

## ORIGINAL RESEARCH

## Remediation and Treatment

# Evaluation of factors affecting tetracycline and diclofenac adsorption by agricultural soils using response surface methodology

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## Abstract

The adsorption process of the pharmaceutical pollutant in the soil is affected by its physicochemical properties and soil properties. In this study, the factors affecting the adsorption of tetracycline and diclofenac onto two different soils (S and M) were investigated using response surface methodology (RSM). The RSM design was used to optimize the five variable factors (pH (2–10), contact time (5–180 min), soil amount (1–10 g/L), temperature (25–45°C)) on the adsorption of tetracycline and diclofenac. The predicted optimal conditions obtained by RSM showed that pH was the most important variable affecting the adsorption of tetracycline and diclofenac. The optimum pH for the adsorption of tetracycline and diclofenac onto the soil samples S and M were found to be 4 and 2, respectively. The adsorbed amounts of tetracycline and diclofenac onto the soils S and M were calculated to be 14.82 mg/g, 12.43 mg/g, 189.40 mg/g, and 144.81 mg/g, respectively. In addition, the effects of soil organic matter, salt, and divalent cations on the adsorption of tetracycline and diclofenac onto soils were studied. The removal of soil organic matter slightly increased tetracycline adsorption, while inhibiting diclofenac adsorption. The presence of salt and divalent cations prominently suppressed the adsorption of tetracycline and diclofenac onto soils. A possible complex mechanism was proposed for TC and DCF adsorption, including ion exchange, electrostatic interaction, and some chemical bonds.

## KEYWORDS

adsorption, diclofenac, RSM, soil, tetracycline

## 1 | INTRODUCTION

Pharmaceutical pollutants are released into the environment through various means, including direct disposal of drugs, pharmaceutical production facilities, hospitals, veterinary drug uses, sewage systems, wastewater treatment plants, and wastewater reuse.<sup>1,2</sup> Tetracycline antibiotics (TCs) and diclofenac (DCF), known as a non-steroidal anti-inflammatory drug, are typical drugs widely used in the treatment of human diseases and in the livestock. These two types of compounds cannot be fully metabolized; most of them

enter the environment by means of feces. They can also reach agricultural lands through treatment plant sludge or organic fertilizer application, irrigation with treated wastewater, seepage, and infiltration.<sup>3</sup> TCs may cause direct or indirect toxic effects on microorganisms in the soil, animals, and plants and may trigger the emergence of resistant bacteria.<sup>4</sup> DCF is more likely to persist in the aquatic environment due to its hydrophilicity and stability. If aquatic species are subjected to prolonged exposure of DCF at various trophic levels of the food web, this can create an increased ecological risk at all trophic levels.<sup>5</sup>

It has been reported that such compounds accumulate in soils due to the continuous inflow of pollutants and the sorption properties of the soil.<sup>6</sup> For example tetracyclines have been found in soil samples of the Chinese province of Shandong (0.5–2.5 µg/kg), in the agricultural fields of Spain (<600 µg/kg) and on the surface soils of Singapore (<80.6 µg/kg), and on the surface water (up to 1.3 mg/L) and ground-water (up to 0.75 mg/L) of the Beiyun River in Beijing, China; diclofenac, on the other hand, has been detected in the potential agricultural areas in Ontario, Canada.<sup>7–11</sup>

The adsorption process plays a major role in the transport, bioaccumulation, and degradation of their pollutants and ultimately their fate in the environment.<sup>8–10,12</sup> Therefore, understanding the adsorption mechanism of TC and DCF in the soil is significant for determining its ecotoxicity, migration, and conversion. Many studies have focused on the removal of TC and DCF from waters by low-cost and effective adsorbent materials, such as Fe<sub>3</sub>O<sub>4</sub>/clinoptilolite nanocomposite,<sup>13</sup> chitosan,<sup>14</sup> algae,<sup>15</sup> Fe<sub>2</sub>O<sub>3</sub>-scallop shell nanocomposite,<sup>16</sup> goethite,<sup>17</sup> pine bark biochar<sup>18</sup> and biowaste compounds.<sup>19</sup> However, studies of TC adsorption by soils are few and limited in content. To our knowledge, soil adsorption of DCF has not been studied in the literature.<sup>20–23</sup> Thus, studying adsorption of TC and DCF from aqueous solution onto soils is crucial for removing pharmaceutical contamination.

The adsorption process in the soil is affected by the physico-chemical properties of pharmaceuticals (e.g., molecular structure, solubility, and hydrophobicity) and soil properties (e.g., soil composition, surface structure, charge properties), especially pH and the content of components that can hold these pollutants (organic matter, clay, non-crystalline minerals).<sup>22,24</sup> The soil adsorption, which is affected by the temperature and pH, significantly affects the concentration of organic pollutants. In addition, as the pollutant is increasingly retained in soil over time, contact time affects the exposure of living organisms and the toxicology of the pollutant.<sup>25</sup>

In light of the literature reviewed above, this study aims to investigate the soil environmental parameters (pH, contact time, soil amount, temperature, initial pollutant concentration) and potential interaction mechanisms affecting TC and DCF adsorption in two agricultural soils. To understand this situation better, the interactions between the independent variables (soil environmental parameters) and the adsorption mechanism were discussed. The response surface methodology approach was used to analyze the relative importance and interacting effects of the soil environmental parameters affecting the adsorption of TC and DCF onto the soil, and the analysis of variance (ANOVA) was performed. Soil organic matter, salt, and cations are important factors in the adsorption of pharmaceuticals by soils. Therefore, in addition to these analyses, the effects of soil organic matter, salt (NaCl) and divalent cations (Mg<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) on the soil behavior and mechanism of adsorbing TC and DCF were investigated. As a result, this comprehensive study on the modeling and optimization of adsorption of TC and DCF by soil will contribute to the literature in terms of understanding and evaluating soil adsorption systems.

## 2 | MATERIAL AND METHODS

### 2.1 | Chemicals and materials

Tetracycline hydrochloride (TC) and Diclofenac sodium salt (DCF) were purchased from Sigma-Aldrich and all chemicals were of high purity and analytical grade. TC stock solution was prepared by dissolving solid into ultrapure water. DCF stock solution was prepared by dissolving solid into a little methanol followed by the addition of ultrapure water. The pharmacological and physico-properties of TC and DCF are listed in Table S1 (in Data S1).

Top soil samples were collected from agricultural lands in Sivas (soil S) and Malatya (soil M), Turkey at a depth of 0–20 cm. These samples were air dried in a laboratory, passed through a 2 mm sieve, homogenized, and stored in bottles until being analyzed.

### 2.2 | Soil characterization

The elemental composition of the soils was determined using XRF (X-ray fluorescence). The point of zero charge (pHpzc) of soils was obtained as follows: (i) the soil previously suspended in 0.1 mol L<sup>-1</sup> KCl solution was adjusted to pH 1 to 12 with NaOH or HCl solution and was kept at room temperature for 24 h. (ii) The final pH, which was the same as the initial pH, was called as pHpzc.

### 2.3 | Adsorption conditions

The experiments were conducted in 250 ml Erlenmeyer flasks and all flasks were kept in an orbital shaker at a speed of 180 rpm and subsequently centrifuged at 4000 rpm for 15 min. The final concentrations of TC and DCF were determined by utilizing a UV-Visible spectrophotometer (Spectroquant Pharo 300, Merck) at the wavelength of λ<sub>max</sub> 357 nm and λ<sub>max</sub> 285 nm, respectively. Limit of detection (LOD) values of TC and DCF are calculated to be 0.29 mg/L and 0.07 mg/L, respectively (LOD = 3.3 SD/a where, SD is the standard deviation of the intercept and a is average slope). In the experimental studies, pH (2–10), contact time (5–180 min), soil amount (1–10 g/L), temperature (25–45°C), and initial pollutant concentration (5–300 mg/L) were varied. Experiments were designed in various combinations to examine the synergistically interacting factors affecting the adsorption of TC and DCF by soil. The adsorption of TC and DCF by the flask was tested before all experiments and the results showed that their influence was negligible. The blank experiment was performed with the TC and DCF solutions without sorbent. All sample run procedures and conditions were the same to ensure the same experimental conditions. The adsorbed amount of TC or DCF by the soils S and M (q<sub>s</sub>, mg/g) and adsorption rate (%) were calculated according to the Equations (1) and (2), respectively.

$$q_s = \frac{(C_o - C_e)V}{m}, \quad (1)$$

**TABLE 1** Independent variable intervals for the Box–Behnken experimental design

Variables	Symbols		Coded levels (TC)			Coded levels (DCF)		
	Uncoded	Coded	−1	0	1	−1	0	1
Solution pH	$X_1$	$x_1$	2	6	10	2	6	10
Soil amount (g/L)	$X_2$	$x_2$	1	5.5	10	1	5.5	10
Temperature (°C)	$X_3$	$x_3$	25	35	45	25	35	45
Time (min)	$X_4$	$x_4$	5	92.5	180	5	92.5	180
Initial pollution concentration (mg/L)	$X_5$	$x_5$	5	152.5	300	5	152.5	300

$$\text{Adsorption rate (\%)} = \frac{(C_o - C_e)}{C_o} \times 100, \quad (2)$$

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

The effects of soil organic matter, salt (NaCl) and divalent cations ( $Mg^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ ) on the adsorption of TC and DCF by soil were studied under the predicted optimal conditions based on RSM. All experiments were performed in duplicated.

## 2.4 | Statistical experimental design

To investigate the effect of the complex soil environment on the adsorption of TC and DCF, a subset of RSM known as the Box–Behnken design was applied for the five input variables (pH, contact time, soil amount, temperature, and initial pollutant concentration). The experimental conditions in terms of pH (2–10), contact time (5–180 min), soil amount (1–10 g/L), environmental temperature (25–45°C), and initial pollutant concentration (5–300 mg/L) for the adsorption of TC and DCF were established by considering the concentrations reported in the literature. The Design Expert 7.0.0 (Trial version Stat Ease Inc. Minneapolis USA) computer program was used for the model fitting, regression analysis, and process optimization. The analysis of variance (ANOVA) was used in order to ensure a good model. Adsorption rate (%) was considered as responses variable. The model proposed 46 experiments for each experimental design. The five independent process variables, namely pH, contact time, soil amount, environmental temperature, and initial pollutant concentration were segregated into three levels with a coded value (−1, 0, +1) (Table 1). The extreme star points −1 (− $\alpha$ ) and +1 (+ $\alpha$ ) were selected for each process variables based on the experimental range.

## 2.5 | Effect of soil organic matter (SOM) on adsorption process

The soil organic matter was removed by the  $H_2O_2$  peroxidation method.<sup>26</sup> Ten grams of soil sample was transferred to a 250 ml

beaker, and 20 ml of  $H_2O_2$  at different concentrations (0.1 M, 0.5 M, and 1 M) was added. The suspension was stirred at room temperature and kept in a 70–80°C water bath to allow the reaction to proceed. The process was repeated until the frothing was completely reduced and no reaction was observed with the addition of more  $H_2O_2$ . Excess  $H_2O_2$  was removed by heating. After the suspension was centrifuged and washed a few times with distilled water, it was dried, crushed, and sieved. These soils were named as  $S_{SOM-0.1}$ ,  $S_{SOM-0.5}$ ,  $S_{SOM-1}$  (SOM free soil S),  $M_{SOM-0.1}$ ,  $M_{SOM-0.5}$ ,  $M_{SOM-1}$  (SOM free soil M) and these were used in the experiments under the predicted optimal conditions based on RSM.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Soil characteristics

The XRF analysis results of the soils S and M are shown in Table S2 (in Data S1). According to Table S2, Ca dominates the soil S while Si dominates the soil M. These analysis results indicated that quartz for soil M and calcite for soil S as predominant phases.<sup>25</sup> Ca is the dominant cation in the exchange mechanism. The percentages of Na, K, and Mg in the soil S were 0.0349, 0.2053, and 1.5709 while those values in the soil M were 0.7201, 3.9787, and 2.3601, respectively. The percentages of Fe oxides and Al in the soils S and M were 2.8137, 3.0004, 10.4724, and 19.0701, respectively. The percentage of P in the soils S and M were 0.0613 and 0.5514, respectively. P percentage is related to persistent organic and inorganic fertilizations in agricultural lands.<sup>23</sup> The pH values of the studied soils in water were found to be  $pH_{\text{soil S}}$  6.27 and  $pH_{\text{soil M}}$  3.87, respectively. In addition, the  $pH_{\text{pzc}}$  values were determined as 5.57 for the soil S and 3.37 for the soil M. The fact that the  $pH_{\text{pzc}}$  value was lower than  $pH_{\text{soil}}$  indicates that negative charges were dominant in these soils.<sup>23</sup>

### 3.2 | Optimization and statistical analysis (ANOVA) using RSM

Tables S3 and S4 have been given the observed values of the adsorption rate (%) of TC and DCF by the soils S and M and the adsorption rate (%) predicted by the model (in Data S1). The predicted model data

were quite close to the observed values, and there is a good correlation between observed results and predicted values. The  $R^2$  values for the TC-soil S, TC-soil M, DCF-soil S and DCF-soil M studies were 0.9250, 0.9661, 0.9275, and 0.9906, respectively. The closer the value of  $R^2$  was to 1, the better the correlation between predicted and observed values. Linear equations related to the parameters affecting the adsorption of TC and DCF by the soils S and M were obtained using RSM and in Equations (3), (4), (5), and (6) are presented, respectively. These equations showed the experimental affinity between the independent variables and the adsorption rate (%).

$$\begin{aligned} \text{TC adsorption rate by the soil S (\%)} = & -102.07313 + 1.56916X_1 \\ & + 4.95X_2 + 4.832X_3 + 0.418X_4 \\ & + 0.317X_5 - 0.0428X_1 - 2.992 \\ & \cdot 10^{-3}X_1X_4 + 3.813 \cdot 10^{-3}X_1X_5 \\ & + 2.944 \cdot 10^{-5}X_2X_5 + 0.1121X_1 \\ & - 0.4468X_2 - 0.0507X_3^2 - 6.31 \\ & \cdot 10^{-4}X_4^2 - 9.546 \cdot 10^{-4}X_5^2, \end{aligned} \quad (3)$$

$$\begin{aligned} \text{TC adsorption rate by the soil M (\%)} = & -1.11905 - 4.782X_1 + 10.5388X_2 - 0.0834X_3 + 0.3129X_4 \\ & + 0.0189X_5 - 0.3736X_1X_2 - 0.102X_1X_3 - 0.0142X_1X_4 - 3.389 \\ & \cdot 10^{-3}X_1X_5 - 0.1714X_2X_3 + 0.0154X_2X_4 + 0.01317X_2X_5 - 3.314 \\ & \cdot 10^{-3}X_3X_4 - 7.355 \cdot 10^{-4}X_3X_5 - 2.072 \cdot 10^{-5}X_4X_5 + 0.978X_1^2 \\ & - 0.169X_2^2 + 0.0312X_3^2 - 6.371X_4^2 - 2.44 \cdot 10^{-5}X_5^2, \end{aligned} \quad (4)$$

$$\begin{aligned} \text{DCF adsorption rate by the soil S (\%)} = & -166.59761 - 42.6797X_1 - 2.9338X_2 - 0.786X_3 - 1.196 \cdot 10^{-3}X_4 \\ & + 0.0526X_5 - 0.0787X_1X_2 + 0.327 \cdot 10^{-3}X_1X_3 - 2.2 \cdot 10^{-3}X_1X_4 \\ & - 0.012X_1X_5 - 0.082X_2X_4 - 0.4468X_2 - 0.0507X_3^2 - 6.31 \\ & \cdot 10^{-4}X_4^2 - 9.546 \cdot 10^{-4}X_5^2 + 2.1X_1^2 + 0.364X_2^2 + 5.85 \cdot 10^{-4}X_3^2 \\ & + 9.08X_4^2 - 5.87X_5^2, \end{aligned} \quad (5)$$

$$\begin{aligned} \text{DCF adsorption rate by the soil M (\%)} = & 68.588 - 31.528X_1 + 3.459X_2 - 2.582X_3 - 0.0472X_4 + 0.2695X_5 \\ & + 0.13083X_1X_2 + 0.0155X_1X_3 + 1 \cdot 10^{-2}X_1X_4 - 0.0127X_1X_5 \\ & - 5.555 \cdot 10^{-3}X_2X_3 - 6.349 \cdot 10^{-4}X_2X_4 - 0.0231X_2X_5 + 2 \\ & \cdot 10^{-3}X_3X_4 - 6.77 \cdot 10^{-4}X_3X_5 + 1.897X_1^2 - 0.04X_2^2 - 0.036X_3^2 \\ & + 4.582 \cdot 10^{-5}X_4^2 - 2.44 \cdot 10^{-5}X_5^2. \end{aligned} \quad (6)$$

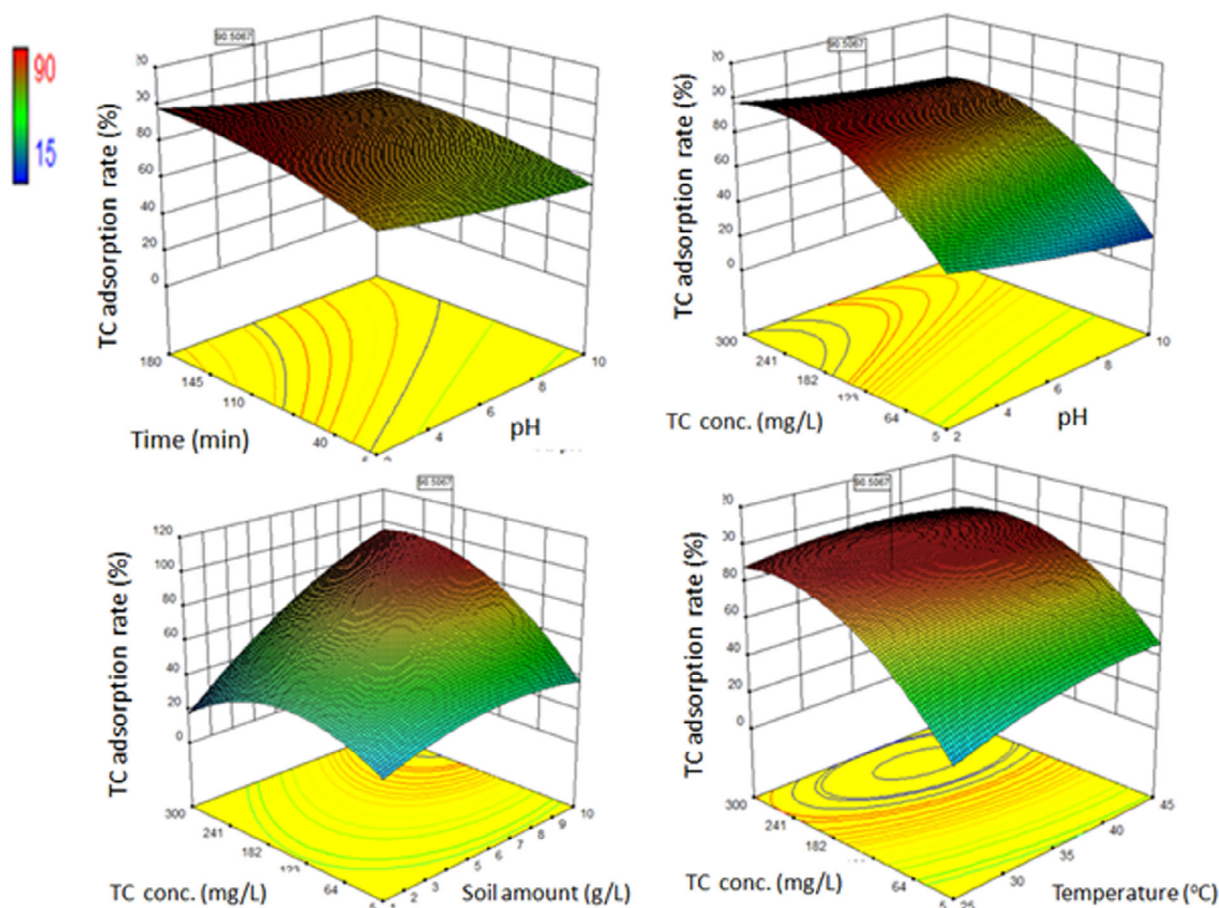
Among the different models proposed, ANOVA was applied to the quadratic equation model due to greater compatibility with the data and the details are given in Table S5 (Data S1). The significance of the regression model was evaluated using the  $F$ -value (Fischer distribution),  $p$ -value (null-hypothesis test) and the sum of the squares (SS). If the  $p$ -values are fewer than 0.05 and the  $F$  values are greater than 4–5, the results obtained from the model are significant.<sup>13</sup> In addition, the sum of squares (SS) values of the variables may be high. This indicates the importance of the variables. The  $F$ -values of the model were 54.3, 3421.6, 54.65, and 5004.6 for the TC-soil S, TC-soil M, DCF-soil S and DCF-soil M. The  $p$ -value of the model for all

studies is 0.0001. These results suggest that the model is acceptable. According to the  $p$ -values listed in Table S5, the expressions, including A (pH), B (soil amount), C (temperature), D (time), E (initial pollution concentration), AB, AC, AD, AE, BC, BD, BE, CD, CE, DE,  $A^2$ ,  $B^2$ ,  $C^2$ ,  $D^2$ , and  $E^2$ , are meaningful. In addition, the values for the adjusted  $R^2_{\text{Adj}}$  and predicted  $R^2_{\text{Pred}}$  also confirm the validity of the model. The  $R^2_{\text{Adj}}$  values for the TC-soil S, TC-soil M, DCF-soil S, and DCF-soil M were 0.865, 0.9390, 0.8619, and 0.9831, respectively, indicating the high significance of the model. The  $R^2_{\text{Pred}}$  values for TC-soil S, TC-soil M, DCF-soil S, and DCF-soil M were 0.8600, 0.8640, 0.7620, and 0.9638. Their close values indicate a good agreement between the predicted and observed values for TC and DCF adsorption. This agreement in other studies has also been reported.<sup>14,27–29</sup> The object of RSM is to detect which experimental parameters generate signals, that is, which are large in comparison to any noise.<sup>30</sup> For “Precision adeq”, the signal/noise ratio should be above 4.<sup>31,32</sup> These rates for TC-soil S, TC-soil M, DCF-soil S, and DCF-soil M studies were found to be 15.877, 29.516, 8.207, and 41.906, respectively. The smaller the standard deviation values in the study, the more compatible is the study with the model. The standard deviation values of the predicted and actual deposition rate for the TC-soil S, TC-soil M, DCF-soil S, and DCF-soil M in the quadratic model were found as 6.95, 3.91, 13.12, and 3.42, respectively. As shown in ANOVA results (Table S5), the mean values of the TC-soil S, TC-soil M, DCF-soil S, and DCF-soil M were respectively found as 57.6, 42.35, 31.66, and 39.00. Relatively higher mean values for the quadratic equations (Equations (3)–(6)) obtained from the model indicate that the linear parameters present in these equations also had significant effects on the experimental results. The difference between the mean values and the optimum values in the whole design shows that the design was affected by the independent variables. Lower coefficient of variation values of CV for the TC-soil S, TC-soil M, DCF-soil S, and DCF-soil M indicated a greater reliability of the experiment.<sup>30</sup> The smaller the PRESS value, the higher the model fit.<sup>33</sup> The PRESS values for TC-soil S, TC-soil M, DCF-soil S, and DCF-soil M studies were found as 4830.38, 1524.93, 16641.95, and 1128.01, respectively.

As a result, the ANOVA test showed that the RSM model was compatible with the quadratic model for the TC-soil S, TC-soil M, DCF-soil S, and DCF-soil M studies. The quadratic model equations obtained by RSM shows that the input parameters affected each other.

### 3.3 | Optimum conditions and validation experiments

According to the proposed model, the optimization was performed based on the maximum adsorption rate (%) of TC and DCF onto the soils S and M. The predicted optimal conditions for the TC-soil S and TC-soil M were pH of 4, soil amount of 10 g/L, TC concentration of 178 mg/L, time of 140 min and temperature of 30°C, which resulted in 90.51% and 71.73% adsorption rate, respectively. The predicted optimal conditions for the DCF-soil S were pH of 2, soil amount of



**FIGURE 1** The 3d graph showing the change in TC adsorption by the soil S with RSM: (a) time-pH; (b) initial TC concentration-pH; (c) initial TC concentration-soil amount; (d) initial TC concentration-temperature

1 g/L, DCF concentration of 287 mg/L, time of 127 min and temperature of 25°C, which resulted in a 72.80% adsorption rate. The predicted optimal conditions for the DCF-soil M were pH of 2, soil amount of 1 g/L, DCF concentration of 152.5 mg/L, time of 92.5 min and temperature of 35°C, which resulted in a 95.92% adsorption rate. Under optimal conditions, adsorbed amounts ( $q_s$ ) of TC and DCF by the soils S and M were 16.02 mg/g, 12.84 mg/g, 203.77 mg/g, and 144.90 mg/g, respectively.

Validation experiments were conducted with the parameters as suggested checking the accuracy of the predicted optimal conditions based on the RSM results. The adsorption rates (%) for the TC and DCF onto the soils S and M were found to be 83.27%, 69.88%, 65.99%, and 94.99%, respectively. The adsorbed amounts ( $q_s$ ) of TC and DCF by the soils S and M were 14.82 mg/g, 12.43 mg/g, 189.40 mg/g, and 144.81 mg/g, respectively.

The experimental values agreed with the values obtained from RSM. The optimized adsorption rates (%) for the TC and DCF onto the soils S and M had a small deviation of 7.24%, 2.92%, 5.74% and 0.93%, respectively from the predicted value.

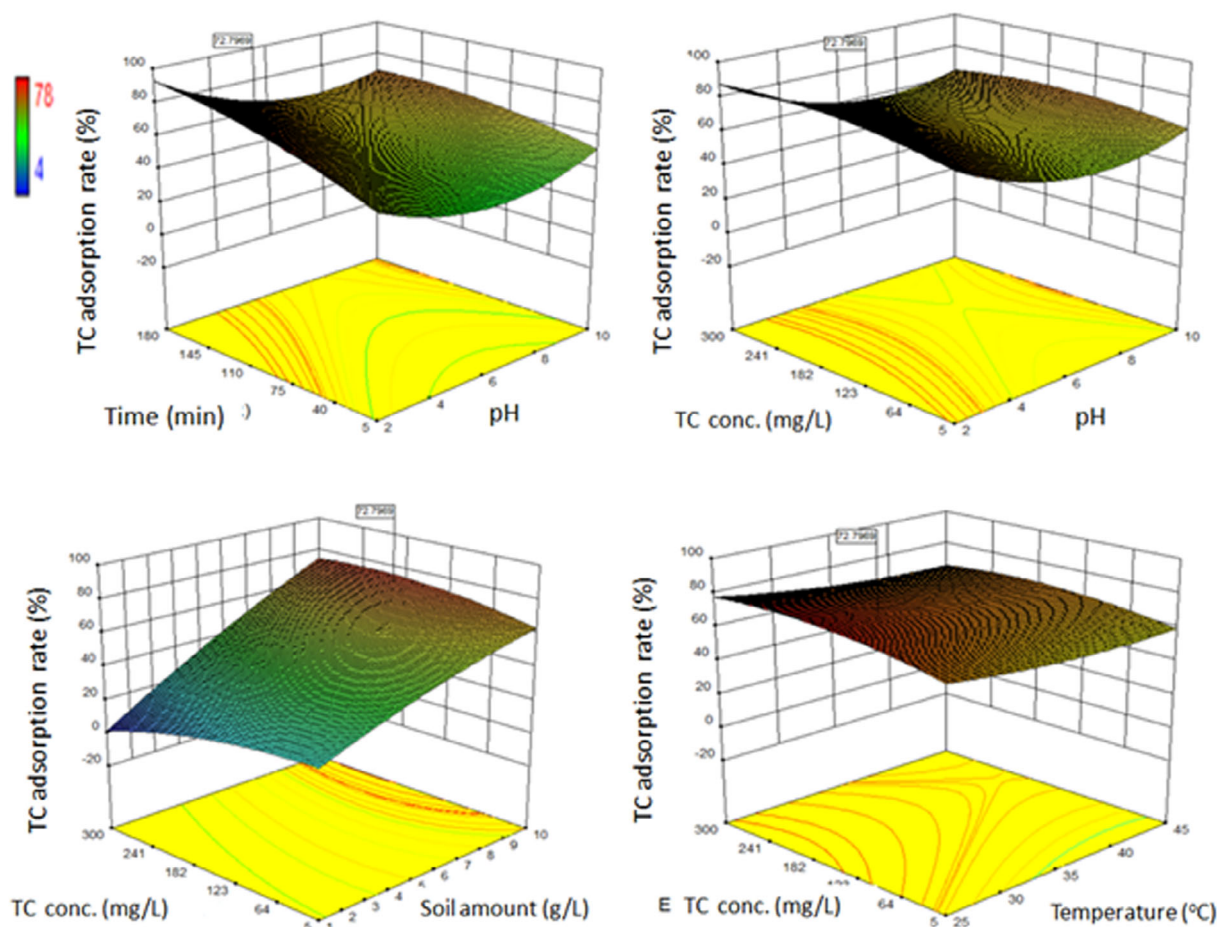
It was observed that the adsorption rates (%) and adsorbed amounts ( $q_s$ ) of TC and DCF were affected by all variables. Similarly, Topal and Arslan,<sup>14</sup> Hiew et al.,<sup>27</sup> Dehghan et al.,<sup>34</sup> and Wu et al.<sup>35</sup>

reported that the process variables had effects on the adsorption process.

### 3.4 | Interactions among independent variables

In this study, the effects of solution pH, soil amount, environmental temperature, contact time and initial pollution concentration on the adsorption of TC and DCF from aqueous solution onto the soils S and M were investigated, which is shown in Figures 1, 2, 3, and 4. The three-dimensional response surfaces plots in Figures 1-4 were generated using Equations (3), (4), (5), and (6).

According to Figures 1a, 2a, 3a, and 4a, the adsorption rates (%) of TC and DCF increased as the solution pH decreased and the contact time increased. All in experiments, with increasing contact time, the adsorption rate increased up to a certain period and then the rate of increase became smoother due to the equilibrium phase between the pollutant and soil. The higher adsorption rate at the beginning can be explained by many active adsorption sites on the adsorbent surface and then the decrease and equilibrium of the adsorption rate due to the decrease in these sites.<sup>36</sup> The environmental pH values may affect the adsorption behavior of pharmaceutical compounds in the soil. pH



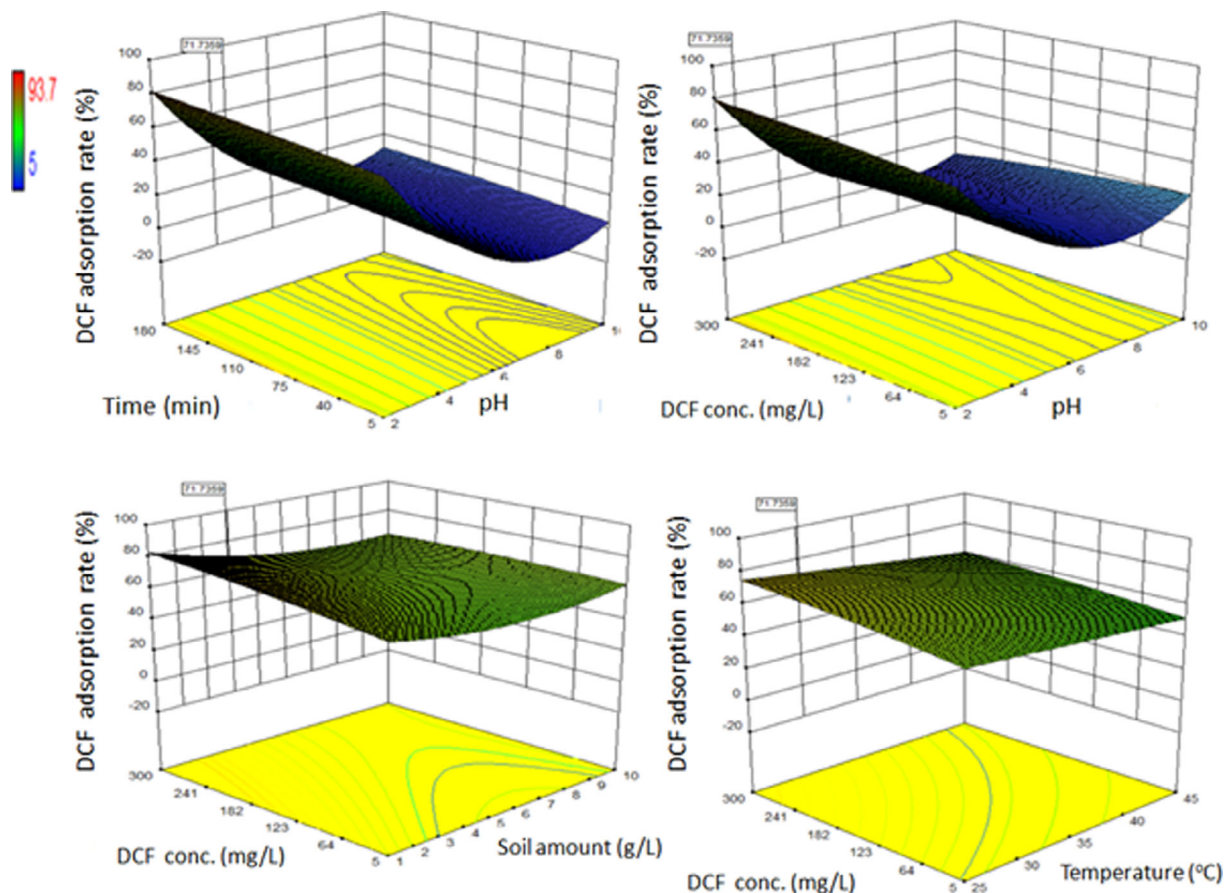
**FIGURE 2** The 3d graph showing the change in TC adsorption by the soil M with RSM: (a) time-pH; (b) initial TC concentration-pH; (c) initial TC concentration-soil amount; (d) initial TC concentration-temperature

values affect the characteristics of both pharmaceutical compounds and the soil itself.<sup>27</sup> Increasing soil pH usually causes an increase in dissolved organic matter.<sup>37</sup> TC and DCF are bound to be dissolved in organic matter in a solution at high pH. This is a factor that decreases TC and DCF adsorption in soils. At the same time, antibiotics can be found in different types (cations, anions, or zwitterions) in soils with different pH values.<sup>38</sup> TC is an amphoteric compound with three ionizable groups and pKa values of approximately 3.3, 7.7, and 9.7. There are four types of TC ions, including  $\text{TCH}_3^+$  ( $\text{pH} < 3.3$ ),  $\text{TCH}_2^0$  ( $3.3 < \text{pH} < 7.7$ ),  $\text{TCH}^-$  ( $7.7 < \text{pH} < 9.7$ ), and  $\text{TC}^{2-}$  ( $\text{pH} > 9.7$ ), under different pH conditions.<sup>9,39</sup> Moreover, the  $\text{pH}_{\text{pzc}}$  (point of zero charge) values of soils are needed to evaluate the effects mechanism of pH on the adsorption of TC and DCF by soils; when  $\text{pH} > \text{pH}_{\text{pzc}}$ , soil surfaces are negatively charged; when  $\text{pH} < \text{pH}_{\text{pzc}}$ , they are positively charged.<sup>40,41</sup> The  $\text{pH}_{\text{pzc}}$  values for the soils S and M were 5.57 and 3.37, respectively. In this case, soils with a pH value below the  $\text{pH}_{\text{pzc}}$  are in the cationic form, and with the values above it, they are in the anionic form. At a pH of 4, at which the best TC adsorption took place by the soils S and M, TC was in the zwitterionic and/or cationic form, the soil S was in the cationic form, and the soil M was in the anionic form. Thus, it can be said that the adsorption process between TC and soil S is under the influence of ion exchange and electrostatic

interaction, while the adsorption process between TC and soil M is under the influence of electrostatic interaction. Aristilde et al.<sup>42</sup> reported that the adsorption capacity of TC in the soil containing montmorillonite might increase at low pH values ( $< 7.0$ ). As the pH value increased, the adsorption capacity of TC gradually decreased. Furthermore, Peruchi et al.<sup>43</sup> reported that fluoroquinolones existed as zwitterionic under acidic conditions and could form complexes with soil metals. This phenomenon might occur in our study. Other studies also reported similar results.<sup>17,35</sup>

The pKa value of DCF is 4.15.<sup>44</sup> At a pH of 2, the best DCF adsorption took place by the soils S and M, the DCF compound and the soils S and M were in the cationic form. In this case, it can be said that the adsorption process between DCF and the soils S and M is under the effects of ion exchange. Studies with DCF have reported similar results.<sup>10,27</sup>

In Figures 1b, 2b, 3b, and 4b, the adsorption rates (%) of TC and DCF increased as the solution pH decreased and the initial TC concentration increased. The formation of parabolic lines shows the presence of second-order effects. The high initial pollution concentration provided the driving force for the organic molecule to overcome various mass transfer resistances in the transition from the aqueous phase to the solid phase.<sup>36</sup> This resulted in higher randomness between pollutants and soil. Therefore, the adsorption of TC and DCF by the soils



**FIGURE 3** The 3d graph showing the change in DCF adsorption by the soil S with RSM: (a) time-pH; (b) initial DCF concentration-pH; (c) initial DCF concentration-soil amount; (d) initial DCF concentration-temperature

increased.<sup>45</sup> Similar results have been reported in the literature for adsorption of organic pollutants.<sup>22,24</sup>

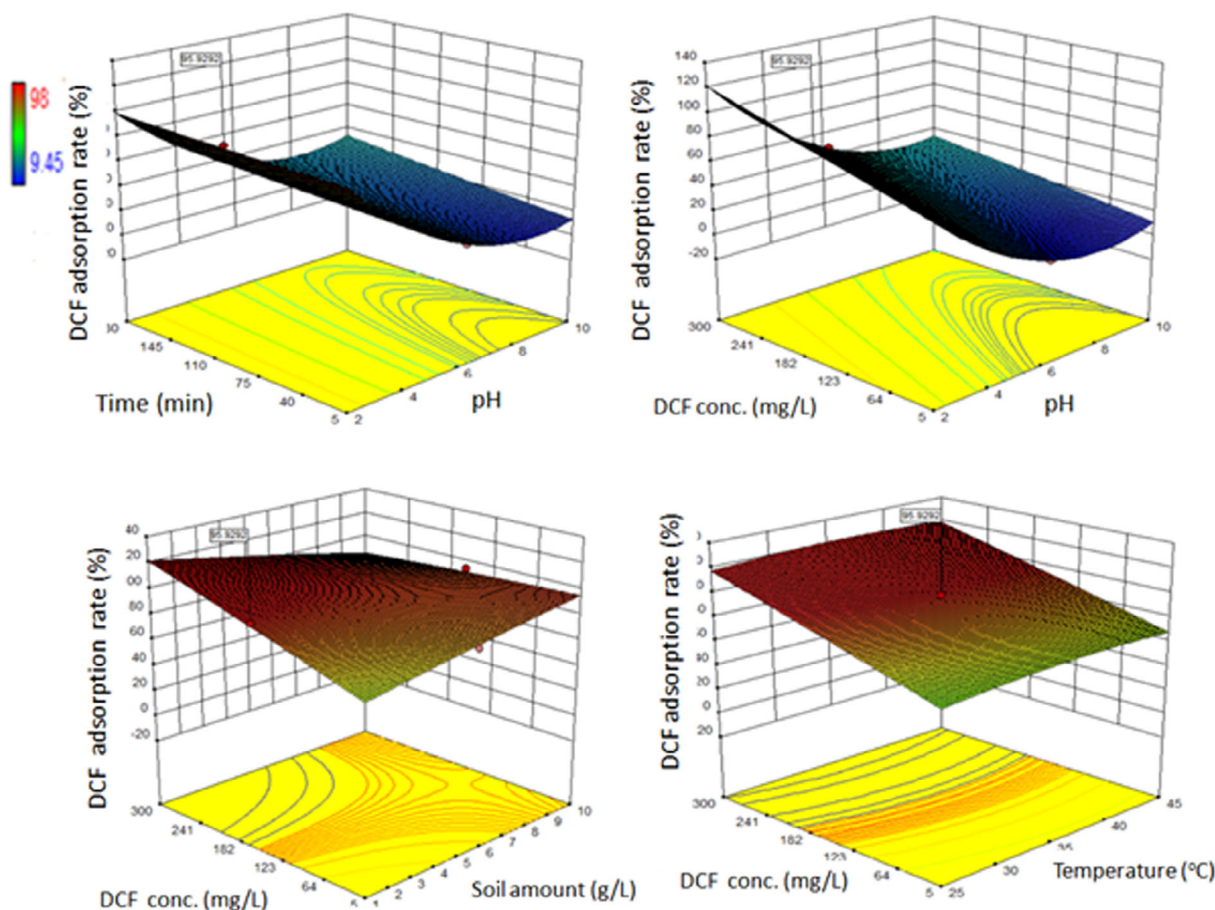
Figures 1c, 2c, 3c, and 4c show the effects of initial pollution concentration and soil amount on the adsorption rate (%). The adsorption rate (%) of TC and DCF increased with increasing pollution concentration and soil amount for both soils. This is an expected situation. Because a higher amount of soil contains more surface area and more functional groups, this ensures that pollutant is adsorbed more.<sup>46-49</sup>

Figures 1d, 2d, 3d, and 4d show the effects of the initial pollution concentration and temperature on the adsorption rate (%). The role of temperature on the adsorption properties of the system is crucial because there are daily and seasonal fluctuations in the actual environmental temperature.<sup>45</sup> According to Figures 1d and 2d, the TC adsorption rate (%) decreased as the TC concentration and temperature increased. Parabolic lines appeared with increasing initial TC concentration, which indicates that the initial TC concentration has a quadratic effect on TC adsorption by the soil S. The three-zone effects were observed from the contour surfaces in Figure 2d. This shows that different responses were obtained for TC adsorption at different TC concentrations and temperatures. Also, the decrease in the adsorption rate with increasing temperature suggests an exothermic sorption process.<sup>47,50</sup> These results are consistent with previous studies on pharmaceuticals.<sup>14,28</sup> A similar characteristic behavior was

observed in DCF adsorption by the soil S (Figure 3d). In Figure 4d, the DCF adsorption rate (%) for the soil M increased with increasing initial DCF concentration and temperature. The four-zone effects were observed from contour surfaces, which implies that different responses were obtained for DCF adsorption by the soil M at different DCF concentration and temperature values. This may be due to the interaction between the molecular structure of DCF and ionic structures in the soil M. Therefore, the adsorption of DCF in soil M is likely to be endothermic, which agrees with the finding of Jenkins et al.<sup>51</sup> and Gao et al.<sup>25</sup> for atrazine, imazapyr, and menadione in soil, respectively. In addition, in endothermic adsorption, an increase in temperature causes a decrease in solution viscosity. Thus, the adsorbed pollutant shows a good diffusion rate through the outer boundary layer and in inner adsorbent particle pores.<sup>36</sup>

### 3.5 | The effects of soil organic matter (SOM) on the adsorption process

Soil organic matter (SOM) generally refers to organic compounds containing carbon in the soil. Many functional groups (e.g., carbohydrates, nitrogenous compounds, lignin, and some fat-soluble substances) on the surface of SOM may play an important role in the transport,



**FIGURE 4** The 3d graph showing the change in DCF adsorption by the soil M with RSM: (a) time-pH; (b) initial DCF concentration-pH; (c) initial DCF concentration-soil amount; (d) initial DCF concentration-temperature

transformation, and immobility of pollution in the soil.<sup>9,24,36,52</sup> Many studies have demonstrated that the components of the soils and sediments and their physicochemical properties (soil and sediment composition, surface structure, charge properties, organic matter content, etc.) can affect the adsorption behavior of TC and DCF.<sup>24,52–55</sup> The adsorption experiments were carried out at the predicted optimal conditions based on the RSM (Table S4) (in Data S1). The adsorption capacities ( $q_s$ ) of the soils S and M before and after the removal of SOM were given in Table S6 (in Data S1).

According to Table S6, the adsorbed amount of TC on the soils S and M with SOM were slightly lower than those on the soils S and M after the removal of SOM, which suggests that SOM in the soils has slightly inhibited the adsorption of TC. However, the adsorbed amount of DCF on the soils S and M after removing SOM sharply approached zero. As the main mineral component of the soils S and M, calcite and quartz have not contributed to the DCF adsorption. SOM is possibly the main contribution to DCF adsorption onto the soils.<sup>52</sup> The mechanisms of interaction between some antibiotics and SOM have been investigated previously.<sup>9,56,57</sup> The reason for these two different phenomenon has been reported by the researchers as the differences in the potential adsorption sites (e.g.,  $-\text{COO}^-$ ), composition and structure (hydrophilicity, hydrophobicity) of SOM.<sup>24,57</sup>

### 3.6 | The effect of salt and divalent cations on adsorption process

Monovalent (e.g.,  $\text{Na}^+$  and  $\text{K}^+$ ) and multivalent metal ions (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$ ) coexisting in soil have important effects on the adsorption behavior of antibiotics. Monovalent metal ions can often compete for adsorption sites with cationic or zerovalent antibiotics.<sup>9,58</sup> The effects of different concentrations of salt (NaCl) and divalent cations ( $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ) on the adsorption of TC and DCF by the soils S and M were investigated. The adsorption experiments were carried out at the predicted optimal conditions based on the RSM (Table S7) (in Data S1). The adsorption capacities ( $q_s$ ) of the soils S and M were given in Table S7 (in Data S1). According to Table S7, the adsorption capacities ( $q_s$ ) of the soils S and M for TC and DCF decrease as the concentrations of salt (NaCl) and divalent cations ( $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ) increases. The reduction in the adsorption capacities of the soils S and M may be due to the occupation of their adsorption sites by divalent cations and ions derived from NaCl.<sup>13</sup> A similar inhibitory effect on the adsorption of antibiotics has been observed in the presence of some multivalent metal ions at low soil pH values.<sup>47,59–61</sup> For example, in the report of Aristilde et al.,<sup>42</sup> the TC adsorption capacity of soil was shown to significantly decrease in



the presence of divalent cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) at  $\text{pH}_{\text{soil}} < 7.0$ .<sup>46,47</sup> In another study, Pei et al.<sup>61</sup> stated that  $\text{Cu}^{2+}$  inhibits tylosine adsorption in soil due to electrostatic competition.

## 4 | CONCLUSIONS

In this study, the effects of soil environmental parameters on the adsorption of TC and DCF by the soils collected from two different agricultural lands in Turkey were examined in the laboratory. The results of the ANOVA test showed that the effects of the studied variables including pH, contact time, soil amount, temperature, and initial pollutant concentration on TC and DCF adsorption, were significant. It was determined that the parameter that affects the process the most is pH, and the parameter that affects the process the least is environment temperature. The optimum pH values in the adsorption of TC and DCF by the soils S and M were 4 and 2, respectively. Increasing pH of the solution adversely affected the adsorption of TC and DCF by the soil. This situation attributed to the increase in solubility of organic matter with increasing pH value. At the optimal conditions, the adsorption rates (%) for the TC-soil S, TC-soil M, DCF-soil S and DCF-soil M were calculated to be 83.27%, 69.88%, 65.99% and 94.99%, respectively. TC adsorption was not affected by SOM removal. SOM is possibly the main contribution to DCF adsorption onto the soil. In addition, the adsorption of TC and DCF onto soils with different physicochemical properties was inhibited by salt ( $\text{NaCl}$ ) and divalent cations ( $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ) in the medium. According to all the data obtained, a complex mechanism may exist in the TC and DCF adsorption process by S and M soils, including ion exchange, electrostatic interaction and some chemical bonds. This comprehensive study on the modeling and optimization of the adsorption process of TC and DCF can provide valuable insights into understanding and evaluation of soil adsorption systems.

### AUTHOR CONTRIBUTIONS

**Ulker Asli Guler:** Thesis advisor (conceptualization, funding acquisition, investigation, methodology, project administration, resources, software, supervision, validation, visualization, original draft, writing, review & editing); **Eliza Tuncel:** Master thesis (investigation; data curation, formal analysis); **Mehtap Ersan:** Assistant thesis advisor (methodology, original draft; writing, review & editing).

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### CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

### DATA AVAILABILITY STATEMENT

All data generated or analyzed during this study are included in this published article (and its supplementary information files). Data openly available in a public repository that issues datasets with DOIs.

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