Experimental data and model prediction of tetracycline adsorption and desorption in agricultural soils

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Abstract

In this work, tetracycline (TC) adsorption and desorption were studied, identifying those soil properties that most influenced the process. Batch experiments were carried out on 63 crop soils, which showed a wide range of values in their physicochemical characteristics. Adsorption curves fitted well to the Freundlich equation, with K_F values varying between 901 and 9202 L^n μmol^{1-n} kg^{-1}. TC retention on soils was high, with adsorption values always higher than 58%, and desorption lower than 9%. Bivariate correlations and multiple linear regressions were performed to identify those soil variables having a greater influence on TC adsorption and desorption. The results indicate that organic carbon, clay, exchangeable aluminum, available phosphorus, effective cation exchange capacity contents, and pH are the main characteristics affecting TC adsorption and desorption. The models, developed by means of multiple linear regression, gave satisfactory and robust predictions for TC adsorption and desorption, using easily determinable soil characteristics as input.

Keywords: adsorption/desorption; antibiotics; modeling; soils; tetracycline.

1. Introduction

There is a worldwide growing concern regarding the presence of antibiotic residues in different environmental compartments, including soils, crops, water and air, mainly due to the development and spread of microorganisms resistant to these compounds (Carvalho and Santos, 2016), which generates global hazards for humans, animals, and the whole environment (Kuppusamy et al., 2018).

Tetracycline antibiotics (TCs) are one of the most widely used in veterinary medicine. In Europe, TCs were the most consumed veterinary antibiotics in 2014, representing 33.4% of total sales (European Medicines Agency, 2016). Its low cost, wide spectrum, and high antimicrobial activity favor their utilization to prevent and control diseases, as well as to promote animal growth, where allowed (Daghrir and Drogui, 2013).

Among TCs, tetracycline (TC) is the most frequently used in veterinary medicine (López-Peñalver et al., 2012). Once administered to animals, 80-90% is excreted through feces and urine (Kumar et al., 2005), reaching soils by spreading of slurries and manures (Kemper, 2008), where TC residues are commonly detected (Ezzariai et al., 2018; Hamscher et al., 2002; Li et al., 2013a; Martínez-Carballo et al., 2007; Widyasari-Mehta et al., 2016; Ji et al., 2012), as well as in amended soils (Chen et al., 2011; Hu et al., 2010; Li et al., 2011). Recently, we detected TC concentrations of up to 0.9 mg kg^{-1} in manures and up to 0.6 mg kg^{-1} in agricultural soils of Galicia (NW Spain) (Conde-Cid et al., 2018a).

Once TC reaches the soil, processes such as adsorption, leaching, and degradation take place. The adsorption-desorption process is considered the most relevant regarding TC mobility, eventual transport to water bodies, and plant uptake (Pikkemaat et al., 2016). TC residues have been detected in surface waters (Charuaud et al., 2019; Kolpin et al., 2002; Lindsey et al., 2001; Wang et al., 2017), groundwater (Mackie et al., 2006), and crops (Marco et al., 2013; Hu et al., 2010; Mullen et al., 2019; Conde-Cid et al., 2018a), thus entering the food chain.

Some studies have been carried out to investigate TC adsorption on soil components, such as clays (Figueroa et al., 2004; Xu et al., 2014; Pils and Laird, 2007; Zhao et al., 2011b; Zhao. et al., 2012; Wang et al., 2010a), iron oxyhydroxides (Zhao et al., 2011a; Tanis et al., 2008), humic substances (Sun et al., 2010; Zhao et al 2011a; Zhao et al., 2012; Pils and Laird, 2007; Gu et al., 2007), and sediments (Wang et al., 2010a; Ji et al., 2016; Chen et al., 2016; Zhang et al., 2010). Other studies have focused on TC adsorption on whole soils (Bao et al., 2013; Figueroa-Diva et al., 2010; Li et al., 2015; Fernández-Calviño et al., 2015a, b; Wan et al., 2010; Sassman and Lee, 2005; Jia et al., 2008; Zhang et al., 2010; Teixidó et al., 2012). However, these studies were carried out with a reduced number of soil samples (up to a maximum of 13 soils, in the case of Teixidó et al., 2012), and most of them investigated adsorption but not desorption, which is crucial to elucidate the degree of reversibility of the process.

Taking all this into account, in this work we used batch type experiments to study TC adsorption and desorption in 63 different agricultural soils. Data derived from these experiments were used to build adsorption curves by plotting TC adsorbed (q_a, µmol kg^{-1}) versus TC concentration remaining dissolved in the equilibrium (C_{eq}, µmol L^{-1}). Different models were used to describe these kinds of curves, such as Temkin, Dubinin-Radushkevich, Flory-Huggins, Halsey, and Brunauer-Emmer-Teller (BET); however, Freundlich and Langmuir models are those most largely used. The Freundlich equation is very useful for heterogeneous sorbent surfaces, such as those of soils, while the Langmuir equation usually shows good fitting for adsorption of inorganic and organic substances, even having evident theoretical limitations (Barrow, 1999).

The main objective is to determine which soil characteristics have a greater influence on the adsorption-desorption process. The secondary objective is to develop a statistically robust model to predict TC adsorption behavior, using pedo-transfer functions where soil characteristics are the input values, facilitating the identification of vulnerable soils.

2. Materials and methods

2.1. Chemical reagents

All chemicals were of high purity analytical grade, from Panreac (Barcelona, Spain), unless acetonitrile, which was HPLC grade, from Fisher Scientific (Madrid, Spain). To carry out HPLC quantifications, all solutions were prepared using milliQ water, obtained through a Millipore equipment (Millipore, Madrid, Spain). Tetracycline hydrochloride (purity of 97.4%) was from Sigma Aldrich (Barcelona, Spain). Table S1 (Supplementary Material) shows the main chemical characteristics of the antibiotic. The TC molecule is characterized by a high water solubility (231 mg L^{-1}, Table S1, Supplementary Material), and by a low value for the distribution coefficient octanol/water (log K_{OW} = -1.37, Table S1), making it hydrophilic.

The TC molecule is amphoteric, with three different acid dissociation constants (pK_a, Table S1), allowing its presence as cation, zwitterion and/or anion as a function of pH.

2.2. Soil samples

Representative soil samples were taken from 63 agricultural plots located in Galicia (NW Spain). For each plot, 10-20 subsamples of the surface layer of soil (0-20 cm depth) were taken in a zigzag manner, using an Edelman probe, then mixing to obtain a single (≈2 kg) representative sample for each plot. Once in the laboratory, these samples were air dried, sieved by 2 mm, homogenized and stored in polyethylene bottles.

Standard methods where used to determine soil characteristics (Tan, 1996). Specifically, sand (2-0.05 mm), silt (0.05-0.002 mm), and clay (<0.002 mm) contents were quantified by using the wet sieving and pipetting methods. Soil pH was determined in water and 0.1 M KCl (soil ratio: 1: 2.5) using a combined glass electrode (Crison pHmeter, model 2001, Crison, L'Hospitalet de Llobregat, Barcelona, Spain). Total soil organic carbon (SOC) and nitrogen (TSN) were determined by elemental analysis in a LECO CHN-1000 (LECO Corporation, St. Joseph, MI, USA). Exchangeable basic cations (Ca_e, Mg_e, Na_e and K_e) were displaced with 0.2 M NH_4Cl (Sumner and Miller, 1996), while exchangeable Al (Al_e) was displaced with 1 M KCl (Bertsch and Bloom, 1996), then determining by flame atomic absorption or emission spectroscopy (AAnalyst 200, Perkin Elmer, Boston, MA, USA). The effective cation exchange capacity (eCEC) was estimated as the sum of the exchangeable basic cations and Al_e. Available phosphorus was extracted using 0.5 M $NaHCO_3$ and determined by using the phosphomolybdic complex method, with a UV-visible spectrophotometer (UV-1201, Shimadzu, Kioto, Japan) (Olsen and Sommers, 1996).

2.3. Quantification of tetracycline

To quantify TC, a previously described procedure (López-Peñalver et al., 2010; Fernández-Calviño et al., 2015a, b) was used, with slight modification. TC quantification was performed in all suspensions by means of a HPLC liquid chromatograph (Dionex Corporation, Sunnyvale, USA), complemented with a P680 quaternary pump, an ASI-100 auto-sampler, a TCC-100 thermostatized column compartment, and a UVD170U detector. To perform chromatographic separations, a Luna C18 column (150 mm long; 4.6

mm internal diameter; 5 µm particle size), obtained from Phenomenex (Madrid, Spain), and a guard column (4 mm long; 2 mm i.d.; 5 µm particle size), packed with the same material as the column, were used. The injection volume was 50 µL, and the flow rate 1.5 mL min^{-1}, with a mobile phase constituted by acetonitrile (phase A), and 0.02 mol L^{-1} oxalic acid/0.01 mol L^{-1} triethylamine (phase B). A linear gradient elution program was run from 5 to 32% of phase A (and 95 to 68% of phase B) within 10.5 min. The initial conditions were re-established in 2 min and held for 2.5 min. The total analysis time was 15 min, with a retention time of 8.0 minutes, and the wavelength used for TC detection was 360 nm. The values for the limit of detection (LOD) and for the limit of quantification (LOQ) were 0.08 µM and 0.27µM, respectively. They were calculated as follows:

$$LOD = \frac{3\ x\ Height\ signal\ to\ noise\ x\ Concentration\ of\ the\ standard}{Height\ of\ signal\ peak\ for\ the\ standard}$$

$$LOQ = \frac{10\ x\ Height\ signal\ to\ noise\ x\ Concentration\ of\ the\ standard}{Height\ of\ signal\ peak\ for\ the\ standard}$$

2.4. TC adsorption and desorption

Batch experiments were carried out to study TC adsorption and desorption in the equilibrium. Specifically, samples of 1 g of soil were weighed in 50 mL polypropylene centrifuge tubes, and suspended in 40 mL of a TC solution. TC concentrations of 5, 10, 25, 50, 100, 200, and 400 µmol L^{-1} were used, with all of them containing 0.005 M $CaCl_2$ as background electrolyte. The resulting suspensions were shaken for 24 h at 50 rpm on a rotary shaker, at room temperature (25 ± 2 °C), then centrifuged for 10 min at 4000 rpm. Previously performed kinetic tests indicated that 24 h were sufficient to reach equilibrium. Afterwards, the supernatant was passed through 0.45 µm pore size nylon syringe-filters (Fisherbrand, Madrid, Spain), followed by TC quantification by means of HPLC, as indicated above (section 2.3.), and by pH measurement. The amount of TC adsorbed was calculated as the difference between the amount initially added and that present in the equilibrium solution.

Regarding desorption, soil precipitates corresponding to those fractions previously subjected to the adsorption process were weighed, in order to quantify the occluded solution, then being re-suspended in 40 mL of 0.005 M $CaCl_2$. Afterwards, the resulting suspensions were shaken, centrifuged, filtered and analyzed in the same manner as indicated above for the adsorption phase.

To study the effect of temperature on adsorption and desorption, three selected soils (soils 27, 28 and 41) were subjected to the same batch-type experiments described above, but working at three different temperatures (288, 298 and 308 ºK).

All the experiments were carried out in triplicate. Previously, control samples consisting in blanks without soil were also tested to check any eventual loss of TC, resulting in TC loss always lower than 3% due to abiotic degradation and/or adsorption to the centrifuge tubes during the experiments. In addition, previous experiments allowed discarding eventual biotic degradation of TC by soil microorganisms (Conde-Cid et al., 2018b).

2.5. Data analysis and statistical treatment

All data obtained in the adsorption experiments were described by means of the Freundlich (Eq. 1) and Langmuir (Eq. 2) models:

$$q_a = K_F C_{eq}^n \qquad \text{(Eq. 1)}$$

$$q_a = \frac{K_L C_{eq} q_m}{1+K_L C_{eq}} \qquad \text{(Eq. 2)}$$

where q_a (µmol kg^{-1}) is the amount of antibiotic adsorbed on the soil at equilibrium; C_{eq} (µmol L^{-1}) is the concentration of antibiotic present in the solution at equilibrium; 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.

Desorption was expressed as the amount of TC desorbed (µmol kg^{-1}), and as the percentage of TC desorbed, compared to the amount previously adsorbed.

To carry out the adjustments of the adsorption models to the experimental data, the statistical software R, version 3.1.3 (R core Team, 2015), and the *nlstools* package for R (Baty et al., 2015), were used. In addition, the SPSS 15.0 software was used to perform bivariate Pearson correlations among adsorption and desorption data and soil variables, as well as multiple linear regression analysis.

3. Results and discussion

3.1. Characteristics of soil samples

The main characteristics of the 63 soils studied are shown in Table S2 (Supplementary Material). Regarding texture, it was sandy-clay loam for 23 soils, sandy loam for 22 soils, clay loam for 2 soils, loam for 8 soils, and silt loam for 8 soils. Sand contents varied between 22 and 70% (average 53%), while silt contents varied from 12 to 62% (average 27%); however, clay contents were similar for most soils, varying between 14 and 34% (average 20%). All soils were acidic, with pH in water (pH_w) between 4.1 and 7.1 (average 5.2). The values for pH in KCl (pH_{KCl}) were always lower than those of pH_w, varying between 3.7 and 6.4 (average 4.6), indicating a predominance of negative charges in all soils. Soil organic carbon (SOC) and TSN contents were highly variable, ranging from 1.07 to 10.92% for SOC (average 2.78%), and from 0.09 to 0.84% for TSN (average 0.25%). Similarly, eCEC was also highly variable, ranging from 3.88 to 30.31 $cmol_c\ kg^{-1}$ (average 7.74). For most soils, calcium was the cation dominating in the exchange complex. Finally, available phosphorus ranged from 26.28 to 317.61 mg kg^{-1} (average 136.25).

Tetracycline was detected in just 4 of the 63 soil samples. Specifically, TC concentrations were 0.2 mg kg^{-1} for soils 21 and 45, 0.3 mg kg^{-1} for soil 27, and it was detected for soil 43, but below the quantification limit.

As shown in Table S3 (Supplementary Material), Pearson's r values indicate that pH_w correlated positive and significantly with Ca_e ($r = 0.742$, $p<0.001$)), Mg_e ($r = 0.563$, $p<0.001$), eCEC ($r = 0.668$, $p<0.001$) and silt content (0.654, $p<0.001$), and negatively with Al_e ($r = -0.613$, $p<0.001$), P_{Olsen} ($r = -0.428$, $p<0.001$), and sand content ($r = -0.610$, $p<0.001$). The behavior was similar for pH_{KCl}, significantly correlating with Ca_e, Mg_e, eCEC, silt, Al_e, P_{Olsen} and sand (with r values 0.865, 0.602, -0.693, 0.796, -0.290, -0.607 and 0.647, respectively), and also significantly correlating with Na_e ($r = 0.302$, $p<0.05$) and K_e ($r = 0.303$, $p<0.05$) (Table S3). SOC correlated positive and significantly with Ca_e ($r = 0.304$, $p<0.05$), Mg_e ($r = 0.412$, $p<0.001$), Na_e ($r = 0.348$, $p<0.001$), eCEC ($r = 0.396$, $p<0.001$), TSN ($r = 0.866$, $p<0.001$), and clay content ($r = 0.384$, $p<0.001$) (Table S3). Regarding sand content, it correlated negative and significantly with parameters related to the exchange complex, such as Ca_e ($r = -0.600$, $p<0.001$), Mg_e ($r = -0.507$, $p<0.001$), eCEC ($r = -0.586$, $p<0.001$), as well as with TSN ($r = -0.365$, $p<0.001$) and silt ($r = -0.955$, $p<0.001$), while the correlation was positive and significant with Al_e ($r = 0.317$, $p<0.05$) and P_{Olsen}

($r = 0.330$, $p<0.001$) (Table S3). Finally, the clay content correlated positive and significantly with Na_e ($r = 0.315$, $p<0.05$), Al_e ($r = 0.258$, $p<0.05$), TSN ($r = 0.397$, $p<0.001$), and SOC ($r=0.384$, $p<0.001$), whereas the correlation was negative and significant with silt ($r = -0.259$, $p<0.05$) (Table S3, Supplementary Material).

3.2. TC adsorption

Figure 1 shows adsorption curves for 12 of the soils, as example of the 63 soils studied, whereas Figure S1 (Supplementary Material) shows TC adsorption curves for all soils (n = 63). In all cases, adsorbed TC increased with the increase in TC added. Adsorption curves in this work corresponded to Giles H-type (Giles et al., 1974) (Figures 1 and S1), characterized by a high affinity between the adsorbent surface and the adsorbate (Calvet, 1989), indicating a strong interaction between TC and the surface of different soil components. In all cases, TC adsorbed was higher than 58% with respect to the amount initially added. Average TC adsorption on soils was 97%, which is clearly high. Other authors found strong interactions among TC and different soil components, with high adsorption capacities (Teixidó et al., 2012; Figueroa et al., 2004; Fernández-Calviño et al., 2015a, b; Pils and Laird, 2007).

Adsorption curves were well described by the Freundlich and Langmuir models (Table 1). Freundlich's model successfully described TC adsorption for all soils (n = 63), with R^2 values between 0.831 and 0.999 (average 0.976), while the Langmuir model satisfactorily described TC adsorption for 47 of the 63 soil (≈ 75% of the samples), with R^2 values between 0.965 and 0.999 (average 0.990). Previously, other authors observed that Freundlich's model satisfactorily described TC adsorption curves in whole soils (Sassman and Lee, 2005; Zhang et al., 2010; Teixidó et al., 2012; Wan et al., 2010; Li et al., 2015), in clays (Figueroa et al., 2004; Xu et al., 2014; Zhao et al., 2012; Zhao et al., 2011a, b; Wang et al., 2010a; Pils and Laird, 2007), or in iron oxyhydroxides (Zhao et al., 2011a), and in humic substances (Zhao et al., 2011b; Pils and Lair, 2007; Sun et al., 2010), in all cases with R^2 values close to 1.

In the present study, Freundlich's affinity coefficient (K_F) values ranged from 901 to 9202 L^n μmol^{1-n} kg^{-1} (equivalent to 731 and 7103 L^n mg^{1-n} kg^{-1}). Previously, Teixidó et al. (2012) obtained K_F values between 240 and 1601 L^n mg^{1-n} kg^{-1}, while Zhang et al. (2010) reported values between 778 and 2375 L^n mg^{1-n} kg^{-1} for TC adsorption on soils. In view of that, it is clear that the range of variation for K_F in the present work is much higher than in those previous studies, probably due to the large number of soil samples here used (n = 63).

Values for the n parameter were below 1 in all cases, varying between 0.18 and 0.90 (average 0.43), indicating that adsorption curves are non-linear and concave, as shown in Figures 1 and S1. This fact indicates that the number of available adsorption sites for TC decreases as the concentration of added TC increases. This situation takes place when the adsorbent surface is heterogeneous, as is the case of soils, causing that high energy adsorption sites are occupied first, followed by low energy adsorption sites (Sukul et al., 2008). Previously, Teixidó et al. (2012) reported n values between 0.59 and 0.92 for TC adsorption, being between 0.49 and 0.74 in a study from Sassman and Lee (2005). Other authors also found similar n values for other antibiotics in the group of TCs, such as oxytetracycline (OTC) (Jones et al., 2005; Teixidó et al., 2012) or chlortetracycline (CTC) (Teixidó et al., 2012; Li et al., 2015).

Regarding the Langmuir model, K_L values for TC varied between 0.02 and 0.90 L μmol^{-1} (average 0.28) (Table 1), which are similar to those reported by Teixidó et al. (2012) (K_L between 0.18 and 1.67 L μmol^{-1}, average 0.75). However, they are slightly higher than those observed by Li et al. (2010) when studying TC adsorption on two different soils, with K_L values of 0.038 and 0.067 L μmol^{-1}. In addition, values obtained for the parameter q_m in this work (8784 and 29800 μmol kg^{-1}, Table 1) were clearly higher than those found by Teixidó et al. (2012) (q_m between 587 and 4458 μmol kg^{-1}, average 1769, n = 13), although similar to those reported by Li et al. (2010) (q_m between 12310.25 and 21339.16 μmol kg^{-1}).

Taking into account parameters from the Freundlich equation, TC adsorption to soils was higher in quantity and affinity than that of sulfonamides and macrolides (Srinivasan et al., 2014; et al., 2014; Liu et al., 2017; Chen et al., 2017), which was also shown by adsorption parameters from the Langmuir equation (Vithanage et al., 2014). However, adsorption on soils is higher for other antibiotics, such as fluoroquinolones (Teixidó et al., 2014; Kong et al., 2014).

Another way of studying adsorption is by using the partition coefficient (K_d), which facilitates comparing different adsorbent materials (Na et al., 2019; Szulejko et al., 2019; Vikrant and Kim, 2019), and is calculated using the following equation:

$$K_d = AC/FC$$

where *AC* is the adsorption capacity (µmol kg^{-1}); *FC* is the final concentration in solution after 24 h of contact (µmol L^{-1}), and K_d is the partition coefficient (L kg^{-1}).

Na et al. (2019) indicate that the partition coefficient (K_d) is less sensitive to the initial concentration than the adsorption capacity, which allows a better comparison to other studies.

Table 2 shows K_d values for different initial concentrations of TC (25, 100 and 400 µmol L^{-1}), as well as adsorption capacity and adsorption percentages, which are close to 100% for the lower initial concentrations (25 and 100 µmol L^{-1}), but clearly decreasing for initial concentration of 400 µmol L^{-1}, although generally remaining higher than 80% (Table 2). As expected, the amount of TC adsorbed (q_a) increases as a function of added TC. Assuming the maximum added concentration as the q_{a400}, it can be seen that TC adsorption values oscillate between 8541 and 14839 µmol kg^{-1} (17.8-30.9 mg g^{-1}) (Table 2). Compared to other materials, these values are intermediate, as lower scores can be found for silica oxide and a granular nitrifying material, and higher scores were reported for carbon nanotubes and activated biochar, among various other (Li et al., 2013b; Li et al., 2018a).

The lowest scores for K_d corresponded to the highest initial concentration of TC, indicating a certain flattening in adsorption curves. Sun et al. (2010) found K_d values in the range 1300-9100 L kg^{-1} for different humic acids and initial concentrations between 1.80 and 46.2 µmol L^{-1} (Table 3), which are of the same order than those in the current work for an initial TC concentration of 25 µmol L^{-1} (Table 2 and Table 3). Also, Bao et al. (2013) reported K_d values of between 838 and 15278 L kg^{-1} for initial concentrations of 2.1 and 52.1 µmol L^{-1} in two different soils (an Alfisol and an Ultisol). However, these values are dependent on soil characteristics, mainly pH, SOC and CEC (Sasdman and Lee, 2005). In fact, Li et al. (2015) reported lower scores (close to 200 L kg^{-1}, Table 3) for a soil with high pH and low SOC content.

3.3. Relation between TC adsorption and soil properties

To elucidate the influence of soil characteristics on TC adsorption onto soils, a bivariate Pearson's correlation was performed among adsorption parameters from the Freundlich equation (K_F and *n*) and chemical characteristics of the different soils (n = 63). Table S4 (Supplementary Material) shows Pearson´s r coefficients obtained from this analysis. The K_F parameter correlated positively and significantly ($p<0.05$) with contents in SOC (r = 0.624), TSN (r = 0.553), clay (r = 0.526), and Al_e (r = 0.405). Furthermore, the K_F parameter was negatively and significantly ($p<0.05$) correlated with pH_{KCl} (r = -0.273). Figure 2 shows the main correlations observed among K_F values and different soil variables. Freundlich's *n* parameter was significantly correlated with all soil variables here studied, with the exception of available phosphorus and clay content. Other authors also observed that TC adsorption positively correlated with SOC content (Zhang et al., 2010) and clay content (Jones et al., 2005), and negatively with pH (Zhang et al., 2010).

Furthermore, for an initial TC concentration of 400 µmol L^{-1}, K_d significantly correlated with soil parameters such as TSN (r = 0.803), SOC (r = 0.847), Mg_e (r= 0.368), Na_e (r = 0.310), eCEC (r = 0.270), and clay (r = 0.443).

In addition, with the objective of developing a model to predict TC adsorption using soil characteristics as input, a multiple linear regression was carried out, establishing the Freundlich affinity coefficient (K_F) as dependent variable, and soil characteristics as independent variables. As a result, 59.5% of the variance of K_F was explained by the independent variables SOC, eCEC, clay, and P_{Olsen} (Eq. 3). SOC was the variable explaining a greater percentage of the variance of K_F, with 38%.

$$K_F = (944.271 \pm 653.824) + (575.197 \pm 92.310) *SOC - (120.691 \pm 25.811) *eCEC + (104.232 \pm 31.794) *Clay - (3.976 \pm 1.895) *P_{Olsen} \qquad \text{(Eq. 3)}$$

F = 23.728; $p<0.000$; adjusted $R^2 = 0.595$

Similarly, a multiple linear regression was also performed establishing the Freundlich linearity index (*n*) as the dependent variable, and soil characteristics as independent variables. As a result, 60% of the variance of *n* was explained by the independent variables eCEC, SOC, and silt (Eq. 4). Among them, eCEC was the variable that explained a greater percentage of the variance of *n*, with 46.7%.

$$n = (0.254 \pm 0.034) + (0.006 \pm 0.003) *eCEC + (0.037 \pm 0.009) *SOC + (0.003 \pm 0.001) *Silt - (0.051 \pm 0.020) *Al_e \qquad \text{(Eq. 4)}$$

F = 24.277; $p<0.000$, adjusted $R^2 = 0.600$

These results are similar to those obtained by Teixidó et al. (2012), who studied TCs adsorption in 13 soils, and performed a principal components analysis, obtaining that the soil characteristics that had a greater influence on TCs adsorption were pH, SOC, eCEC, texture, K, Na, Al, Fe, and P.

In order to verify the efficacy of the proposed models, they were used for all soil samples studied in this work, then comparing K_F and n values predicted and those obtained from the adsorption experiments. Figure 3 shows the relations between observed and predicted values. The model proposed for K_F (Eq. 3) satisfactorily predicted K_F value for 50 of the 63 soils studied, while the model proposed for n (Eq. 4) satisfactorily predicted n values for 55 of the 63 soils.

Taking into account both the Pearson bivariate correlation analysis, and the multiple linear regression analysis, it is shown that the soil characteristics that have a greater importance in TC adsorption are SOC, TSN, clay, Al_e, P_{Olsen}, and eCEC contents, and pH value.

Several authors (Zhang et al., 2010; Zhao et al., 2011a, b; Zhao et al., 2012; Gu et al., 2007; Sun et al. al., 2010), previously suggested that soil organic matter plays a positive role on TC adsorption, in accordance with our results. In addition, Zhao et al. (2011b) studied the effect of humic acids (HA) on TC adsorption, finding that 100 mg L^{-1} of HA increased TC adsorption on kaolinite, from 111.5 to 130.4 mmol kg^{-1}. At the pH values (5.1 ± 0.6) of our experiments on TC adsorption, cationic and zwitterionic TC species are dominant in the medium, and they can be complexed with deprotonated (negatively charged) sites present in HA (mainly carboxyl groups) through electrostatic forces or hydrogen bonds (Zhao et al., 2012). In this sense, Sun et al. (2010) also stated that the TC molecule has multiple polar functional groups, including hydroxyl, ketone and amino, which can strongly interact with the respective functional groups (acids) present in the HA, through hydrogen bonds.

Clay content is another soil characteristic showing a positive influence on TC adsorption, in concordance with that previously observed by other authors. Specifically, Sassman and Lee (2005) studied TC, OTC and CTC adsorption on 8 different soils, finding high adsorption in acid soils with high clay contents. This influence was also observed by Jones et al. (2005) for OTC, and by Teixidó et al. (2012) for CTC and doxycycline. As in the case of organic matter, at acidic pH values the cationic and zwitterionic species of TC could interact with clay surfaces, which, at the acidic pHs of the present study, and in soils with variable charge, have a predominance of negative charge.

Another soil property having strong influence was Al_e content, which in our study favored TC adsorption. In this sense, it is well known that TCs can form complexes with metal ions, such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Zn^{2+}, Fe^{3+} and Al^{3+} (Pikkemaat et al., 2016). Therefore, aluminum could be combined with negatively charged sites on clay surfaces, or with negatively charged functional groups of organic matter, acting as a bridge between zwitterionic and/or anionic TC species and soil particles (Zhang et al., 2010). This is in agreement with that observed by D'Angelo (2017), who studied TC adsorption in organic materials and found that those containing higher Al^{3+} and Fe^{3+} concentrations were the ones that showed higher adsorption, due to the formation of ternary complexes between Al^{3+} or Fe^{3+} and the phenolic diketone and tricarbonylamide systems of the TC molecule. Mackay and Canterbury (2005) studied OTC adsorption in HA and observed that the addition of Al increased adsorption, because Al allowed the formation of ternary complexes between functional groups of the negatively charged organic matter and zwitterionic and/or anionic OTC species.

It is well known that the adsorption of antibiotics is strongly influenced by soil pH (Thiele-Bruhn, 2003). In our study, an increase in soil pH caused a decrease in TC adsorption, and vice versa. Other authors observed that TC adsorption decreased with the increase in the pH of the medium (Teixidó et al., 2012; Zhang et al., 2010; Sassman and Lee, 2005). Specifically, Sassman and Lee (2005) evaluated the influence of pH on TC adsorption to a sediment, obtaining a K_d value of approximately 1800 L kg^{-1} at pH 3.5, while at pH 5.5 it was clearly smaller, approximately 900 L kg^{-1}. As noted above, the TC molecule is amphoteric and has three acid-base dissociation constants (pK_a, Table S1) causing that, depending on the pH of the medium, one or other species predominate. At very acidic pHs, the dominant TC species is cationic, but as the pH of the medium increases, the proportion of cationic species decreases and the proportion of zwitterionic species increases, until a pH of approximately 5.5, from which the proportion of zwitterionic species begins to decrease and the proportion of anionic species increases. Therefore, it is expected that TC adsorption became greater at acidic pHs, where the predominant TC species are cationic and zwitterionic, and where the surfaces of the organic components of the soil, as well as those of clays, have predominantly negative charges.

Regarding the available phosphorus content, those soils having higher concentrations showed lower TC adsorption, and vice versa. These results are in agreement with that observed by Wang et al. (2010b), who obtained K_F values of 9210 and 3730 L^n mg^{1-n} kg^{-1} for two soils in absence of P, while K_F values decreased to 5700 and 2470 L^n mg^{1-n} kg^{-1} in the presence of 31 mg P L^{-1}. These authors concluded that, at pH values lower than 4, the presence of phosphorus can cause changes in the characteristics of the surface of soil components, increasing negative charges, resulting in an increase in TC adsorption, but, at pH values higher than 4 (as in our case), the presence of phosphorus leads to a decrease in adsorption, due to competition between phosphorus and TC for the same adsorption sites.

Finally, soil eCEC had a negative effect on *K_F*, as previously observed by Zhang et al. (2010). In our study, this effect is probably due to Ca^{2+}, which is the major cation of the exchange complex in most of our soils. Teixidó et al. (2012) obtained a negative correlation between *K_d* and Ca content in soils. Although Ca^{2+} can promote TC adsorption due to the formation of ternary complexes between the metal, TC molecules and the negatively charged surfaces of the soil, the presence of Ca^{2+} at high concentrations and in acidic conditions can strongly compete for cation exchange sites with cationic and/or zwitterionic TC species, thus causing a decrease in TC adsorption (Sun et al., 2010). This competitive effect between Ca^{2+} and TCs antibiotics has been previously observed by several authors (Figueroa et al., 2004; Laak et al., 2006; Mackay and Canterbury, 2005). Specifically, Figueroa et al. (2004) demonstrated that the presence of Ca^{2+} caused a decrease in OTC adsorption on montmorillonite at acidic pH values, due to competition for adsorption sites, while at neutral and alkaline pHs the presence of Ca^{2+} favored OTC, adsorption due to the formation of bridges between OTC anionic species and negatively charged surfaces of montmorillonite.

Sithole and Guy (1987) indicated that TC is able to interact with soil organic matter by three mechanisms: a) ionic exchange between H^+ and protonated amines belonging to TC, which has low probability of taking place at the pH values prevailing in the current study; b) TC interacting with divalent cations previously adsorbed to organic particles, with exchangeable cations (mainly Al, Ca and Mg) being able to act as cationic bridges favoring bonds between TC and negatively charged soil particles, giving ternary complexes pH-dependent; c) H bonds between phenolic and carboxylic groups belonging to humic acids (main components in soil organic matter) and TC polar groups, although this kind of bonds decreases as a function of increasing pH. Mechanisms b) and c) are consistent with our results, taking into account that OC, exchangeable cations and pH have great importance in TC adsorption. In addition, cationic bridges can also favor bonds between TC and clays present in soils, causing an increased relevance for mechanism b), being affected by both OC and clay contents, further explaining results obtained in the current study.

3.4. TC desorption

Table 4 shows the amounts of TC desorbed for each of the initial concentrations used, as well as the percentages of desorption with respect to the amount of TC previously adsorbed. Desorption did not take place for the two lowest TC concentrations added (5 and 10 μmol L^{-1}). The amount of TC desorbed increased with the increase in TC concentration added. Desorption was very low for all soils and concentrations used, indicating that TC adsorption is highly irreversible. In fact, in all cases TC desorbed represented 9% or lower of the amount previously adsorbed.

These results are in agreement with those from Fernández-Calviño et al. (2015b), who studied TC, OTC and CTC adsorption/desorption in two different soils, obtaining 8 and 9% as desorption percentages for TC. Munira and Farenhorst (2017), as well as Pils and Laird (2007), found TC desorption from soils lower than 1%. Also relevant, TC is more strongly retained by soils than antibiotics of other groups, such as sulfonamides and macrolides, as reported by Białk-Bielińska et al. (2012), who found desorption between 13.4 and 96.8% for sulfadimethoxine, and between 14.3 and 71.6% for sulfaguanidine, while Hu et al. (2019) found desorption between 30.3 and 52.1% for sulfadiazine, and between 43.7 and 48.3% for sulfamethoxazole. In relation to macrolides, Rabølle and Spliid (2000) reported desorption between 26 and 69% for tylosin. However, the desorption behavior observed for TC is similar to that of fluoroquinolones, which also have a high affinity for soil components. In this sense, Leal et al. (2012) found desorption lower than 0.22% for norfloxacin, ciprofloxacin and enrofloxacin.

3.5. Relation between TC desorption and soil characteristics

In order to identify those soil characteristics that have a greater influence on TC desorption, a bivariate Pearson correlation was performed among desorption data (amounts and percentages of desorption) and soil characteristics. Table S5 (Supplementary Material) shows Pearson's r coefficients obtained from the analysis. As shown, both the quantity and the percentage of TC desorption correlated positively and significantly with pH, Ca_e, silt, and eCEC, while they correlated negatively and significantly with Al_e, SOC, sand, and clay. The fact that desorption correlates negatively and significantly with both sand content and clay content is due to the circumstance that 7 of the soils used in this work (soils 14, 28, 51, 59, 60, 61 and 62) present a positive and significant correlation between sand and clay contents ($r = 0.923$, $n = 7$), having very similar percentages of sand and clay. However, if these soils are not included in the analysis, both the quantity and the percentage of desorption for an initial concentration of 400 μM of TC correlate negatively and significantly with clay content ($r = 0.273$ for the amount desorbed, $r = 0.321$ for percent desorption, $n = 55$), whereas they do not correlate significantly with sand content.

A multiple linear regression analysis was performed using desorbed TC quantities (*TC_{des}*) and percentages (*$\%_{des}$*) as dependent variables, and soil characteristics as independent variables. This analysis was carried out just for desorption data corresponding to the highest initial TC concentration (400 µmol L^{-1}), due to TC desorption being very low. As a result, 29.4% of the variance of the desorbed quantity was explained by the independent variables pH_{KCl} and Mg_e (Eq. 5). Considering these two variables, pH_{KCl} was the one that explained a greater percentage of the variance, with 21.7%.

$$TC_{des}\ (C_0 = 400\ \mu mol\ L^{-1}) = (-485.140 \pm 147.602) + (182.321 \pm 34.959) *pH_{KCl} - (74.657 \pm 27.138) *Mg_e \qquad \text{(Eq. 5)}$$

F = 13.709; p<0.000; adjusted R^2 = 0.294

In addition, 28.0% of the variance of the percentage of TC desorption was explained by the independent variables pH_{KCl} and SOC (Eq. 6). Considering these two variables, pH_{KCl} was the one that explained a greater percentage of the variance, with 17.5%.

$$\%_{des} = (-1.359 \pm 1.124) + (0.980 \pm 0.237) *pH_{KCl} - (0.319 \pm 0.102) *SOC \qquad \text{(Eq. 6)}$$

F=12.865; p<0.000; R^2 ajustado = 0.280.

Figure 4 shows that representing predicted values versus those observed, both the amount and the percentage of TC desorbed were predicted satisfactorily for 49 of the 63 soils studied (approximately 78%). Those variables that correlated positively with TC adsorption (SOC, clay and Al_e), correlated negatively with TC desorption. On the other hand, other variables such as pH and eCEC, which had correlated negatively with TC adsorption, show positive correlation with TC desorption. In general, soil variables that correlate positively with TC adsorption, correlate negatively with desorption, and vice versa.

Predictive models for TC desorption indicate that the most important variables are SOC, Mg_e, and pH. Specifically, increased pH values would favor desorption, which is coherent with adsorption mechanism commented above, indicating that increased pH values reduce the probability of developing bonds through ternary complexes TC-Cation-OM (or –Clay), also decreasing H bonds between TC and humic acids present in soils.

3.4. Relation between TC adsorption and desorption

The relation between adsorption and desorption was confirmed by means of a correlation analysis between the Freundlich K_F parameter and desorption values (quantity and percentage) (Table S6, Supplementary Material), showing that the K_F parameter was negatively and significantly correlated with the amount of TC desorbed, and with the percentage of desorption, for all the initial concentrations of TC used in this analysis (25, 50, 100, 200 and 400 μmol L^{-1}), with values of r between -0.375 and -0.676. Therefore, those soils presenting a greater capacity of TC adsorption were those showing less TC desorption, and vice versa, evidencing the strong irreversibility of TC adsorption in soils.

The association between K_F and desorption values is also shown by the existence of a potential relation between desorption (quantity and percentage) and the Freundlich affinity coefficient (K_F) (Figure 5), with values of r greater than those found when performing a linear relation (r between -0.655 and -0.820). From a value of K_F around 5000 L^n μmol^{1-n} kg^{-1}, TC desorption remains low and practically constant, suggesting that desorption is apparently controlled by the degree of affinity of the previous TC adsorption process.

3.5. Effect of temperature on TC adsorption-desorption

Fitting of experimental data to the Freundlich and Langmuir models for three different temperatures are shown in Table S7 (Supplementary Material). TC adsorption increased in all cases as a function of increased temperature. Specifically, at 288 ºK the values of Freundlich's K_F were 2051, 3109 and 3865 L^n μmol^{1-n} kg^{-1} for soils 27, 28 and 41, respectively, while they clearly increased at 308 ºK, being 6958 L^n μmol^{1-n} kg^{-1} for soil 27, 6752 L^n μmol^{1-n} kg^{-1} for soil 28, and 7049 L^n μmol^{1-n} kg^{-1} for soil 41. Furthermore, Langmuir's q_m and K_L parameters also increased in all cases as a function of increased temperature (Table S7, Supplementary Material).

From experimental results, Gibbs ΔG^0 values were calculated for the adsorption process, as follows:

$$\Delta G^0 = -RTlnK \qquad \text{(Eq.7)}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K degrees) and K (L kg^{-1}) is an equilibrium constant obtained by mathematical multiplication of the Langmuir parameters q_m (μmol kg^{-1}) and K_L (L μmol^{-1}).

Gibbs free energy ΔG^0 is also related to enthalpy (ΔH^0) and entropy (ΔS^0), as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \text{(Eq. 8)}$$

Following Yao et al. (2010), ΔH^0 (J mol^{-1}) and ΔS^0 (J mol^{-1} K^{-1}) were calculated by plotting ΔG^0 versus temperature.

In all cases, negative values were obtained for ΔG^0, indicating the feasibility of the process and the spontaneous nature of adsorption in the range of temperature from 288 to 308 ºK (Table 5). In addition, the absolute values of ΔG^0 increase as a function of increased temperature, indicating that TC adsorption is also higher with that increase. This is further confirmed taking into account the positive values obtained for ΔH^0 (Table 5), indicating that TC adsorption in the studied soils is endothermic. Finally, the positive values obtained for ΔS^0 in all cases (Table 5) indicate the increasing randomness at the solid-solution interface during TC adsorption in the studied soils.

Regarding the effect of temperature on TC adsorption, conflicting effects have been described, which will depend on the adsorbent material, as well as on the range of temperatures tested. On the one hand, a decrease in adsorption takes place as a function of increasing temperature, as has been described for different adsorbent materials, such as kaolinite (Li et al., 2010), suspended organic matter from swine wastewater (Lou et al., 2018), or marine sediments (Wang et al., 2010a). These investigations also gave negative values for ΔH^0, indicating an exothermic nature for TC adsorption. On the other hand, other authors reported an opposite effect, with increasing TC adsorption as a function of increasing temperature (Tanis et. al, 2008; Fan et al., 2016), which in fact is coincident with our findings (increased TC adsorption for increasing temperature, as well as endothermic nature, in view of the positive values of ΔH^0). In this regard, Bao et al. (2013) indicate that, for increasing temperature, water molecules sometimes can be affected more easily than organic pollutants, with increasing adsorption of organic pollutants on minerals surfaces. Other authors reported different effects on TC adsorption as a function of the range of temperature considered, taking into account that it would be an optimal temperature value to favor adsorption. Specifically, D´Angelo (2017) studied the effect of temperature on TC adsorption in poultry litter and municipal biosolids used for soil amendment, finding a significant increase in TC adsorption when temperature rose from 8 to 20 ºC, while at 30 ºC TC adsorption was equal or lower than at 20 ºC.

Regarding desorption, its values decreased in all cases as a function of increased temperature (Table S8, Supplementary Material). As specific examples, for the highest TC concentration added (400 µmol L^{-1}), TC desorbed at 288 ºK was 7.7%, 2.2%, and 2.2% for soils 27, 28 and 41, respectively, while it decreased to 0.5% for all three soils when temperature was set at 308 ºK (Table S8, Supplementary Material). Similarly, Bao et al. (2013) found a decrease in desorption as a function of increased temperature for one of the two soils they studied.

5. Conclusions

The antibiotic TC was strongly retained onto the studied soils (n=63), reaching adsorption values close to 100% in most cases. In addition, TC adsorption was highly irreversible, with desorption percentages always lower than 9%. Soil characteristics having a greater influence on TC adsorption were SOC, clay, Al_e, available P, and eCEC contents, and soil pH. This strong retention makes difficult TC transport from soil to water, as well as plant uptake, especially in acidic soils with high organic matter, clay and exchangeable aluminum contents. However, higher risks of TC transfer and pollution affect to alkaline soils, poor in organic matter and with low contents in clay and exchangeable Al, where TC is more mobile. The models here proposed to predict TC adsorption and desorption can aid in the identification of vulnerable soils. The proposed models have a high robustness and allow carrying out a prediction of TC adsorption and desorption using easily determinable soil characteristics as input. In addition, thermodynamic studies showed that adsorption was spontaneous and endothermic, with increased temperature resulting in higher adsorption and lower desorption. Overall, the results obtained in this work contribute to a better knowledge of the behavior of TC in soils and the overall environment.

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Table 1. Model fitting for tetracycline adsorption in the equilibrium (estimation ± standard error). K_F is the Freundlich adsorption coefficient; n (dimensionless) is the Freundlich's linearity index; K_L is a Langmuir constant relative to the adsorption energy; q_m is the maximum adsorption capacity. R^2: correlation coefficient between experimental and model data. * significant at a P-value of 0.05; ** significant at a P-value of 0.01; *** significant at a P-value of 0.001. na: no adjust allowed.

Soil	**Freundlich**			**Langmuir**		
	K_F (L^n μmol^{1-n} kg^{-1})	**n**	**R^2**	**K_L (L μmol^{-1})**	**q_m (μmol kg^{-1})**	**R^2**
1	$2195 \pm 401^{**}$	$0.45 \pm 0.05^{***}$	0.973	$0.12 \pm 0.01^{***}$	$14750 \pm 522^{***}$	0.996
2	$1352 \pm 264^{**}$	$0.54 \pm 0.05^{***}$	0.987	na	na	
3	$2395 \pm 374^{**}$	$0.45 \pm 0.05^{***}$	0.983	na	na	
4	$3167 \pm 550^{**}$	$0.37 \pm 0.05^{***}$	0.961	$0.26 \pm 0.02^{***}$	$14100 \pm 405^{***}$	0.996
5	$3089 \pm 788^{*}$	$0.37 \pm 0.07^{**}$	0.909	$0.28 \pm 0.07^{*}$	$13900 \pm 1144^{***}$	0.966
6	$2481 \pm 331^{***}$	$0.49 \pm 0.04^{***}$	0.986	$0.12 \pm 0.04^{*}$	$16630 \pm 1784^{***}$	0.980
7	$3308 \pm 545^{**}$	$0.33 \pm 0.04^{***}$	0.966	$0.20 \pm 0.02^{***}$	$14610 \pm 520^{***}$	0.997
8	$5725 \pm 733^{**}$	$0.49 \pm 0.07^{**}$	0.977	$0.58 \pm 0.10^{*}$	$18390 \pm 1122^{***}$	0.994
9	$6068 \pm 886^{*}$	$0.47 \pm 0.09^{*}$	0.987	na	na	
10	$3852 \pm 549^{***}$	$0.31 \pm 0.04^{***}$	0.989	$0.21 \pm 0.08^{*}$	$13950 \pm 1334^{***}$	0.981
11	$2956 \pm 691^{*}$	$0.39 \pm 0.07^{**}$	0.943	$0.23 \pm 0.07^{*}$	$13930 \pm 1164^{***}$	0.976
12	$1966 \pm 284^{***}$	$0.44 \pm 0.04^{***}$	0.988	na	na	0.965
13	$3189 \pm 444^{***}$	$0.27 \pm 0.04^{***}$	0.974	$0.29 \pm 0.09^{*}$	$10720 \pm 768^{***}$	0.980
14	$4038 \pm 530^{***}$	$0.32 \pm 0.04^{***}$	0.973	$0.40 \pm 0.05^{***}$	$13740 \pm 482^{***}$	0.997
15	$2979 \pm 336^{***}$	$0.33 \pm 0.03^{***}$	0.988	$0.16 \pm 0.04^{**}$	$12820 \pm 785^{***}$	0.992
16	$2386 \pm 355^{**}$	$0.28 \pm 0.03^{***}$	0.979	$0.15 \pm 0.04^{*}$	$9514 \pm 597^{***}$	0.989
17	$2352 \pm 256^{***}$	$0.35 \pm 0.03^{***}$	0.995	na	na	
18	$1794 \pm 234^{***}$	$0.38 \pm 0.03^{***}$	0.988	na	na	
19	$3587 \pm 751^{**}$	$0.18 \pm 0.05^{*}$	0.888	$0.60 \pm 0.10^{**}$	$8784 \pm 393^{***}$	0.990
20	$3906 \pm 654^{**}$	$0.32 \pm 0.05^{**}$	0.957	$0.37 \pm 0.05^{***}$	$13850 \pm 534^{***}$	0.994
21	$3054 \pm 252^{***}$	$0.42 \pm 0.03^{***}$	0.995	$0.14 \pm 0.05^{*}$	$15880 \pm 1655^{***}$	0.984
22	$3291 \pm 343^{***}$	$0.41 \pm 0.03^{***}$	0.986	$0.19 \pm 0.03^{***}$	$15730 \pm 697^{***}$	0.997
23	$3995 \pm 627^{**}$	$0.31 \pm 0.05^{**}$	0.981	$0.26 \pm 0.06^{**}$	$14180 \pm 949^{***}$	0.991
24	$3399 \pm 553^{**}$	$0.28 \pm 0.04^{**}$	0.989	na	na	
25	$1702 \pm 213^{***}$	$0.42 \pm 0.03^{***}$	0.995	na	na	
26	$2394 \pm 221^{***}$	$0.36 \pm 0.02^{***}$	0.995	na	na	
27	$2760 \pm 352^{***}$	$0.30 \pm 0.03^{***}$	0.977	$0.22 \pm 0.06^{*}$	$10500 \pm 681^{***}$	0.985
28	$4554 \pm 266^{***}$	$0.61 \pm 0.03^{***}$	0.994	$0.26 \pm 0.02^{***}$	$22770 \pm 1029^{***}$	0.999
29	$3912 \pm 567^{***}$	$0.32 \pm 0.04^{***}$	0.987	$0.24 \pm 0.07^{*}$	$14030 \pm 1200^{***}$	0.985
30	$4072 \pm 547^{***}$	$0.34 \pm 0.04^{***}$	0.991	na	na	
31	$5200 \pm 585^{***}$	$0.31 \pm 0.04^{***}$	0.987	$0.50 \pm 0.10^{*}$	$14920 \pm 1088^{***}$	0.989
32	$3779 \pm 531^{***}$	$0.33 \pm 0.04^{***}$	0.990	$0.20 \pm 0.07^{*}$	$14310 \pm 1472^{***}$	0.980
33	$4060 \pm 652^{**}$	$0.37 \pm 0.05^{***}$	0.962	$0.38 \pm 0.06^{**}$	$15270 \pm 734^{***}$	0.990
34	$3218 \pm 470^{**}$	$0.41 \pm 0.05^{***}$	0.977	$0.21 \pm 0.02^{***}$	$15290 \pm 489^{***}$	0.998
35	$2844 \pm 531^{**}$	$0.44 \pm 0.06^{***}$	0.949	$0.26 \pm 0.02^{***}$	$13560 \pm 414^{***}$	0.997
36	$3053 \pm 398^{***}$	$0.37 \pm 0.04^{***}$	0.974	$0.28 \pm 0.05^{**}$	$12400 \pm 612^{***}$	0.992
37	$3414 \pm 396^{***}$	$0.41 \pm 0.04^{***}$	0.978	$0.32 \pm 0.06^{**}$	$13840 \pm 759^{***}$	0.990
38	$3014 \pm 419^{***}$	$0.37 \pm 0.04^{***}$	0.985	na	na	
39	$1939 \pm 180^{***}$	$0.43 \pm 0.03^{***}$	0.994	na	na	
40	$2072 \pm 370^{**}$	$0.47 \pm 0.05^{***}$	0.982	na	na	
41	$6623 \pm 174^{***}$	$0.47 \pm 0.02^{***}$	0.998	$0.70 \pm 0.20^{*}$	$18220 \pm 1663^{***}$	0.990
42	$3873 \pm 296^{***}$	$0.34 \pm 0.02^{***}$	0.991	na	na	
43	$4114 \pm 553^{***}$	$0.36 \pm 0.05^{***}$	0.970	$0.41 \pm 0.05^{***}$	$14360 \pm 565^{***}$	0.996
44	$3864 \pm 393^{***}$	$0.39 \pm 0.04^{***}$	0.987	$0.31 \pm 0.08^{*}$	$14810 \pm 1127^{***}$	0.987
45	$4901 \pm 617^{***}$	$0.37 \pm 0.05^{***}$	0.965	$0.70 \pm 0.10^{**}$	$14780 \pm 696^{***}$	0.992
46	$3501 \pm 478^{***}$	$0.40 \pm 0.05^{***}$	0.831	$0.33 \pm 0.04^{***}$	$14240 \pm 498^{***}$	0.995
47	$4228 \pm 525^{***}$	$0.37 \pm 0.05^{***}$	0.973	$0.44 \pm 0.06^{***}$	$14390 \pm 626^{***}$	0.995
48	$3240 \pm 405^{***}$	$0.45 \pm 0.04^{***}$	0.979	$0.25 \pm 0.03^{***}$	$15280 \pm 569^{***}$	0.996
49	$9202 \pm 393^{***}$	$0.65 \pm 0.05^{***}$	0.987	$0.70 \pm 0.09^{***}$	$24710 \pm 1600^{***}$	0.997
50	$1476 \pm 131^{***}$	$0.70 \pm 0.03^{***}$	0.997	$0.04 \pm 0.01^{*}$	$28850 \pm 4324^{**}$	0.994
51	$1508 \pm 310^{**}$	$0.49 \pm 0.05^{***}$	0.977	$0.07 \pm 0.01^{**}$	$14250 \pm 826^{***}$	0.992
52	$2793 \pm 578^{**}$	$0.45 \pm 0.06^{***}$	0.952	$0.22 \pm 0.03^{***}$	$15120 \pm 598^{***}$	0.994
53	$2387 \pm 296^{***}$	$0.54 \pm 0.04^{***}$	0.989	$0.11 \pm 0.03^{*}$	$18560 \pm 1840^{***}$	0.988
54	$2468 \pm 474^{**}$	$0.57 \pm 0.07^{**}$	0.974	$0.14 \pm 0.02^{**}$	$18830 \pm 1266^{***}$	0.994
55	$4848 \pm 994^{**}$	$0.60 \pm 0.10^{**}$	0.946	na	na	
56	$2447 \pm 457^{**}$	$0.50 \pm 0.06^{***}$	0.969	$0.15 \pm 0.02^{***}$	$16250 \pm 774^{***}$	0.994
57	$901 \pm 54^{***}$	$0.71 \pm 0.02^{***}$	0.999	$0.02 \pm 0.00^{***}$	$28070 \pm 2428^{***}$	0.999
58	$4320 \pm 583^{***}$	$0.37 \pm 0.05^{***}$	0.987	$0.29 \pm 0.07^{**}$	$16090 \pm 1155^{***}$	0.991
59	$1619 \pm 290^{**}$	$0.58 \pm 0.05^{***}$	0.983	$0.06 \pm 0.01^{***}$	$19010 \pm 1187^{***}$	0.995
60	$1509 \pm 83^{***}$	$0.70 \pm 0.02^{***}$	0.999	$0.04 \pm 0.01^{*}$	$29800 \pm 4997^{**}$	0.996
61	$6223 \pm 550^{***}$	$0.27 \pm 0.03^{***}$	0.990	$0.90 \pm 0.30^{*}$	$14720 \pm 1298^{***}$	0.980
62	$1335 \pm 153^{***}$	$0.59 \pm 0.03^{***}$	0.997	$0.03 \pm 0.01^{*}$	$20750 \pm 2924^{**}$	0.993
63	$3530 \pm 471^{***}$	$0.90 \pm 0.09^{***}$	0.979	na	na	

Table 2. Adsorption capacity, adsorption percentages and partition coefficients (K_d) for three different initial TC concentrations (25, 100 and 400 µmol L^{-1}); q_a: amount of tetracycline adsorbed; %: adsorption percentage.

Soil	q_{a25}	$\%_{25}$	K_{d25}	q_{a100}	$\%_{100}$	K_{d100}	q_{a400}	$\%_{400}$	K_{d400}
	(µmol kg^{-1})		**(L kg^{-1})**	**(µmol kg^{-1})**		**(L kg^{-1})**	**(µmol kg^{-1})**		**(L kg^{-1})**
1	629	97.6	1647	3309	97.8	1758	12902	85.4	234
2	615	96.4	1072	3253	97.1	1326	12435	84.0	205
3	619	98.6	1980	3289	99.1	4512	13075	88.3	295
4	622	98.5	2531	3313	98.9	3491	13080	87.4	276
5	609	97.4	1433	3250	98.9	3593	12879	86.1	245
6	634	98.4	2534	3278	98.8	3229	13615	91.0	401
7	638	100.0	-	3272	98.6	2833	12554	83.1	197
8	638	100.0	-	3285	100.0	10951	14822	98.1	2073
9	630	97.8	1808	3250	96.0	967	14434	98.4	2397
10	644	100.0	-	3351	99.0	4092	12975	86.7	259
11	638	100.0	-	3286	99.1	4118	12896	87.1	264
12	612	98.0	1862	3232	98.4	2332	12387	83.6	200
13	631	100.0	-	3249	98.9	3488	10836	74.6	113
14	625	100.0	-	3261	99.3	5209	13095	88.4	299
15	638	100.0	-	3285	98.0	1973	12032	80.4	163
16	638	100.0	-	3204	96.6	1103	9421	63.6	69
17	638	100.0	-	3220	98.0	1918	11462	75.9	126
18	627	97.4	1470	3242	96.8	1187	10473	70.0	92
19	638	100.0	-	3282	98.9	3651	8541	57.7	53
20	631	100.0	-	3290	99.2	4696	13124	86.9	265
21	644	100.0	-	3250	98.9	3523	13459	90.9	390
22	938	99.4	6582	3885	98.2	2210	13675	91.0	404
23	644	100.0	-	3308	98.7	3105	13122	87.7	283
24	631	100.0	-	3319	99.1	4141	11714	79.9	154
25	625	100.0	-	3183	95.9	929	11378	75.3	122
26	631	100.0	-	3245	97.8	1764	11741	78.5	145
27	926	99.1	4338	3833	97.5	1557	10614	72.0	100
28	929	99.4	7081	3903	99.2	4924	14852	98.1	2075
29	638	100.0	-	3253	99.0	3938	12964	88.4	296
30	631	100.0	-	3328	99.3	5815	13381	91.2	404
31	625	100.0	-	3302	99.5	8519	13891	93.8	591
32	644	100.0	-	3320	99.1	4303	13072	88.3	295
33	625	100.0	-	3262	99.3	5432	13947	92.3	481
34	638	100.0	-	3298	98.4	2474	13288	91.5	413
35	848	98.5	2718	3430	98.6	2908	11935	91.8	414
36	834	98.8	3252	3306	98.9	3367	11576	89.1	300
37	851	98.8	3383	3415	99.2	4810	12509	92.7	486
38	804	100.0	-	3451	99.2	5259	11757	89.6	321
39	790	98.2	2010	3343	97.1	1330	10982	84.5	200
40	832	98.6	2755	3421	98.4	2443	12115	89.0	310
41	929	99.9	30237	3917	99.7	12800	14637	98.6	2675
42	926	99.6	9747	3921	99.3	5807	13473	89.8	350
43	861	100.0	-	3415	99.2	4752	13121	92.6	504
44	828	100.0	-	3386	99.3	5796	13225	93.4	563
45	836	100.0	-	3427	99.5	8268	13411	95.6	867
46	825	98.8	3110	3380	99.1	4519	12922	92.1	465
47	844	100.0	-	3453	99.3	5649	13046	94.0	609
48	833	98.7	2941	3309	99.0	3722	13105	93.4	565
49	927	99.6	10840	3937	99.7	13764	14839	99.4	6899
50	622	96.5	1114	3158	97.1	1273	14122	93.5	573
51	597	94.5	680	3202	95.6	852	11910	80.4	161
52	617	97.7	1665	3277	98.8	3177	13401	90.5	372
53	622	97.6	1615	3273	98.7	2875	13894	92.9	517
54	621	97.3	1442	3302	98.6	2712	13979	94.4	658
55	622	98.5	2638		99.8		14418	98.3	2243
56	628	97.5	1567	3300	98.5	2614	13527	91.3	413
57	597	96.4	1019	3024	92.9	505	13029	88.8	309
58	631	100.0	-	3353	99.1	4301	14135	93.6	581
59	615	95.5	842	3167	95.4	822	13213	90.1	353
60	618	97.8	1746	3271	96.7	1163	13891	93.8	591
61	631	100.0	-	3345	99.8	22285	14136	94.5	681
62	625	100.0	-	3137	95.5	823	13069	87.4	274
63	614	98.1	2055	3286	99.0	4032	14478	98.7	2965

Table 3. Partition coefficient (K_d) values obtained in this work as well as in other studies for tetracycline adsorption in soils and other adsorbent materials. C_0: initial concentration of tetracycline.

Material	C_0 (µmol L^{-1})	K_d (L kg^{-1})	Reference
Soil	25	680 - 30237	This work
Soil	100	505 – 22285	This work
Soil	400	53 - 6899	This work
Soil	2.1	838 - 1813	Bao et al. (2010)
Soil	52.1	1450 - 5474	Bao et al. (2010)
Soil	2.1	1270 - 2471	Bao et al. (2010)
Soil	52.1	876 - 15278	Bao et al. (2010)
Soil	1.1 – 4.2	154 - 210	Li et al. (2015)
Soil	0.4 - 65.0	3102 - 312447	Sassman and Lee (2005)
Soil humic acid	1.8 - 46.2	1300 - 3100	Sun et al. (2010)
Coal humic acid	1.8 - 46.2	1700 - 9100	Sun et al. (2010)
Montmorillonite	10	5850 - 20000	Xu et al. (2014)
Polyethylene	1.8 - 46.2	170 - 320	Sun et al. (2010)
Polystyrene	1.8 - 46.2	60 - 150	Sun et al. (2010)
Polyamide	1.0 - 15.6	356	Li et al. (2018b)

Table 4. Amount of TC desorbed (μmol kg^{-1}) for each initial concentration used. The percentage of desorption with respect to the amount previously adsorbed is shown into brackets. C_0: initial TC concentration.

Soil	**C_0 (μmol L^{-1})**				
	25	**50**	**100**	**200**	**400**
1	13.9 (2.2)	27.8 (2.0)	60.7 (1.8)	72.1 (1.1)	311.4 (2.4)
2	13.6 (2.2)	26.0 (1.9)	41.5 (1.3)	237.8 (3.9)	713.0 (5.7)
3	19.5 (3.1)	20.3 (1.4)		195.7 (3.0)	617.9 (4.7)
4	16.6 (2.7)	36.7 (2.6)		97.8 (1.4)	130.1 (1.0)
5	11.0 (1.8)	17.7 (1.2)	47.2 (1.5)		128.4 (1.0)
6	16.4 (2.6)	16.3 (1.1)	30.5 (0.9)		181.8 (1.3)
7	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	57.7 (0.8)	
8	0.0 (0.0)	14.7 (1.0)		20.8 (0.3)	121.9 (0.8)
9	0.0 (0.0)	0.0 (0.0)	16.2 (0.5)		199.6 (1.4)
10	0.0 (0.0)	0.0 (0.0)	21.8 (0.7)	61.3 (0.9)	163.7 (1.3)
11	0.0 (0.0)	0.0 (0.0)	12.9 (0.4)	61.0 (0.9)	250.5 (1.9)
12	0.0 (0.0)	0.0 (0.0)	20.4 (0.6)	121.0 (1.9)	262.6 (2.1)
13	0.0 (0.0)	0.0 (0.0)	20.6 (0.6)	127.1 (1.9)	234.0 (2.2)
14	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	32.3 (0.5)	225.6 (1.7)
15	0.0 (0.0)	0.0 (0.0)	31.0 (0.9)	96.3 (1.4)	202.7 (1.7)
16	0.0 (0.0)	0.0 (0.0)	30.4 (0.9)	151.7 (2.4)	167.3 (1.8)
17	0.0 (0.0)	0.0 (0.0)	8.5 (0.3)	143.4 (2.6)	301.9 (2.6)
18	0.0 (0.0)	0.0 (0.0)	36.6 (1.1)	82.8 (1.3)	96.7 (0.9)
19	0.0 (0.0)	0.0 (0.0)	16.5 (0.5)	54.8 (0.8)	288.0 (3.4)
20	0.0 (0.0)	0.0 (0.0)	0.8 (0.0)	11.3 (0.2)	124.7 (1.0)
21	0.0 (0.0)	0.0 (0.0)	1.9 (0.1)	32.7 (0.5)	101.9 (0.8)
22	1.9 (0.2)	5.9 (0.3)	27.9 (0.9)	83.8 (1.1)	275.7 (2.2)
23	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	23.3 (0.3)	93.6 (0.7)
24	0.0 (0.0)	13.1 (0.9)	22.4 (0.7)	85.6 (1.3)	285.9 (2.4)
25	0.0 (0.0)	17.2 (1.2)	55.0 (1.7)	155.5 (2.6)	423.7 (3.7)
26	0.0 (0.0)	15.1 (1.0)	49.8 (1.5)	130.6 (2.0)	389.2 (3.3)
27	0.0 (0.0)	9.4 (0.5)	26.7 (0.7)	109.6 (1.4)	322.5 (3.2)
28	0.0 (0.0)	4.2 (0.3)	12.3 (0.3)	39.6 (0.5)	99.4 (0.7)
29	0.0 (0.0)	14.4 (1.0)	21.4 (0.7)	64.7 (0.9)	219.8 (1.7)
30	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	72.0 (1.0)	268.1 (2.0)
31	0.0 (0.0)	0.0 (0.0)	16.7 (0.5)	41.3 (0.6)	210.1 (1.5)
32	0.0 (0.0)	14.7 (1.0)	25.8 (0.8)	90.8 (1.3)	290.4 (2.2)
33	0.0 (0.0)	0.0 (0.0)	18.9 (0.6)	48.3 (0.7)	218.3 (1.6)
34	0.0 (0.0)	0.0 (0.0)	37.8 (1.1)	65.2 (1.0)	291.6 (2.2)
35	0.0 (0.0)	16.0 (1.0)	30.3 (0.9)	67.5 (1.0)	269.7 (2.3)
36	10.3 (1.2)	14.2 (0.9)	20.6 (0.6)	41.0 (0.6)	172.8 (1.5)
37	0.0 (0.0)	11.2 (0.7)	14.9 (0.4)	39.7 (0.6)	162.7 (1.3)
38	0.0 (0.0)	10.6 (0.7)	17.0 (0.5)	78.8 (1.2)	255.4 (2.2)
39	10.0 (1.3)	18.7 (1.2)	46.3 (1.4)	240.6 (3.8)	526.3 (4.8)
40	0.0 (0.0)	15.9 (1.0)	31.1 (0.9)	171.5 (2.7)	348.5 (2.9)
41	0.0 (0.0)	2.9 (0.1)	7.1 (0.2)	22.3 (0.3)	100.8 (0.7)
42	0.0 (0.0)	5.4 (0.3)	14.7 (0.4)	73.5 (1.0)	262.4 (1.9)
43	11.1 (1.3)	14.7 (0.9)	18.4 (0.5)	48.4 (0.7)	265.7 (2.0)
44	0.0 (0.0)	10.6 (0.7)	15.5 (0.5)	47.0 (0.7)	251.4 (1.9)
45	0.0 (0.0)		14.1 (0.4)	29.7 (0.4)	160.7 (1.2)
46	0.0 (0.0)	10.9 (0.7)	17.0 (0.5)	45.7 (0.7)	229.6 (1.8)
47	0.0 (0.0)	9.9 (0.6)	14.6 (0.4)	35.3 (0.5)	181.2 (1.4)
48	0.0 (0.0)	12.6 (0.8)	22.3 (0.7)	59.7 (0.9)	217.8 (1.7)
49	0.0 (0.0)	2.6 (0.1)	3.4 (0.1)	13.3 (0.2)	35.6 (0.2)
50	15.7 (2.5)	19.7 (1.4)	54.1 (1.7)		455.1 (3.2)
51	27.8 (4.7)	43.9 (3.1)	80.5 (2.5)	390.4 (5.9)	1053.8 (8.8)
52	0.0 (0.0)	12.9 (0.9)	31.9 (1.0)	77.5 (1.1)	321.9 (2.4)
53	0.0 (0.0)	19.3 (1.4)	22.8 (0.7)	134.9 (2.0)	357.3 (2.6)
54	11.6 (1.9)	20.9 (1.5)	50.5 (1.5)	138.7 (2.0)	495.3 (3.5)
55	0.0 (0.0)	11.0 (0.8)		15.0 (0.2)	92.2 (0.6)
56	9.6 (1.5)	15.6 (1.1)	31.5 (1.0)	99.1 (1.4)	333.7 (2.5)
57	16.1 (2.7)	25.8 (1.9)	83.5 (2.8)	235.8 (3.6)	610.6 (4.7)
58	11.4 (1.8)	13.4 (0.9)	17.3 (0.5)	56.7 (0.8)	232.7 (1.6)
59	14.4 (2.3)	27.9 (1.9)	77.0 (2.4)	189.3 (2.8)	417.2 (4.4)
60	0.0 (0.0)	21.9 (1.5)	57.5 (1.8)	147.7 (2.2)	417.2 (3.0)
61	0.0 (0.0)	0.0 (0.0)	14.8 (0.4)	25.2 (0.4)	379.8 (2.7)
62	0.0 (0.0)	26.2 (1.9)	21.4 (0.7)	61.4 (0.9)	533.1 (4.1)
63	19.6 (3.2)	21.9 (1.5)	19.4 (0.6)	30.3 (0.4)	40.6 (0.3)

Table 5. Thermodynamic parameters for the adsorption of TC onto three of the agricultural soils studied.

Soil	**T (K)**	**ΔG^0 (KJ mol^{-1})**	**ΔH^0 (KJ mol^{-1})**	**ΔS^0 (J mol^{-1} K^{-1})**	**R^2**
27	288	-16.74	101.73	409.43	0.949
	298	-19.19			
	308	-24.93			
28	288	-19.28	54.01	254.12	0.996
	298	-21.52			
	308	-24.36			
41	288	-20.42	45.29	228.98	0.969
	298	-23.42			
	308	-25.00			

Figure 1. TC adsorption curves at equilibrium. q_a (µmol kg^{-1}): amount of TC adsorbed by the soil in the equilibrium; C_{eq} (µmol L^{-1}): TC concentration in the solution at equilibrium. In all cases, size of standard errors is lesser than that of symbols.

Figure 2. Main correlations found between K_F parameter and different soil variables for all the studied soils (n = 63). SOC: soil organic carbon; Al_e: exchangeable aluminum; pH_{KCl}: pH in potassium chloride.

Figure 3. Relations between observed Freundlich's K_F (A) and n (B) adsorption parameters, and those predicted using the proposed models. Dashed lines indicate 10% of the total value of the axis.

Figure 4. Relations between the amounts of desorbed TC (q_{des}) expected and observed (A), and between percentage of TC desorption ($\%_{des}$) expected and observed (B), for the initial concentration of 400 µmol L^{-1}. Dashed lines indicate 10% of the total value of the axis.

Figure 5. Relations found between percentage of TC desorption ($\%_{des}$) and the quantity (q_{des}) of desorbed TC and the Freundlich affinity constant (K_F) for the initial concentration of 200 µmol L^{-1} (A and B) and 400 µmol L^{-1} (C and D).