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EXPERIMENTAL DATA AND MODELING FOR THE ADSORPTION/DESORPTION OF TETRACYCLINE AND DICLOFENAC ON THE AGRICULTURAL SOILS

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Abstract

Original scientific paper

The adsorption-desorption characteristics of tetracycline and diclofenac onto two different agricultural soils (S1 and S2) were investigated using the batch equilibrium method. The adsorption experiments were used to optimize the two variable parameters (contact time (5-120 min), initial pollutant concentration (5-300 mg/L)) on the adsorption of tetracycline and diclofenac. The adsorption kinetics for tetracycline and diclofenac onto soil are well described by a bi-exponential adsorption model characterized by fast and slow adsorption rates. Non-linear adsorption curves fitted well to the Langmuir, Freundlich and Temkin equations. The maximum adsorption capacity (q_m) of tetracycline and diclofenac onto the soils S1 and S2 were calculated to be 55.90 mg/g, 41.92 mg/g, 26 mg/g and 6.42 mg/g, respectively. K_d, Koc, foc and q_a values were calculated. The adsorption efficiency of tetracycline and diclofenac by the soils S1 and S2 was over 97%. The K_d parameters for the adsorption of tetracycline and diclofenac onto the soils S1 and S2 were found to be 3537 L/kg, 654 L/kg, 1669 L/kg and 3105 L/kg, respectively. The reversibility of the adsorption process was evaluated by desorption experiments using different concentrations of HDTMA and Triton-x surfactants. The desorption rates were higher for diclofenac than for tetracycline.

Keywords: *Adsorption, desorption, diclofenac, soil, tetracycline.*

TARIM TOPRAKLARINDA TETRASİKLİN VE DİKLOFENAK ADSORPSİYONU/DESORPSİYONU İÇİN DENEYSEL VERILER VE MODELLEME

Özet

Orjinal bilimsel makale

Tetrasiklin ve diklofenakın iki farklı tarım toprağına (S1 ve S2) adsorpsiyon-desorpsiyon özellikleri kesikli denge yöntemi kullanılarak araştırılmıştır. Adsorpsiyon deneyleri, tetrasiklin ve diklofenak adsorpsiyonunda iki değişken parametreyi (temas süresi (5-120 dakika), başlangıç kirletici konsantrasyonu (5-300 mg/L)) optimize etmek için kullanılmıştır. Tetrasiklin ve diklofenak için toprak adsorpsiyon kinetiği, hızlı ve yavaş adsorpsiyon oranları ile karakterize edilen iki üslü bir adsorpsiyon modeli ile tanımlanmıştır. Non-linear adsorpsiyon izoterm eğrileri, Langmuir, Freundlich ve Temkin modellerine iyi uyum sağlamıştır. S1 ve S2 topraklarına tetrasiklin ve diklofenakın maksimum adsorpsiyon kapasitesi (qm) sırasıyla 55.90 mg/g, 41.92 mg/g, 26 mg/g ve 6.42 mg/g olarak hesaplanmıştır. Kd, Koc, foc ve qa değerleri hesaplanmıştır. Tetrasiklin ve diklofenakın S1 ve S2 toprakları tarafından adsorpsiyon etkinliği %97'nin üzerindedir. S1 ve S2 topraklarına tetrasiklin ve diklofenak adsorpsiyonu için Kd parametreleri sırasıyla 3537 L/kg, 654 L/kg, 1669 L/kg ve 3105 L/kg olarak bulunmuştur. Adsorpsiyon işleminin tersinebilirliği, farklı konsantrasyonlarda HDTMA ve Triton-x yüzey aktif maddeler kullanılarak desorpsiyon deneyleriyle değerlendirilmiştir. Desorpsiyon oranları diklofenak için tetrasikline göre daha yüksek bulunmuştur.

Anahtar Kelimeler: *Adsorpsiyon, desorpsiyon, diklofenak, tetrasiklin, toprak.*

1 Introduction

Many pharmaceuticals and healthcare products are significant pollutants released into the environment because of their active usage for human health and veterinary practices [1]. These active compounds are completely or partially discharged to the receiving environment without being treated in wastewater treatment plants. Pharmaceuticals in bodies of water are classified as one of the emerging pollutant of concern groups as they are widely used and cause environmental pollution [2]. The environmental processes of these pharmaceuticals are sorption, decomposition, photodegradation, and hydrolysis [3]. Among them, soil

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adsorption of pharmaceuticals is the primary factor that affects the interaction between pharmaceuticals and soil component. The higher adsorption capacity, the purification process is the more effective. The parameters such as (i) the chemistry of compound, (ii) the amount of relevant matter, (iii) the climate factors such as temperature, and (iv) the type of soil (e.g., pH, soil organic matter (SOM) content, clay content) are essential to evaluate the distribution of a pharmaceutical compound between soil and aqueous phases [4-6]. Diclofenac, one of such pharmaceutical compounds and widely used for rheumatoid arthritis may have harmful effects on various environmental species at ≤1 μg/L concentration. Recently, diclofenac was included in the lists for the environmental monitoring of chemicals published by the European Commission (EU) [7]. Tetracyclines, one of the antibiotics widely used in human and veterinary medicine, are frequently found in surface waters, groundwater and soil [8]. When an antibiotic reaches the soil, it may stay there for a while, diffuse into the surface waters or enter the food chain by accumulating in plant tissues. There are also some studies on the emergence of bacterial resistance to antibiotics [9, 10].

Soil adsorption and desorption of organic chemicals are the main processes that characterize the mobility and transport of pollutants within the soil environment [11]. Since tetracyclines and diclofenacs enter the environment mostly through wastewater, most studies on their environmental fate so far have focused on their behavior during wastewater treatment processes and their interaction with sewage [8, 12, 13, 14]. Few studies have been done on their behavior in soil [7, 15, 16]. To protect surface and ground waters and aquatic organisms from tetracycline and diclofenac pollution, it is obligation to evaluate the sorption/desorption properties of these compounds in the soil environment. In addition, their behavior in the soil is important because sewage sludge is applied as agricultural fertilizer. Soils have great variety. Therefore, it is essential to examine different soil samples with different physicochemical properties to better understand tetracycline and diclofenac behavior and fate in the soil environment in terms of their adsorption/desorption.

Taking all this into account, in this work we used batch type experiments to study tetracycline and diclofenac adsorption and desorption in two agricultural soils with different physical and chemical propetries.

The data obtained from these experiments were used to generate adsorption curves by plotting the adsorbed pollutant (q_a, mg/g) and the pollutant concentration remaining in equilibrium (C_e, mg/g). Different models such as Langmuir, Freundlich and Dubinin-Radushkevich models were used to describe such curves. This study allowed us to evaluate the effect of pollutant exposure time, initial pollutant concentration and exogenous surfactants (HDTMA and TritonX-100) on the adsorption of tetracycline and diclofenac in soil. Morover, the effects of pH and adsorption coefficients (K_d, Koc, foc and q_a) on the adsorption of tetracycline and diclofenac by the soil are discussed in detail.

2 Experimental

2.1 Chemicals

Tetracycline (TC) ($C_{22}H_{24}N_2O_8$) (>95) and diclofenac (DCF) ($C_{14}H_{11}C_{l2}NO_{2)}$ (≥98.5) were provided from Sigma-Aldrich and all chemicals were of high purity and analytical grade. The TC molecule is defined by a high S_w, and low Kow. TC is hydrophilic and amphoteric. The three different dissociation constants are presence as cationic at pH<3.3, zwitter anions at 3.3< pH< 7.7 and negative ions at pH>7.7. TC stock solution was prepared using milliQ water. DCF including one-COOH group and pKa is 4.15 [7]. DCF stock solution was dissolved in a little methanol (CH_30H) and then added milliQ water. The chemical properties of the TC and DCF are showed in Table 1.

Table 1. The chemical properties of the pharmaceutical compounds [7], [17], [18].

Compound Name	Chlortetracycline Oxytetracycline Tetracycline	Diclofenac
Molecular Formula	$C_{22}H_{24}Cl_2N_2O_8$ $C_{22}H_{24}N_2O_9$ $C_{22}H_{24}N_2O_8$	$C_{14}H_{11}C_{l2}NO_2$
Molecular Weight (Da)	444.5-527.6	296.16
Water Solubility at 25 °C (mg/L)	230-52000	2.37
Log K_{ow}	-1.37	4.51
pKa	3.3/7.7/9.3	4.15
Henry law constant ($Pa.m^3/mol$)	$1.7.10^{-26}$- $4.8.10^{-25}$	$4.79.10^{-7}$

2.2 Soil Samples and Characteristics

The samples were collected from soils at a depth of 0-20 cm from agricultural land in two cities (Sivas (S1) and Malatya (S2)) of Turkey. After removing foreign matter, the soil samples were kept in the laboratory at room temperature for drying, passed through a 2 mm sieve, and stored in glass bottles. The soil elemental composition was found through the XRF analysis. The elemental composition of the soils is shown in Table 2.

Table 2. The elemental composition of the Sivas agricultural soil (S1) and Malatya agricultural soil (S2).

Name	S1	S2	Name	S1	S2
	%	%		%	%
Ca	42.76	1.26	Cr	0.05	0.03
Si	8.75	51.32	S	0.04	0.16
Al	3.00	19.07	Na	0.04	0.72
Fe	2.81	10.47	Ni	0.03	0.03
Mg	1.57	2.36	Pb	0.02	0.01
Ti	0.22	0.82	Cl	0.01	0.03
K	0.21	3.98	Zn	0.01	0.03
Sr	0.12	0.02	Zr	-	0.03
Mn	0.08	0.25	Cu	-	0.03
P	0.06	0.56	Rb	-	0.02
Ba	0.05	0.34	Ga	-	0.06

2.3 Adsorption/Desorption Experiments

The batch adsorption experiments were conducted in 250 mL Erlenmeyer and all Erlenmeyer were hold in a incubator shaker (Gerhard) at 180 rpm and after centrifuged (Hettich EBA21) for 15 min. All experiments were performed in duplicated. The Erlenmeyer containing 1 g soil and 100 mL TC or DCF (50 mg/L) solution at pH 4.0 were shaken at different contact time (5-10-15-30-45-60-90-120 min) for adsorption kinetic studies. The isotherm studies were conducted at a constant pH 4.0 and temperature of 25 °C. 1 g soil were added to 250 mL Erlenmeyer and then spiked with 100 mL working solution to produce eight different initial concentrations (5, 10, 25, 50, 100, 150, 200 and 300 mg/L) for TC or DCF in the aqueous solution. Desorption studies were conducted after adsorption. After removing the supernatants, the soil samples for desorption experiments were resuspended in 50 mL of Triton X-100 (nonionic surfactant) ($C_{16}H_{26}O_2$) (0,1-0,5-1M) and Hexadecyltrimethylammonium bromide (HDTMA; cationic surfactant) ($CH_3(CH_2)15N(Br)(CH_3)_3$) solutions (0,1-0,5-1M). The samples were equilibrated for 24 h and then centrifuged for 15 min, and residual TC and DCF in the aqueous solution determined. TC (λ 357 nm) and DCF (λ 285 nm) concentration were determined by UV-Visible spectrophotometer (Spectroquant Pharo 300, Merck).

The amount of pollutant adsorbed by the unit soil was calculated using Eq. (1).

$$q_a = \frac{(C_0 - C_e)V}{m}$$

where, C_o and C_e are initial and final concentration of pollutant in the aqueous phase, m is soil amount, V is the volume of the aqueous solution, respectively.

The pH of the TC and DCF solutions was measured using the WTW (Inolab) pHmeter. The pHmeter was adjusted with solutions of NaOH (Sigma Aldrich) and HCl (Merck, 37%).

3 Results and Discussion

3.1 Adsorption Kinetics

The kinetic models are important because they control the time to equilibrium and the efficiency of the process. It also defines the uptake rate of the pollutant on the adsorbent surface [19]. This study, the kinetic models of TC and DCF on the soils S1 and S2 was investigated. As shown in Fig. 1, both TC and DCF reached adsorption equilibrium by approximately 45 min after application.

To explain the adsorption process of TC and DCF on the soils S1 and S2, bi-exponential model was selected to fit the kinetic data (Eq. (2)). The bi-exponential model is often used to correlate the two-step kinetics of the adsorption. This model describes two different adsorption sites, defined as fast and slow adsorption, both chemically and mathematically [20].

$$q_t = q_a - q_1 \exp(-k_{D1}t) - q_2 exp(-k_{D2}t) \qquad (2)$$

where q_t and q_a are the adsorption capacity at time t and equilibrium, respectively (mg/g); q_1 (mg/g) and k_{D1} (min^{-1}) are two parameters showing the adsorption capacity and the adsorption rate of the rapid step; q_2 (mg/g) and k_{D2} (g/mg.min) are the corresponding parameters of the slow step [19, 20].

According to Figure 1; the model prediction was in good agreement with the experimental data and the parameters are showed in Table 3.

The adsorption capacities (q_t) at time t=0 for TC and DCF were <1.0, indicating that important adsorption occurred at the very short time. The kinetic model suggested a rapid initial transfer of TC and DCF to the soil surface boundary layer followed by a two-step diffusional transport to the interior [20]. In the first 10 min., TC and DCF concentrations in S1 soil were approximately 76-96% of the initial concentration and their concentrations in S2 soil were approximately 50-92% of the initial concentration (Figure 1).

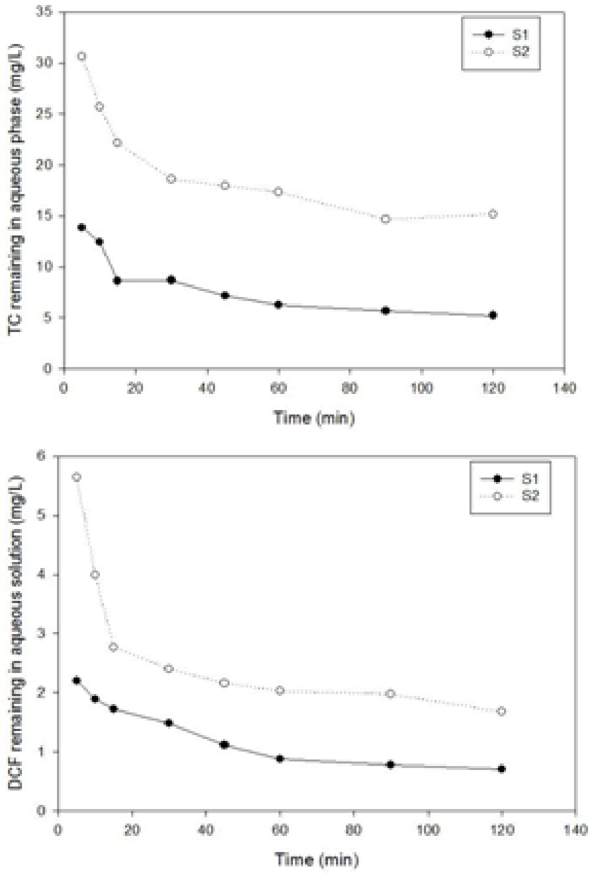

Figure 1. Adsorption behaviors of TC and DCF on the soils S1 and S2 (pH 4, Co=50 mg/L, 10 g/L soil amount, 25 °C).

Table 3. The parameters of a bi-exponential model.

	S1						
	q_a	q_1	**q_2**	k_{D1}	k_{D2}	R_1^2	R_2^2
TC	**4.48**	3.07	**4.53**	0.007	0.111	0.624	0.999
DCF	**49.12**	38.74	**49.26**	0.023	0.549	0.601	0.999
	S2						
	q_a	q_1	**q_2**	k_{D1}	k_{D2}	R_1^2	R_2^2
TC	**3.48**	3.02	**3.64**	0.002	0.054	0.862	0.999
DCF	**47.60**	36.62	**47.84**	0.023	0.189	0.604	0.999

At 120 min., the TC and DCF concentrations on the soils S1 and S2 were approximately 89-99% and 70-97% of the initial concentrations, respectively. The fast adsorption in the first 10 min. can be attributed to the rapid complexation of the soil with organic chemicals [21]. Slow sorption rates (k_{D2}) were found to be higher than fast sorption rates (k_{D1}) for TC and DCF (Table 3). The q_2 values obtained by calculation was close to the actual values, indicating that TC and DCF adsorption in the soils S1 and S2 is not simply a single-step phenomenon, but is affected by several factors, including the physicochemical characteristics of the soils and the nature of the TC and DCF [4]. This is consistent with the previous studies [20, 22].

3.2 Adsorption Isotherms

The data obtained from isotherm experiments are explained by Freundlich (Eq. (3)), Langmuir (Eq. (4)) and Temkin (Eq. (5)) models [23]:

$$q_a = K_F C_e^{1/n} \tag{3}$$

$$q_a = \frac{K_L C_e q_m}{1 + K_L C_e} \tag{4}$$

$$q_a = \frac{RT}{b}\ln(AC_e) \tag{5}$$

where q_a (mg/L) is the amount of adsorbate adsorbed onto the soil at equilibrium; C_e (mg/L) is the concentration of the adsorbate in the solution at equilibrium; K_F (mg/g) is the affinity; n is the index; K_L (L/mg) is a Langmuir constant, and q_m (mg/g) is maximum adsorption capacity. Finally, b (g.kJ/mg.mol) is the Temkin isotherm constant; A (L/mg) is the equilibrium binding constant; T (K) is temperature, and R is the universal gas constant (8.314 J/mol.K). All of the isotherms are nonlinear. In Fig. 2 are given TC and DCF adsorption curves for the soils S1 and S2.

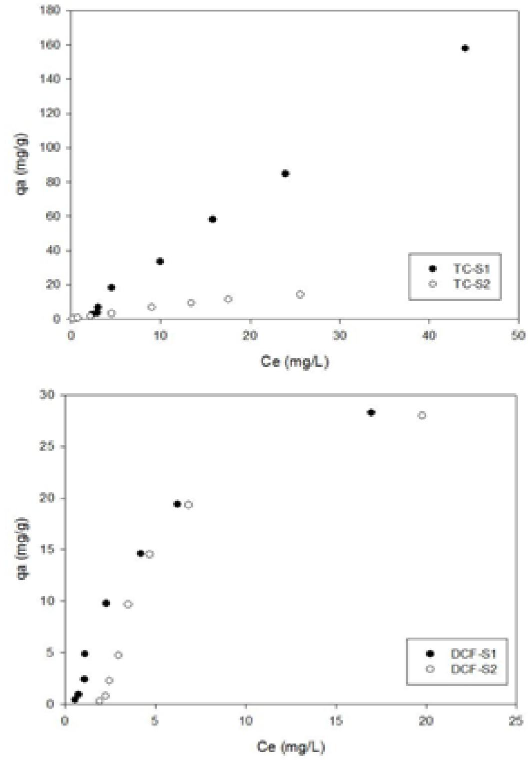

Figure 2. Adsorption curves for TC and DCF in two selected agricultural soil samples (pH 4, 120 min, 10 g/L soil amount, 25 °C).

Firstly, the amount of adsorbed TC and DCF increased with the increase in the initial concentration of adsorbate added. Then it began to reach equilibrium. TC and DCF adsorption curves for the soils S1 and S2 are L-type and S-type, respectively [24]. L-type curves indicate that site availability decreases as the adsorbate concentration increases. According to the results of the literature; L-type curves are often observed. Likewise, mineral and organic cations as well as different soils and sediments adsorb solutes according to L-isotherms [25]. An S-type curve means that the adsorption becomes easier as the adsorbate concentration increases. Literature shows that S-type curves are observed in montmorillonites and sometimes in other clay types. Thus, it can be discussed that S-type curves will be characteristic of the adsorption of organics onto clay surfaces [26]. Weber et al. (1986) have reported that adsorption of fluridone was characterized by an S-type isotherm in soils having a high montmorillonite content and a low SOM content [26]. Langmuir, Freundlich and Temkin isotherms very well described the adsorption mechanism with $0.751 \leq R^2 \leq 0.987$, $0.734 \leq R^2 \leq 0.983$ and $0.724 \leq R^2 \leq 0.993$, respectively (Table 4).

Table 4. Langmuir, Freundlich and Temkin isotherm model parameters.

Model	S1		S2	
	TC	DCF	TC	DCF
Langmuir				
q_m	55.90	44.92	26.00	6.42
K_L	0.005	0.107	0.084	0.042
R^2	0.984	0.987	0.751	0.921
Freundlich				
k_F	2.11	4.92	2.73	2.92
n	0.88	1.56	1.45	1.28
R^2	0.983	0.965	0.734	0.903
Temkin				
A	0.70	1.53	1.31	0.54
b	0.094	0.294	0.525	0,193
R^2	0.813	0.993	0.724	0.981

The n parameter indicates the reactivity and heterogeneity of the active sites of the adsorbents. When n=1 the adsorption is linear, while when n>1 the adsorption process is chemical in nature, and when n<1 there are heterogeneous sites of high adsorption energy with adsorption being predominantly physical and the high energy sites are the first to be occupied [4]. The value of n was highest at DCF-S1 with a value of 1.56 and lowest at TC-S1 with a value of 0.88. A larger k_F meant that the adsorbate was easier to adsorb in the soil [27]. The k_F values of TC and DCF ranged from 2.11 (TC-S1) to 4.92 (DCF-S1). According to Vijayaraghavan et al., (2006), the highest adsorption capacity and affinity between adsorbent and adsorbate are associated to the highest K_F values and to the lowest n values. In general, soils with high organic material have more functional groups than soils with low organic material [28]. The differences in k_F values are thought to be related to these edaphic parameters [29]. Therefore, it indicates a higher adsorption capacity and higher affinity for soils with high organic matter content [4].

The q_m values (mg/g) obtained from Langmuir model for the adsorption of TC and DCF on the soils S1 and S2 were 55.90, 26.00, 44.92 and 6.42, respectively. K_L for TC and DCF varied between 0.0050 and 0.1071

L/mg. The comparison of TC and DCF adsorption capacities of soils and other adsorbent materials used in the studies is given in Table 5. The organic matter and mineral component of the soil is important in adsorption by the soil.

Table 5. The adsorption capacity values obtained in this study as well as in other studies for TC and DCF adsorption in soils and other adsorbent materials.

	Adsorbent	q_m (mg/g)	References
TC studies	Soil	0.26-0.42	[30]
	Soil	3.79	[30]
	Soil	0.39	[31]
	Smectit	173-462	[32]
	S1 soil	55.90	Present study
	S2 soil	26.00	Present study
DCF studies	Activated biochar	392.94	[33]
	Montmorillonit	497	[34]
	Bentonite	62.50	[35]
	Granulated active charcoal	200	[36]
	S1 soil	44.92	Present study
	S2 soil	6.42	Present study

The results were also fitted by the Temkin model, which proposed a decrease in the heat of adsorption due to soil-adsorbate interactions. As a result, adsorption of TC and DCF could be described by a uniform distribution of binding energies [37].

According to Langmuir and Freundlich isotherm parameters; it was determined that TC adsorption to soils was higher than that of DCF in terms of amount and affinity. Other authors also reported strong interactions between TC and soil colloids with high adsorption capacities [38-40].

3.3 Roles of pH and adsorption coefficients for adsorption of TC and DCF

In this study, the adsorption process was performed at a pH 4.0 for TC and DCF. At pH 4.0, TC the species is in zwitter anions form. In addition, the pHpzc for the soils S1 and S2 were found to be 5.57 and 3.37, respectively. In this case, the S1 soil has been positively charged while the S2 soil was negatively charged at experimental pH 4.0. More adsorption has been occurred for TC than DCF (q_mTC>q_mDCF). The reason for this, for the soil S1 due to the attraction taking place between TC zwitter anionic species and the surfaces of the different soil, which present a dominance of positive charges at pH 4.0. In addition, the cation exchange mechanism is dominant in the soil S2 for the TC at pH 4.0. According to the literature; It is stated that Ca, Al and Fe form complexes with pharmaceutical compounds and play an important role in the adsorption capacity of soils [41, 42]. In this study; the soils S1 and S2 contained Si 8%, 51%; Ca 42%, 1%; Al 3%, 51% and Fe 2.8%, 19% (exchangeable matter), respectively (Table 2). In addition, an important mechanism in TC and DCF adsorption is cation exchange [43]. The results show that especially soil S1 has a high adsorption capacity for TC and DCF and a rapid adsorption takes place.

K_d or Koc parameters are used to measure the mobility of a substance in the soil. The K_d parameter is an important indicator for comparing the adsorption capacity of an adsorbent, indicating the distribution ratio of pharmaceuticals between the soil phase and solution. Koc is defined as the organic carbon-water partition coefficient. Koc is a very important parameter used to predict the environmental fate and environmental hazard level of a chemical. If a chemical has a very high Koc value (2000 ≤ Koc ≥ 5000), it means that this chemical will be strongly adsorbed to the soil and SOM and will not move in the soil. A very low Koc value (500 ≤ Koc ≥ 2000) means that the chemical will be highly mobile in the soil [4]. The Koc value of a chemical can be calculated from Kow using the equation (6) [44]. TC and DCF compounds are neutral compounds with the log Kow of -1.37 and 4.51:

$$\log K_{OC} = 0.52 * \log K_{OW} + 1.02 \tag{6}$$

In a certain soil organic carbon content (foc), the Koc and single-point soil adsorption coefficient (K_d) values at a specific C_e were calculated as follows [7]:

$$K_d = \frac{q_a}{Ce} \tag{7}$$

$$K_{OC} = \frac{K_d}{foc} \tag{8}$$

K_d, Koc, foc, and q_a values are given in Table 6. According to Table 6, the Koc value of DCF is considerably higher compared to TC. This indicates that DCF is immobile and is tightly bound to the soil. Thus, the use of DCF is to a certain extent less likely to cause groundwater contamination. The q_a values obtained under optimum conditions also confirm this situation. Accordingly, due to low q_a, K_d, and Koc values, it can be thought that TC in agricultural soils will be more mobile than DCF and will be more prone to transporting to underground waters and rivers. Moreover, even in the studies on the adsorption coefficient of DCF in sandy sediments, it has been proven that adsorption takes place, and therefore DCF is less mobile in groundwater [45]. Additionally, due to its solubility lower than 2.37 mg/L in water, most of the DCF is expected to adhere to soil particles. This reveals that DCF can create a source of pollution long after the time of its application to the soil.

Table 6. K_d, Koc, foc, and q_a values.

	TC-S1	TC-S2	DCF-S1	DCF-S2
K_d (L/kg)	3537	654	1669	3105
K_{OC}	2.03		2318	
f_{OC}	1742	322	0.72	1.34
q_a (mg/g)	16.02	12.84	203.77	144.90

3.4 Desorption of TC and DCF

Surfactants can provide mass transfer of organic compounds from the solid phase to the aqueous phase and they can improve desorption of pollutant from contaminated soils [46]. Generally, cationic and nonionic surfactants are adsorbed to soils by ion exchange reactions and hydrogen bond interactions, respectively

[47]. Fig. 3 shows the desorption results of TC and DCF in the soils S1 and S2. According to Fig. 3, desorption rates were higher for DCF than for TC. The desorption process followed immediately after TC adsorption by HDTMA solution for the soils S1 and S2 demonstrated high release values (between 96%-99%). In the DCF desorption process, a large amount of DCF (97%-99%) was released into the solution by both Triton X-100 and HDTMA solutions. The increased rate of desorption with increasing surfactant concentration may be related to competition [46].

3 Conclusion

TC adsorption was found to be much higher than DCF adsorption in the two soils studied. Experimental data of adsorption kinetics on soil for TC and DCF are well explained with a bi-exponential adsorption model. The adsorption process was characterized by fast and slow adsorption rates. The soil minerals (Si, Ca, Al and Fe) were showed significant cation exchange with the TC and DCF. Considering the Langmuir and Freundlich isotherms, TC adsorption to soils was found to be higher in amount and affinity than that of DCF. The K_d, K_{OC}, f_{OC}, and q_a values of TC and DCF affect the mobility of these compounds in the soil (bioavailability, infiltration and transfer to diverse environment and foods, etc.). Desorption rates were very high for DCF than for TC. The adsorption efficiency and desorption rate of TC and DCF by the soils S1 and S2 was over 96%. According to the data obtained; it showed that a high mobility in soil can be expected for TC compounds and soil adsorption is affected by the physicochemical properties of the soil and the different hydrophobic degrees of the pollutants.

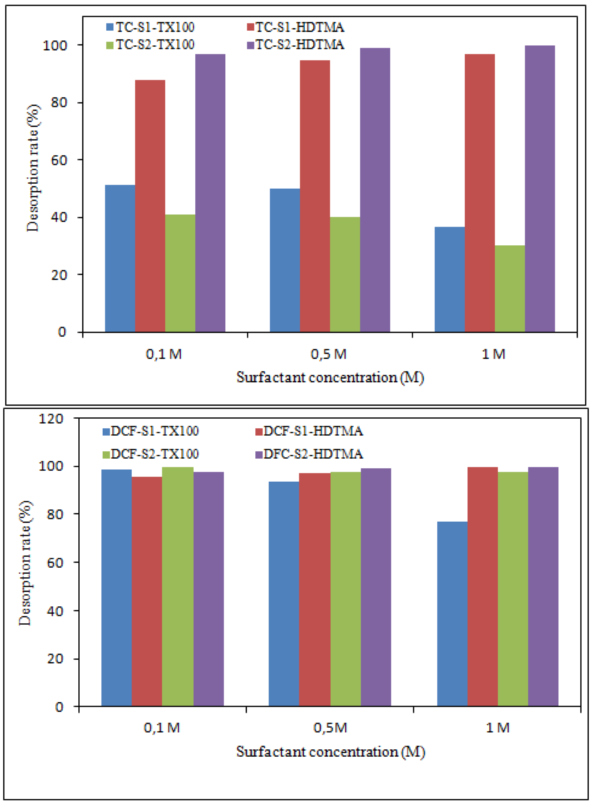

Figure 3. Desorption of TC and DCF from soils S1 and S2 in the presence of surfactants at 24 h contact time.

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Declaration

This study does not require ethics committee permission or any special permission.

References

[1] Mejías, C., Martín, J., Santos, J. L., Aparicio, I., & Alonso, E. (2021). Occurrence of pharmaceuticals and their metabolites in sewage sludge and soil: A review on their distribution and environmental risk assessment. *Trends Environ. Anal. Chem.*, 30, e00125.

[2] Peiris, C., Gunatilake, S. R., Mlsna, T. E., Mohan, D., & Vithanage, M. 2017. Biochar based removal of antibiotic sulfonamides and tetracyclines in aquatic environments: a critical review. *Bioresour. Technol*., 246, 150-159.

[3] Kümmerer, K. (2009). The presence of pharmaceuticals in the environment due to human use-present knowledge and future challenges. *J. Environ. Manage.*, 90, 2354-2366.

[4] Bian, C., Wang, L., Cui, Z., Dong, Z., Shi, X., Li, Y., & Li, B. (2022). Adsorption-desorption and transport behavior of pydiflumetofen in eight different types of soil. *Ecotoxicol. Environ. Saf.*, 234, 113378.

[5] Durak, S. G. (2020). Removal of maxilon golden yellow GL EC 400% from the wastewater by adsorption method using different clays. *Sakarya University Journal of Science*, 24, 5, 1081-1093.

[6] OECD. (2000). Adsorption-desorption using a batch equilibrium method. OECD Guideline for the Testing of Chemicals 106. *Organization for Economic Cooperation and Development*, Paris, France.

[7] Yu, C., Bi, E. (2019). Adsorption site-dependent transport of diclofenac in water saturated minerals and reference soils. *Chemosphere*, 236, 124256.

[8] Shirani, Z., Song, H., & Bhatnagar, A. (2020). Efficient removal of diclofenac and cephalexin from aqueous solution using *Anthriscus sylvestris*-derived activated biochar. *Sci. Total. Environ.*, 745, 140789.

[9] Huijbers, P. M. C., Flach, C. F., & Larsson, D. G. J. (2019). A conceptual framework for the environmental surveillance of antibiotics and antibiotic resistance. *Environ. Int.*, 130, 104880.

[10] Sun, H., Shi, X., Mao, J., & Zhu, D. (2010). Tetracycline sorption to coal and soil humic acids: an examination of humic structural heterogeneity. *Environ. Toxicol. Chem.*, 29, 1934-1942.

[11] Li, Y., Su, P., Li, Y., Wen, K., Bi, G., & Cox, M. (2018). Adsorption-desorption and degradation of insecticides clothianidin and thiamethoxam in agricultural soils. *Chemosphere*, 207, 708-714.

[12] Türk, H., Hanay, Ö. (2017). Nano boyutlu sıfır değerlikli demir ile sulu ortamlarda klortetrasiklin giderim mekanizmasının incelenmesi. *Sakarya University Journal of Science*, 21(5), 1000-1007.

[13] Oral, O., Kantar, C. (2019). Diclofenac removal by pyrite-Fenton process: Performance in batch and fixed-bed continuous flow systems. *Sci. Total Environ.*, 664, 817-823.

[14] Vitiello, G., Iervolino, G., Imparato, C., Rea, I., Borbone, F., De Stefano, L., Aronne, A., & Vaiano, V. (2021). F-doped ZnO nano- and meso-crystals with enhanced photocatalytic activity in diclofenac degradation. *Sci. Total Environ.*, 762, 143066.

[15] Doretto, K. M., Peruchi, L. M., & Rath, S. (2014). Sorption and desorption of sulfadimethoxine, sulfaquinoxaline and sulfamethazine antimicrobials in Brazilian soils. *Sci. Total Environ.*, 476-477, 406-414.

[16] Álvarez-Esmorís, C., Conde-Cid, M., Ferreira-Coelho, G., Fernández-Sanjurjo, M. J., Núñez-Delgado, A., Álvarez-Rodríguez, E., & Arias-Estévez, M. (2020). Adsorption/desorption of sulfamethoxypyridazine and enrofloxacin in agricultural soils. *Sci. Total Environ*., 706, 136015.

[17] Skrásková, K., Santos, L. H. M. L. M., Satínsky, D., Pena, A., Conceiçao, M., Montenegro, B. S. M., Solich, P., & Nováková, L. (2013). Fast and sensitive UHPLC methods with fluorescence and tandem mass spectrometry detection for the determination of tetracycline antibiotics in surface waters. *J. Chromatogr. B.*, 927, 201-208.

[18] Drugbank. Retrieved March 29, 2022 from https://go.drugbank.com/drugs/DB00586.

[19] Silah, H., Gül, Ü. D. (2018). Adsorption of everzol black by using Amberlyst A21: isotherm and kinetic studies. *Sakarya University Journal of Science*, 22(3), 1063-1070.

[20] Zhang, Q., Deng, S., Yu, G., & Huang, J. (2011). Removal of perfluorooctane sulfonate from aqueous solution by crosslinked chitosan beads: Sorption kinetics and uptake mechanism. *Bioresour. Technol.*, 102, 2265-2271.

[21] Torrent, L., Marguí, E., Queralt, I., Hidalgo M., & Iglesias M. (2019). Interaction of silver nanoparticles with mediterranean agricultural soils: Lab-controlled adsorption and desorption studies. *J. Environ. Sci*., 83, 205-216.

[22] Li, F., Fang, X., Zhou, Z., Liao, X., Zou, J., Yuan, B., & Sun, W. (2019). Adsorption of perfluorinated acids onto soils: kinetics, isotherms, and influences of soil properties. *Sci. Total Environ*., 649, 504-514.

[23] Muendo, B.M., Shikuku, V.O., Getenga, Z.M., Lalah, J.O., Wandiga, S.O., & Rothballer, M. (2021). Adsorption-desorption and leaching behavior of diuron on selected Kenyan agricultural soils. *Heliyon*, 7, e06073.

[24] Giles, C.H., Smith, D., & Huitson, A. (1974). A general treatment and classification of the solute adsorption isotherm I. Theoretical. *J. Colloid Interface Sci*., 47, 755-765.

[25] Calvet, R. (1989). Adsorption of organic chemicals in soils. *Environ Health Perspect*., 83, 145-177.

[26] Weber, J.B., Shea, P.H., & Weed, S.B. (1986) Fluridone retention and release in soils. *Soil Sci. Soc. Am. J.*, 50, 582-588.

[27] An, B., Xu, X., Ma, W., Huo, M., Wang, H., Liu, Z., Cheng, G., & Huang, L. (2021). The adsorption-desorption characteristics and degradation kinetics of ceftiofur in different agricultural soils. *Ecotoxicol. Environ. Saf.*, 222, 112503.

[28] Zhou W., Zhang, Y., Li, W., Jia, H., Huang, H., & Li, B. (2019). Adsorption isotherms, degradation kinetics, and leaching behaviors of cyanogen and hydrogen cyanide in eight texturally different agricultural soils from China. *Ecotoxicol. Environ. Saf.*, 185, 109704.

[29] Conde-Cid, M., Ferreira-Coelho, G., Núñez-Delgado, A., Fernández-Calviño, D., Arias-Estévez, M., Álvarez-Rodríguez, E., & Fernández-Sanjurjo, M.J. (2019). Competitive adsorption of tetracycline, oxytetracycline and chlortetracycline on soils with different pH value and organic matter content. *Environmental Research*, 178, 108669.

[30] Conde-Cid, M., Fernandez-Calvino, D., Novoa-Munoz, J.C., Nunez-Delgado, A., Fernandez-Sanjurjo, M.J., Arias-Estevez, M., & Alvarez-Rodriguez, E. (2019). Experimental data and model prediction of tetracycline adsorption and desorption in agricultural soils. *Environmental Research*, 177, 108607.

[31] Zhang, D., Yang, S., Wang, Y., Yang, C., Chen, Y., Wang, R., Wang, Z., Yuan, X., & Wang, W. (2019). Adsorption characteristics of oxytetracycline by different fractions of organic matter in sedimentary soil. *Environmental Science and Pollution Research*, 26, 5668-5679.

[32] Li, Z., Chang, P.H., Jean, J.S., Jiang, W.T., & Wang, C.J. (2010). Interaction between tetracycline and smectite in aqueous solution. *J. Colloid Interface Sci.*, 341, 311-319.

[33] Shirani, Z., Song, H., & Bhatnagar A. (2020). Efficient removal of diclofenac and cephalexin from aqueous solution using Anthriscus sylvestris-derived activated biochar. *Science of the Total Environment*, 745, 140789.

[34] Kaur, M., & Datta, M. (2014). Diclofenac sodium adsorption onto montmorillonite: adsorption equilibrium studies and drug release kinetics. *Adsorption Science & Technology*, 32, 365-387.

[35] Mabrouki, H., & Akretche, D.E. (2016). Diclofenac potassium removal from water by adsorption on natural and pillared clay. Desalin. Water Treat., 57, 6033-6043.

[36] Yehia, A.M., Elbalkiny, H.T., Riad, S.M., & Elsaharty, Y.S. (2019). Monitoring and optimization of diclofenac removal by adsorption technique using in-line potentiometric analyzer. *Microchem. J.*, 148, 521-530.

[37] Khataee, A.R., Vafaei, F., & Jannatkhah, M. (2013). Biosorption of three textile dyes from contaminated water by filamentous green algal *Spirogyra sp*.: kinetic, isotherm and thermodynamic studies. *Int Biodeterior Biodegradation*, 83, 33-40.

[38] Teixido, M., Granados, M., Prat, M.D., & Beltran, J.L. (2012). Sorption of tetracyclines onto natural soils: data analysis and prediction. *Environ. Sci. Pollut. Res*., 19, 3087-3095.

[39] Figueroa, R.A., Leonard, A., & Mackay, A.A. (2004). Modeling tetracycline antibiotic sorption to clays. *Environ. Sci. Technol*., 38, 476-483.

[40] 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.

[41] Conkle, J.L., Lattao, C., White, J.R., & Cook, R.L. (2010). Competitive sorption and desorption behavior for three fluoroquinolone antibiotics in a wastewater treatment wetland soil. *Chemosphere*, 80, 1353-1359.

[42] Zhang, J.O., Dong, Y.H. (2008). Effect of low-molecular-weight organic acids on the adsorption of norfloxacin in typical variable charge soils of China. *J. Hazard. Mater*., 151, 833-839.

[43] Lee, L.S., Carmosini, N., Sassman, S.A.,. Dion, H.M., & Sepulveda, M.S. (2007). Agricultural contributions of antimicrobials and hormones on soil and water quality. *Adv. Agron*., 93, 1-68.

[44] Martinez-Hernandez, V., Meffe, R., Herrera, S., Arranz, E. & de Bustamante, I. (2014). Sorption/desorption tical and personal care products from reclaimed water onto/from a natural sediment. *Sci. Total Environ*., 472, 273-281.

[45] Scheytt, T., Mersmann, P., Lındstadt, R., & Heberer, T. (2005). 1-octanol/water partition coefficients of 5 pharmaceuticals from human medical care: carbamazepine, clofibric acid, diclofenac, ibuprofen, and propyphenazone. *Water Air and Soil Pollution*, 165(1):3-11.

[46] Oleszczuk, P., Xin, B. (2011). Influence of anionic, cationic and nonionic surfactants on adsorption and desorption of oxytetracycline by ultrasonically treated and non-treated multiwalled carbon nanotubes. *Chemosphere*, 8, 1312-1317.

[47] Jin, H., Zhou, W., & Zhu, L. (2013). Utilizing surfactants to control the sorption, desorption, and biodegradation of phenanthrene in soil-water system. *Journal of Environmental Sciences*, 25(7), 1355-1361.