761–770. https://doi.org/10.1897/04-037R.1.

Kemper, N., 2008. Veterinary antibiotics in the aquatic and terrestrial environment. Ecol. Indicat. 8, 1–13. https://doi.org/10.1016/j.ecolind.2007.06.002.

Kim, K., Kim, J., Hyun, S., 2018. Soil attenuation of the leaching potential of mine-related metallic elements (Zn, As, and Cd) under different leachate solute compositions. J. Environ. Manag. 222, 402–408. https://doi.org/10.1016/j.jenvman.2018.05.096.

Kuppusamy, S., Kakarla, D., Venkateswarlu, K., Megharaj, M., Yoon, Y.E., Lee, Y.B., 2018. Veterinary antibiotics (VAs) contamination as a global agro-ecological issue: a critical view. Agric. Ecosyst. Environ. 257, 47–59. https://doi.org/10.1016/j.agee.2018.01.026.

Laak, T.L.T., Gebbink, W.A., Tolls, J., 2006. Estimation of soil coefficients of veterinary pharmaceuticals from soil properties. Environ. Toxicol. Chem. 25, 933–941. https://doi.org/10.1897/05-229R.1.

López-Periago, E., Núñez-Delgado, A., Díaz-Fierros, F., 2002. Attenuation of groundwater contamination caused by cattle slurry: a plot-scale experimental study. Bioresour. Technol. 84 (2), 105–111. https://doi.org/10.1016/S0960-8524(02)00041-X.

Martínez-Carballo, E., González-Barreiro, C., Scharf, S., Gans, O., 2007. Environmental monitoring study of selected veterinary antibiotics in animal manure and soils in Austria. Environ. Pollut. 148, 570–579. https://doi.org/10.1016/j.envpol.2006.11.

Martínez-Mejía, M.J., Sato, I., Rath, S., 2017. Sorption mechanism of enrofloxacin on humic acids extracted from Brazilian soils. Environ. Sci. Pollut. Res. 24, 15995–16006. https://doi.org/10.1007/s11356-017-9210-3.

Munira, S., Farenhorst, A., 2017. Sorption and desorption of glyphosate, MCPA and tetracycline and their mixture in soil as influenced by phosphate. J. Environ. Sci. Health B 1–9. https://doi.org/10.1080/03901234.2017.1361773.

Núñez-Delgado, A., López-Períago, E., Díaz-Fierros-Viqueira, F., 2002. Pollution attenuation by soils receiving cattle slurry after passage of a slurry-like feed solution: column experiments. Bioresour. Technol. 84 (3), 229–236. https://doi.org/10.1016/S0960-8524(02)00050-0.

Oliver, D.P., Li, Y., Orr, R., Nelson, P., Barnes, M., McLaughlin, M.J., Kookana, R.S., 2019. The role of surface charge and pH changes in tropical soils on sorption behaviour of per- and polyfluoroalkyl substances (PFASs). Sci. Total Environ. 673, 197–206. https://doi.org/10.1016/j.scitotenv.2019.04.055.

Park, J.Y., Huwe, B., 2016. Effect of pH and soil structure on transport of sulfonamide antibiotics in agricultural soils. Environ. Pollut. 213, 561–570. https://doi.org/10.1016/j.envpol.2016.01.089.

Parolo, M.E., Savini, M.C., Vallés, J.M., Baschini, M.T., Avena, M.J., 2008. Tetracycline adsorption on montmorillonite: pH and ionic strength effects. Appl. Clay Sci. 40, 179–186. https://doi.org/10.1016/j.clay.2007.08.003.

Pereira-Leal, R.M., Figueira, R.F., Tornisielo, V.L., Regitano, J.B., 2012. Occurrence and sorption of fluoroquinolones in poultry litters and soils from Sao Paulo State. Brazil. Sci. Total Environ. 432, 344–349. https://doi.org/10.1016/j.scitotenv.2012.06.002.

Pereira-Leal, R.M., Ferracciú Alleoni, L.R., Tornisielo, V.L., 2013. Sorption of fluoroquinolones and sulfonamides in 13 Brazilian soils. Chemosphere 92, 979–985. https://doi.org/10.1016/j.chemosphere.2013.03.018.

Pils, J.R., Laird, D.A., 2007. Sorption of tetracycline and chlortetracycline on K- and Ca-saturated soil clays, humic substances, and clay-humic complexes. Environ. Sci. Technol. 41, 1928–1933. https://doi.org/10.1021/es062316y.

Riaz, L., Mahmood, T., Khalid, A., Rashid, A., Muhammad Bashir Ahmed Siddique, M.B. A., Kamal, A., Coyne, M.S., 2018. Fluoroquinolones (FQs) in the environment: a review on their abundance, sorption and toxicity in soil. Chemosphere 191, 704–720. https://doi.org/10.1016/j.chemosphere.2017.10.092.

Santás-Miguel, V., Díaz-Raviña, M., Martín, A., García-Campos, E., Barreiro, A., Núñez-Delgado, A., Fernández-Sanjurjo, M.J., Álvarez-Rodríguez, E., Arias-Estévez, M., Fernández-Calviño, D., 2020. Medium-term influence of tetracyclines on total and specific microbial biomass in cultivated soils of Galicia (NW Spain). Span. J. Soil Sci. 10 (3), 2017–2232. https://doi.org/10.3232/SJSS.2020.V10.N3.05.

Sassman, S.A., Lee, L.S., 2005. Sorption of three tetracyclines by several soils: assessing the role of pH and Cation exchange. Environ. Sci. Technol. 39, 7452–7459.

Tan, K.H., 1996. Soil Sampling, Preparation, and Analysis. Marcel Dekker, New York.

Teixidó, M., Granados, M., Prat, M.D., Beltrán, J.L., 2012. Sorption of tetracyclines onto natural soils data analysis and prediction. Environ. Sci. Pollut. Res. 19, 3087–3095. https://doi.org/10.1007/s11356-012-0954-5.

Vasudevan, D., Bruland, G.L., Torrance, B.S., Upchurch, V.G., Mackay, A.A., 2009. pH-dependent ciprofloxacin sorption to soils: interaction mechanisms and soil factors influencing sorption. Geoderma 151, 68–76. https://doi.org/10.1016/j.geoderma.2009.03.007.

Verlicchi, P., Zambello, E., 2015. Pharmaceuticals and personal care products in untreated and treated sewage sludge: occurrence and environmental risk in the case of application on soil- A critical review. Sci. Total Environ. 538, 750–767. https://doi.org/10.1016/j.scitotenv.2015.08.108.

Wang, Y.J., Jia, D.A., Sun, R.J., Zhu, H.W., Zhou, D.M., 2008. Adsorption and cosorption of tetracycline and copper (II) on montmorillnite as affected by solution pH. Environ. Sci. Technol. 42, 3254–3259.

Wang, M., Li, Z., Hong, H., Wu, Q., 2013. Enrofloxacin uptake and retention on different types of clays. J. Asian Earth Sci. 77, 287–294. https://doi.org/10.1016/j.seaes.2013.02.032.z.

Wang, W., Ma, X., Sun, J., Chen, J., Zhang, J., Wang, Y., Wang, J., Zhang, H., 2019. Adsorption of enrofloxacin on acid/alkali-modified corn stalk biochar. Spectrosc. Lett. https://doi.org/10.1080/00387010.2019.1648296.

Xie, T., Wang, M., Su, C., Chen, W., 2018. Evaluation of the natural attenuation capacity of urban residential soils with ecosystem-service performance index (EPX) and entropy-weight methods. Environ. Pollut. 238, 222–229. https://doi.org/10.1016/j.envpol.2018.03.013.

Xu, X., Ma, W., An, B., Zhou, K., Mi, K., Huo, M., Liu, H., Wang, H., Liu, Z., Cheng, G., Huang, L., 2021. Adsorption/desorption and degradation of doxycycline in three agricultural soils. Ecotoxicol. Environ. Saf. 224, 112675 https://doi.org/10.1016/j.ecoenv.2021.112675.

Yang, C.W., Hsiao, W.C., Chang, B.V., 2016. Biodegradation of sulfonamide antibiotics in sludge. Chemosphere 150, 559–565. https://doi.org/10.1016/j.chemosphere.2016.02.064.

Yang, W., Hu, S., Jing, C., 2012. Enrofloxacin sorption on smectite clays: effects of pH, cations, and humic acid. J. Colloid Interface Sci. 372, 141–147. https://doi.org/10.1016/j.jcis.2012.01.016.

Zhang, G., Liu, X., Sun, K., Zhao, Y., Lin, C., 2010. Sorption of tetracycline to sediments and soils: assessing the roles of pH, the presence of cadmium and properties of sediments and soils. Front. Environ. Sci. Eng. 4, 421–429. https://doi.org/10.1007/s11783-010-0265-3.

Zhang, Z., Sun, K., Gao, B., Zhang, G., Liu, X., Zhao, Y., 2011. Adsorption of tetracycline on soil and sediment: effects of pH and the presence of Cu (II). J. Hazard. Mater. 190, 856–862. https://doi.org/10.1016/j.hazmat.2011.04.017.

Zhao, Y., Geng, J., Wang, X., Gu, X., Gao, S., 2011a. Tetracycline adsorption on kaolinite: pH, metal cations and humic acid effects. Ecotoxicology 20, 1141–1147. https://doi.org/10.1007/s10646-011-0665-6.

Zhao, Y., Geng, J., Wang, X., Gu, X., Gao, S., 2011b. Adsorption of tetracycline onto goethite in the presence of metal cations and humic substances. J. Colloid Interface Sci. 361, 247–251. https://doi.org/10.1016/j.jcis.2011.05.051.

Zhu, F., Jiao, S.J., Shan, Z.J., Kong, D.Y., Ge, F., Wang, N., 2015. Sorption and desorption behavior of doxycycline on a Wushantu soil in TaiHu lake region, China. Fresenius Environ. Bull. 24, 3295–3299.