

Use of commercial adsorbents for the removal of antibiotics from agricultural soil. Process efficacy and interaction mechanisms

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Abstract

Soil contamination by antibiotic residues poses an increasing risk to terrestrial and water ecosystems and human health, particularly due to its contribution to the development and spread of antimicrobial resistance. This study evaluates the effectiveness of a commercial organoclay-based adsorbent (PM199), selected from an initial pool of eight candidate materials, for the immobilization of antibiotics frequently detected in soils. Batch experiments were conducted to evaluate removal efficiency, adsorption kinetics, and equilibrium behaviour under controlled soil-solution contact conditions. Eight antibiotics were analyzed simultaneously, including amoxicillin, trimethoprim, sulfamethoxazole, clindamycin, ofloxacin, tetracycline, ciprofloxacin, and azithromycin. The incorporation of PM199 into the soil (80:20, w/w) significantly improved the retention of amoxicillin, trimethoprim, sulfamethoxazole, and clindamycin, with retention efficiencies ranging from 57.5% to 84.6%, and these compounds were subsequently selected for detailed kinetic and isothermal analyses. Adsorption kinetics were described using a biphasic PFO + PSO model for the four selected antibiotics and a simple PFO model for the remaining compounds, reflecting differences in surface accessibility and rate-limiting mechanisms. The equilibrium data were best described by the Freundlich isotherm, which is consistent with adsorption on an energetically heterogeneous surface. The multicomponent model indicated that competitive interactions among the four antibiotics were limited, suggesting preferential interaction with distinct adsorption sites. Overall, these results support the potential of soils enriched with organoclays as an effective strategy for the simultaneous retention of antibiotic mixtures in contaminated soils, to prevent these highly hazardous pollutants from entering natural water bodies.

1 Introduction

The widespread use of antibiotics in human medicine, veterinary medicine, and agricultural systems has raised growing concerns due to their persistence in the environment and their role in the spread of antimicrobial resistance, which in 2019 was estimated to be directly responsible for 1.27 million deaths annually and it has been associated with nearly 5 million deaths worldwide according to current estimates (Murray et al., 2022). It has been established that agricultural soils serve as a key reservoir and a pathway for the spread of antibiotic resistance genes (ARGs), the abundance and diversity of which have increased significantly due to anthropogenic pressures, particularly through the application of manure, sewage sludge, and irrigation with treated wastewater (Fang et al., 2023; Wu et al., 2023). This accumulation is largely due to the incomplete metabolism of antibiotics in humans and animals, which leads to their release into the soil through faeces and organic waste streams (Wu et al., 2023).

Antibiotics belonging to the same classes analyzed in this study—tetracyclines, sulfonamides, fluoroquinolones, macrolides, β -lactams, and lincosamides—have been widely detected in agricultural soils worldwide. The concentrations reported range from undetectable levels to several thousand $\mu\text{g kg}^{-1}$ in global assessments (Fang et al., 2023), while field-scale studies typically report concentrations in the $\mu\text{g kg}^{-1}$ range, with fluoroquinolones, such as ciprofloxacin and enrofloxacin, followed by tetracyclines and ofloxacin, among the most frequently detected and dominant compounds in manure-affected soils (Zha et al., 2023). Even at sub-inhibitory concentrations, antibiotic residues present in the soil exert selective pressure on microbial communities and promote the spread of resistance genes through horizontal gene transfer, a mechanism that occurs at a high rate in dense microbial communities, especially in biofilm environments, where close cell-to-cell interactions enhance genetic exchange (Michaelis & Grohmann, 2023).

It has been estimated that a significant fraction of administered antibiotics is excreted as unchanged compounds or active metabolites, in proportions ranging from 40% to 90%, depending on the class of drug and the route of administration. These residues subsequently enter the environment through pathways such as hospital and pharmaceutical effluents, agricultural runoff, and the application of manure as fertilizer (Al-Khalaifah et al., 2025; Da Silva Bruckmann et al., 2025; Polianciuc et al., 2020). Consequently, antibiotics are frequently detected in agricultural soils, surface waters, and, in some cases, groundwater, highlighting their widespread distribution and continuous input into different environmental compartments (Fatima et al., 2025; Zeng et al., 2025; Zhu et al., 2024). Although conventional wastewater treatment plants have improved in recent decades, the removal of many antibiotics remains incomplete and highly variable, leading to the discharge of residual compounds into receiving water bodies (Fatima et al., 2025; Guo et al., 2025; Zhu et al., 2024). In this context, biochar-based adsorption has emerged as a promising and cost-effective strategy for immobilizing organic contaminants, including antibiotics, in agricultural soils, owing to its large surface area, functional surface groups, and tunable physicochemical properties (Haider et al., 2022). In agricultural soils, adsorption plays a key role in controlling the retention and mobility of antibiotics, which influences their persistence in the environment and their potential for leaching (Cela-Dablanca et al., 2024). Consequently, a wide range of adsorbent materials has been studied for the removal and immobilization of antibiotics in environmental systems, including activated carbon, biochar, zeolites, and natural or modified clays, due to their high specific surface area and versatile interaction mechanisms (Ajala et al., 2023). Biochar has been shown to significantly enhance antibiotic retention in agricultural soils, reducing the concentrations of sulfonamides and tetracyclines by approximately 55% and 21%, respectively, according to a recent meta-analysis based on multiple experimental studies (Xia et al., 2025). In addition, organoclays have demonstrated promising performance as soil amendments capable of increasing the adsorption of contaminants and mitigating their mobility and leaching, although their efficacy may decrease over time due to aging processes in the soil (López-Cabeza et al., 2024). These materials provide additional sorption sites and alter the physicochemical properties of soils, thereby promoting the immobilization of ionizable organic compounds such as antibiotics and reducing their environmental availability.

However, a significant portion of sorption studies has been conducted using high water-to-soil ratios and antibiotic concentrations higher than those typically found under environmental conditions. These experimental designs do not adequately represent natural soil systems and may bias the estimation of sorption coefficients, limiting the extrapolation of results obtained under simplified conditions to heterogeneous agricultural soils (Franklin et al., 2022). Furthermore, the behaviour of adsorbents when directly applied as soil amendments remains insufficiently understood under realistic agricultural conditions, particularly considering the complex interactions governing adsorption, mobility, and degradation processes (García-Delgado et al., 2023). Within this framework, the present study first evaluates the performance of eight industrial adsorbents directly applied as amendments to an agricultural soil artificially contaminated with a multicomponent mixture of antibiotics frequently detected in agricultural environments. Following a preliminary screening phase, the material with the best results was selected for a more detailed study using batch experiments, which included kinetic and equilibrium analyses, employing a chemical solution representative of soil pore water, to characterize the adsorption process under conditions that simulate the interactions between the soil

and the solution. This integrated approach allows for the evaluation of adsorption kinetics, equilibrium behaviour, and overall efficiency under representative conditions, providing experimental evidence regarding the practical feasibility of using industrial adsorbents as a strategy to mitigate antibiotic contamination in agricultural soils.

2 Materials and Methods

2.1 Agricultural soil

Agricultural soil was collected from the Granada plain in Spain at a depth of 0–25 cm. The geographic coordinates of the sampling site were 37°11'11.87" N and 3°41'26.09" W. The soil had a loamy-clay texture, with a porosity of 48.36% and low permeability ($4.42 \times 10^{-5} \text{ cm s}^{-1}$), indicating limited infiltration capacity. Mineralogical analysis revealed that illite was the predominant clay mineral, followed by smectite and kaolinite. Chemically, the soil was characterized by a slightly alkaline pH (7.4 in KCl and 7.9 in water), a low organic matter content (1.81%), a notable carbonate content (15.4% as CaCO_3), and a moderate to high cation exchange capacity (22.12 meq/100 g of soil).

2.2 Adsorbents

In this study, eight industrial adsorbent materials were evaluated. The materials were purchased commercially and used as supplied by the manufacturer, without any additional physical or chemical modification. Prior to use, all adsorbents were stored in dry conditions and protected from light. The materials correspond to modified clay minerals intended for environmental applications, including sepiolite-type and smectite-type materials (e.g., bentonite, montmorillonite) functionalized with organic compounds to enhance their adsorption capacity toward organic contaminants in environmental matrices. Basic physicochemical characterization data were provided by the manufacturer. Additional characterization was performed by Fourier transform infrared spectroscopy with attenuated total reflectance (ATR-FTIR), and the corresponding spectra are provided in the Supplementary Material (Fig. S1). For clarity, the adsorbents are identified throughout the manuscript using coded labels (A-H).

2.3 Chemicals and reagents

Eight antibiotics commonly used in human and veterinary medicine were selected, representing different pharmacological classes: amoxicillin (AMX), azithromycin (AZM), trimethoprim (TMP), sulfamethoxazole (SMZ), ciprofloxacin (CIP), ofloxacin (OFL), tetracycline (TCN), and clindamycin (CLDM). OFL, TCN, and CLDM are included in the most recent updated watch list of substances for monitoring purposes at the European Union level, in accordance with Article 8b of Directive 2008/105/EC (European Commission, 2025). All solid standards were of analytical grade (> 98% purity) and were purchased from Sigma-Aldrich. Cinchophen (CIN) was employed as a surrogate standard to monitor analytical recovery throughout the extraction and quantification procedure and was supplied by Alfa Aesar. All solvents and additives were of LC-MS grade. Methanol (MeOH) was obtained from VWR Prolabo Chemicals, and formic acid (98%), used as a mobile-phase additive, was supplied by Honeywell. Stock solutions of the target antibiotics were prepared in ultrapure water at a concentration of 100 mg L^{-1} and stored at 4 °C in the dark until experimental use. Ultrapure water ($18.2 \text{ M}\Omega\text{-cm}$) was produced using a Milli-Q Plus® system (Millipore). The physicochemical properties and chemical structures of the antibiotics are provided in the Supplementary Material (Table S1).

2.4 LC-MS analysis

Quantification of the antibiotics in aqueous solutions was performed using an ACQUITY ultrahigh performance liquid chromatography system (Waters, Milford, MA, USA) coupled to a single quadrupole mass spectrometer. Analyses were carried out using electrospray ionization in positive mode (ESI+), and detection was performed in selected ion monitoring (SIM) mode. Detailed information on chromatographic separation and instrumental parameters is provided in the Supplementary Material (Tables S2A and S2B).

2.5 Preliminary experiments

All experiments were conducted under batch conditions at a constant temperature of 20 °C, using polypropylene tubes (67 cm^3) and a rotary shaker (SBS, model AN-2) operating at 13,300 rpm ($16,300 \times g$). Prior to the adsorption experiments, control tests were performed to verify that no significant adsorption of the antibiotics occurred on the walls of the polypropylene tubes or on other components of the experimental setup. Preliminary experiments were then conducted to optimize operating conditions and select the most effective adsorbent material for the immobilization of antibiotics. Initially, the adsorption potential of the antibiotics on the analyzed materials was evaluated using solutions prepared at concentrations ranging from 0.5 to $5 \mu\text{g mL}^{-1}$ and brought into contact with the solid phases under constant stirring. To assess the feasibility of the solid-liquid system, different solution volumes (20, 40, and 50 mL) were tested. The 20 mL and 40 mL volumes resulted in excessively dense suspensions due to the high solid-to-liquid ratio, which hindered adequate dispersion of the adsorbent during stirring and complicated the sampling of the supernatant. In contrast, a 50 mL volume allowed for the formation of a homogeneous and stable suspension, ensuring reproducible experimental conditions. Therefore, 50 mL was selected as the working volume. Subsequently, the adsorbent-to-solution ratio was optimized by evaluating different adsorbent masses (1.0, 2.5, and 5.0 g) in contact with 50 mL of a multicomponent antibiotic solution at a concentration of 2.5 mg L^{-1} each, to identify the best balance between removal efficiency and material consumption. Finally, the adsorption performance of the commercial adsorbent materials and agricultural soil was compared. For this purpose, 2.5 g of each material were contacted with 50 mL of a multicomponent solution containing amoxicillin (10 mg L^{-1}) and the remaining antibiotics (5 mg L^{-1} each). The higher concentration selected for amoxicillin was necessary to ensure adequate chromatographic signal intensity given its comparatively lower response under the analytical conditions employed. The suspensions were agitated for 65 h to ensure complete equilibration under all tested conditions, although preliminary kinetic data indicated that equilibrium was reached at earlier times. Aliquots were collected at predetermined time intervals (5–3900 min) for UHPLC-MS analysis. Once the most efficient commercial adsorbent had been identified, an additional experiment was carried out to optimize the soil-adsorbent mixture by testing different mass proportions ranging from 0:100 to 100:0 (soil:adsorbent, w/w) in increments of 20%, while maintaining a constant total solid mass (2.5 g) and solution volume (50 mL) under the same experimental conditions and contact time.

2.6 Batch experiments

The adsorption behaviour of AMX, TMP, OFL, TCN, SMZ, AZM, and CLDM was evaluated using a batch adsorption system. Aqueous solutions were prepared by dilution from the stock solutions described in Section 2.3. To determine the time required to reach adsorption equilibrium, kinetic experiments were conducted by collecting aliquots at the following time intervals: 5, 30, 45, 60, 120, 360, 720, 1440, 2880, and 3900 min. Samples were centrifuged at 13,300 rpm ($16,300 \times g$) for 2 min, and the supernatant was subsequently analyzed by UHPLC-MS. Kinetic data indicated that equilibrium was reached within 24 h, which was therefore adopted as the contact time for all subsequent adsorption experiments.

Next, adsorption experiments were conducted under the same experimental conditions to evaluate the adsorption capacity and removal efficiency of the adsorbent for each antibiotic. A homogeneous mixture of natural soil and modified organoclay in an 80:20 (w/w) ratio was used as the adsorbent, selected based on the optimization described in Section 2.5. In each experiment, 2.5 g of adsorbent was brought into contact with 50 mL of a multicomponent antibiotic solution at initial concentrations of amoxicillin (10 mg L^{-1}) and the remaining antibiotics (5 mg L^{-1} each), in triplicate, and stirred in the rotary shaker at 13,300 rpm ($16,300 \times g$) for 24 h at 20°C . The adsorbed amount per unit mass of adsorbent (q_e , mg g^{-1}) and the removal efficiency (R , %) were calculated using Eqs. (1) and (2):

$$\text{Eq. (1)} \quad q_e = \frac{(C_o - C_e) V}{m}$$

$$\text{Eq. (2)} \quad R (\%) = \frac{(C_o - C_e)}{C_o} \times 100$$

where C_o and C_e represent the initial and equilibrium antibiotic concentrations (mg L^{-1}), respectively, m is the dry mass of adsorbent (g), and V is the solution volume (L).

The empirical models applied for kinetic, isotherm, and statistical analyses are presented in the following sections.

2.7 Empirical adsorption models

Adsorption kinetics. Adsorption kinetics were evaluated using five empirical models: the pseudo-first order (PFO) model, the pseudo-second order (PSO) model, a mixed PFO-PSO model, the intraparticle diffusion model (Weber-Morris, WM), and the Elovich model (E) (Chu et al. 2025; Musah et al., 2022; Revellame et al., 2020; Tran et al., 2017; Wang and Guo, 2020). These models were selected based on their mathematical formulation and their widespread use for describing adsorption rate behaviour and potential rate-controlling steps. The Weber-Morris model was specifically used to assess the contribution of intraparticle diffusion to the overall adsorption process. Kinetic modelling was performed on single-component systems to allow unambiguous parameter estimation without the confounding effects of competitive adsorption. The mathematical expressions of each model, together with their parameters and bibliographic references, are summarized in Table S3. Kinetic parameters were estimated by non-linear regression using the GRG Nonlinear Solver algorithm in Microsoft Excel, minimizing the sum of squared errors (SSE) between experimental and model-predicted values. Model performance was assessed using the coefficient of determination (R^2), the root means square error (RMSE), and the SSE, which are widely used indicators for evaluating the goodness of fit of nonlinear adsorption models (Suwannahong et al., 2021). **Adsorption isotherms.** Adsorption equilibrium was investigated for AMX, TMP, SMZ, and CLDM using a composite adsorbent consisting of natural soil and industrially modified organoclay. Both single-component and multicomponent systems containing the four antibiotics simultaneously were evaluated to assess potential competitive adsorption effects. Equilibrium data were fitted to three non-linear adsorption isotherm models: Langmuir, Freundlich, and Sips (Ayawei et al., 2017; Mozaffari Majd et al., 2022; Murphy et al., 2023). The Langmuir model assumes monolayer adsorption on a homogeneous surface with a finite number of identical sites, the Freundlich model describes heterogeneous multilayer adsorption, and the Sips model combines features of both, accommodating heterogeneous surfaces with a finite adsorption capacity. The equations, parameters, and original references are summarized in Table S4, and the extended multicomponent formulations are provided in the Supplementary Material (Table S5). Non-linear formulations were selected to preserve the original mathematical structure of the models and avoid parameter distortions introduced by linearized transformations (Vitek et al., 2023). Model performance was assessed using the same statistical indicators described in Section 2.7.1 (R^2 , RMSE, and SSE).

3 Results

3.1 Preliminary batch experiments

Control tests confirmed that there were no significant losses of antibiotics due to the materials used in the experimental setup. Preliminary experiments were conducted to evaluate the influence of the adsorbent-to-solution ratio and the soil-adsorbent composition on adsorption performance, as well as to compare the performance of the materials analyzed. The results are summarized in Fig. 1.

First, the influence of the adsorbent-to-solution ratio on removal efficiency was evaluated (Fig. 1A). No significant differences in removal efficiency were observed among the ratios analyzed ($0.02\text{--}0.10 \text{ g mL}^{-1}$) (Kruskal-Wallis, $H = 1.37$, $p = 0.504$). However, variability increased with lower adsorbent doses. Considering both removal performance and operational feasibility, a ratio of 0.05 g mL^{-1} was selected for subsequent experiments. Next, the effect of the soil-to-adsorbent ratio on removal efficiency was evaluated (Fig. 1B). A progressive decrease in removal efficiency was observed as the soil proportion increased, with a notable decline in the untreated soil system (100:0), which also exhibited high variability. A soil-to-adsorbent ratio of 80:20 (w/w) was selected as a compromise between high removal efficiency and lower adsorbent consumption.

The adsorption performance of the materials analyzed (A-H) and agricultural soil was evaluated comparatively under identical experimental conditions, using a multicomponent antibiotic solution (Fig. 1C). Adsorbents G and H exhibited the highest removal efficiencies, and H (PM199), a commercial organoclay, clearly outperformed all other materials analyzed. Therefore, this material was selected for subsequent kinetic and equilibrium studies.

To evaluate the specific adsorption behaviour of each compound in greater detail, Table 1 summarizes the removal efficiencies obtained for each of the antibiotics in soil, in PM199, and in the soil-PM199 mixture (80:20, w/w).

Table 1
Removal efficiencies (%) of antibiotics in soil, PM199, and the soil/PM199 mixture (80:20, w/w)

Antibiotic	Soil	PM199	Soil/PM199 (80:20, w/w)
AMX*	18.5	100.0	59.1
TMP*	46.9	87.8	57.5
OFL	96.8	98.3	92.9
TCN	97.2	100.0	96.4
CIP	98.1	100.0	96.7
SMZ*	6.1	97.7	84.6
AZM	97.9	98.9	99.4
CLDM*	41.2	97.0	75.2
* Antibiotics selected for subsequent kinetic and equilibrium studies based on the marked improvement in adsorption upon PM199 addition			

AMX, TMP, SMZ, and CLDM showed a marked increase in removal efficiency compared to untreated soil, indicating a significant improvement attributable to the incorporation of PM199. In contrast, OFL, TCN, CIP, and AZM already exhibited high removal efficiencies in the soil matrix (> 96%), with only marginal improvements following the addition of PM199. Therefore, AMX, TMP, SMZ, and CLDM were selected for subsequent kinetic and equilibrium adsorption analyses.

3.2 Adsorption kinetics

The adsorption kinetics of the eight antibiotics onto the soil/PM199 mixture (80:20, w/w) are shown in Fig. 2. Two clearly distinct behaviours were observed among the studied compounds. AMX, TMP, SMZ, and CLDM exhibited a biphasic adsorption pattern, characterized by an initial stage of rapid adsorption followed by a progressively slower approach to equilibrium (Fig. 2A). This behaviour suggests the coexistence of rapid surface interactions and a slower, rate-limiting stage associated with the gradual occupation of energetically heterogeneous adsorption sites. The PFO + PSO mixed model provided the best fit to the experimental data across the entire time interval ($R^2 = 0.978\text{--}0.993$, $RMSE = 0.002\text{--}0.009\text{ mg g}^{-1}$; Table 2a), outperforming the individual PFO and PSO models. This supports the rapid occupation of external surface sites (PFO component) coupled with slower diffusion toward internal sites of higher energy (PSO component). The Elovich model consistently ranked second ($R^2 = 0.921\text{--}0.972$; Table 2b), consistent with the expected energy heterogeneity of the composite adsorbent surface. In contrast, OFL, CIP, AZM, and TCN reached near-maximum adsorption capacity within the first 5 min of contact, with q_t remaining essentially constant thereafter (Fig. 2B), indicating that the adsorption rate exceeded the temporal resolution of the experimental design. Given the near-instantaneous nature of the adsorption process, only the PFO model yielded physically meaningful parameters for this group ($R^2 = 0.984\text{--}0.9996$, $RMSE = 0.0005\text{--}0.003\text{ mg g}^{-1}$; Table 2a), while the remaining models yielded parameters with limited physical interpretability due to the lack of kinetic resolution.

Table 2

a Kinetic parameters obtained by nonlinear least-squares fitting (PFO, PSO and PFO + PSO models) for the adsorption of antibiotics onto soil/PM199 (

Antibiotic	$q_{e, \text{ exp}}$	PFO				PSO				PFO + PSO				
	(mg g^{-1})	q_e	k_1	R^2	RMSE	q_e	k_2	R^2	RMSE	q_{e1}	k_1	q_{e2}	k_2	
Group A														
AMX	0.1783	0.1674	0.0016	0.9320	0.0158	0.1931	0.0102	0.9479	0.0138	0.0220	0.3141	0.1955	0.0051	
TMP	0.0839	0.0708	0.0258	0.7223	0.0122	0.0734	0.6446	0.8166	0.0099	0.0438	0.3614	0.0484	0.0277	
SMZ	0.1654	0.1605	0.0158	0.9852	0.0074	0.1698	0.1285	0.9888	0.0064	0.1196	0.0223	0.0508	0.0852	
CLDM	0.0502	0.0454	0.0164	0.8497	0.0060	0.0481	0.4888	0.9117	0.0046	0.0194	0.3139	0.0333	0.1237	
Group B														
OFL	0.0878	0.0872	0.6958	0.9996	0.0005	—	—	—	—	—	—	—	—	
CIP	0.1101	0.1041	3.5044	0.9872	0.0034	—	—	—	—	—	—	—	—	
AZM	0.0885	0.0861	3.5970	0.9931	0.0021	—	—	—	—	—	—	—	—	
TCN	0.1339	0.1226	3.5879	0.9840	0.0045	—	—	—	—	—	—	—	—	
PFO: q_e (mg g^{-1}), k_1 (min^{-1}). PSO: q_e (mg g^{-1}), k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$). PFO + PSO: q_{e1} , q_{e2} (mg g^{-1}), k_1 (min^{-1}), k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$). RMSE in mg g^{-1} . —: model not applied physically interpretable for Group B). $q_{e, \text{ exp}}$: experimental amount adsorbed at $t = 3900 \text{ min}$														

Table 2

b Kinetic parameters obtained by nonlinear least-squares fitting (Elovich and Weber-Morris models) for the adsorption of Group A antibiotics onto soil/PM199 (80:20, w/w)

Antibiotic	$q_{e, \text{exp}}$ (mg g^{-1})	Elovich				Weber-Morris			
		α	β	R^2	RMSE	K_{id}	C	R^2	RMSE
AMX	0.1783	0.0007	24.26	0.9646	0.01138	0.00288	0.0125	0.9562	0.0126
TMP	0.0839	0.0865	130.74	0.9721	0.00387	0.00096	0.0339	0.7217	0.0122
SMZ	0.1654	0.0168	42.46	0.9209	0.01700	0.00230	0.0591	0.6067	0.0379
CLDM	0.0502	0.0108	170.19	0.9724	0.00258	0.00065	0.0183	0.7337	0.0079

α ($\text{mg g}^{-1} \text{min}^{-1}$) and β (g mg^{-1}) denote the Elovich model parameters. K_{id} ($\text{mg g}^{-1} \text{min}^{-0.5}$) and C (mg g^{-1}) correspond to the Weber–Morris intraparticle diffusion parameters. RMSE is expressed in mg g^{-1} . The Elovich and Weber–Morris models were not applied to Group B antibiotics due to the near-instantaneous adsorption kinetics, which prevented physically meaningful parameter estimation. $q_{e, \text{exp}}$ (mg g^{-1}) represents the experimental adsorption capacity at $t = 3900 \text{ min}$.

Based on the kinetic profiles, a contact time of 1440 min was selected as the operational equilibrium time. Beyond this point, q_t values showed negligible variation, ensuring consistent and representative conditions for subsequent equilibrium isotherm experiments.

3.3 Equilibrium adsorption and isotherm model

To further investigate the adsorption mechanisms of the soil/PM199 system (80:20, w/w), equilibrium isotherms were determined for the antibiotics that showed a clear increase in adsorption compared to untreated soil in the preliminary batch experiments, namely AMX, TMP, SMZ, and CLDM (Table 1). The equilibrium data were fitted by non-linear regression to the Langmuir, Freundlich, and Sips isotherm models. While the Langmuir and Sips models provided satisfactory statistical fits ($R^2 > 0.96$), the calculated maximum adsorption capacities (q_{max}) were significantly higher than the experimentally observed maximum adsorbed amounts. This discrepancy indicates that adsorption saturation was not reached within the concentration range studied, which limits the physical interpretability of the fitted parameters. Furthermore, although these models can be applied to multicomponent systems, the derived parameters should be considered apparent, since competitive interactions between solutes are not explicitly considered. In particular, the concept of maximum adsorption capacity loses relevance under such conditions, since adsorption sites are occupied simultaneously by multiple compounds. In contrast, the Freundlich model yielded the most consistent fit values for all antibiotics ($R^2 = 0.970\text{--}0.999$), providing the most accurate description of the experimental data across the entire concentration range (Fig. 3).

The exponent n was less than one for all compounds, indicating favourable adsorption on a heterogeneous surface. The K_F values, which reflect relative adsorption capacity and affinity, followed the order SMZ > CLDM > TMP > AMX (Table 3).

Table 3
Freundlich isotherm parameters obtained by nonlinear least-squares fitting for the adsorption of Group A antibiotics onto soil/PM199 (80:20, w/w)

AMX	K_F ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$)	n	RMSE (mg g^{-1})	R ²
	0.1600	0.6984	0.0024	0.9966
TMP	0.3295	0.8307	0.0162	0.9696
SMZ	0.4745	0.8279	0.0006	0.9992
CLDM	0.4222	0.7798	0.0020	0.9981

K_F : Freundlich adsorption capacity constant. Values of $n < 1$ indicate favourable adsorption onto a heterogeneous surface.

3.4 Modeling of competitive adsorption

To evaluate adsorption behaviour in the multicomponent system, competitive interactions among the four antibiotics in solution were examined using both component-based and global modelling approaches. The equations of the applied models are provided in the Supplementary Material (Table S5). The SRS model (Sheindorf et al., 1981) was adopted as the theoretical framework to describe solute interactions within the multicomponent system, as reviewed in the context of pharmaceutical adsorption (Amrutha et al., 2023; Girish et al., 2018) and applied in similar studies (Peñafiel & Flores, 2023). Additionally, a global Freundlich-based modelling approach was applied to describe the overall adsorption behaviour of the multicomponent system, following the methodology proposed by Cela-Dablanca et al. (2025).

A two-step modelling strategy was adopted. First, a simplified formulation of the SRS model was applied, assuming that $\alpha_{ij} = 1$, to capture the overall competitive effect by treating all solutes as contributing equally to site occupancy. Subsequently, the full SRS model was implemented to estimate the interaction coefficients (α_{ij}), which allowed for the evaluation of pairwise competitive effects among the antibiotics. This approach allows for the separation of global competitive effects from specific interactions between solutes, providing a more detailed interpretation of the adsorption behaviour of multiple components. Figure 4 presents an integrated overview of the main results obtained from SRS model fitting.

The adsorption isotherms under competitive conditions (Fig. 4A) show that the model satisfactorily reproduces the experimental behaviour of the four antibiotics, with the predicted curves closely following the trend of the experimental data over the entire concentration range. The representation of predicted versus experimental values (Fig. 4B) further confirms this agreement, with most data points located within the $\pm 15\%$ error band relative to the 1:1 line. Slight deviations are observed for AMX and TMP at low equilibrium concentrations. The comparison of individual and competitive Freundlich parameters (Fig. 4C) reveals a systematic reduction in the $K_{F, \text{comp}}$ coefficient under multicomponent conditions for all compounds, with decreases ranging from 29% to 35%, indicating the presence of competitive effects. The interaction factor matrix α_{ij} (Fig. 4D) shows values close to unity for most pairs (0.85–1.22), indicating that competition is present but relatively limited, with the TMP-CLDM pair ($\alpha_{\text{TRI, CLDM}} = 1.220$) exhibiting the most pronounced competitive interaction.

The quality of the model fit was evaluated using the goodness-of-fit parameters summarized in Table 4. High coefficients of determination were obtained for all compounds ($R^2 = 0.9775\text{--}0.9991$), indicating a high degree of agreement between the experimental and predicted values, while the low RMSE values confirm the model's ability to accurately reproduce the experimental data.

Table 4
SRS model parameters for the competitive adsorption of Group A antibiotics onto soil/PM199 (80:20, w/w)

AMX	$K_{F, \text{ind}}$	$K_{F, \text{comp}}$	ΔK_F	n_{ind}	n_{comp}	Δn	R ²	RMSE
	0.1600	0.1134	-29.1	0.6984	0.7204	+ 3.2	0.9969	0.01766
TMP	0.3295	0.2279	-30.8	0.8307	0.8027	-3.4	0.9775	0.04818
SMZ	0.4745	0.3302	-30.4	0.8279	0.8234	-0.5	0.9991	0.00974
CLDM	0.4222	0.2754	-34.8	0.7798	0.7882	+ 1.1	0.9976	0.01604

$K_{F, \text{ind}}$ and $K_{F, \text{comp}}$: Freundlich constants under individual and competitive conditions, respectively ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$); ΔK_F : relative change in K_F (%); n_{ind} and n_{comp} : Freundlich heterogeneity parameters; Δn : relative change in n (%), Bold values indicate R²; RMSE: root mean square error (mg g^{-1}).

To assess the extent of competitive interactions in the quaternary system in greater detail, a global modelling approach based on the Freundlich model was applied, following Cela-Dablanca et al. (2025). In this approach, the total equilibrium adsorption capacity (Q_e, T) is expressed as a function of the total equilibrium concentration ($C_{e, T}$), without explicitly accounting for interactions between solutes.

The global Freundlich model showed good agreement between experimental and predicted values ($R^2 = 0.9963$, RMSE = 0.0781), with fitted parameters $K_F = 0.2184$ and $n = 0.7898$. The comparable fitting quality and predictive performance relative to the SRS model, despite the absence of explicit interaction terms, indicate that competitive interactions among the four antibiotics are present but relatively limited and do not significantly alter the overall adsorption behaviour of the system.

4 Discussion

Preliminary experiments showed that the incorporation of PM199 significantly increased the removal efficiency of AMX, TMP, SMZ, and CLDM compared to unmodified soil. Specifically, the soil-PM199 mixture (80:20, w/w) showed an approximately threefold increase in AMX retention and a 1.2-fold increase in TMP retention, while CLDM showed a more pronounced increase, approximately 1.8-fold, compared to natural soil. The effect was particularly pronounced in the case of SMZ whose removal increased from very low values in the unamended soil to over 80%, representing an increase of nearly an order of magnitude. These results indicate that the system's retention capacity is strongly influenced by the nature of the incorporated adsorbent material. This behaviour is consistent with previous studies reporting greater adsorption of antibiotics in soils amended with clay materials or organoclays. For example, López-Cabeza et al. (2024), reported that the incorporation of a commercial organoclay (Cloisite® 10A) significantly increased SMZ adsorption compared to unamended soil. These findings highlight that soil amendment with functionalized clay materials can substantially improve the retention capacity of soils, potentially reducing the mobility of antibiotics in the environment.

These results can be explained by considering the properties of both the incorporated adsorbent and the soil. The FTIR spectrum of PM199 (Figure S1, Supplementary Material) confirms the presence of an organically modified silicate matrix that combines mineral surfaces with organic domains, thereby expanding the range of possible interaction mechanisms with antibiotics and enhancing the natural retention capacity of the soil. This type of organoclay has been widely used as an adsorbent in environmental remediation processes, including the immobilization of mercury species in contaminated soils and aquatic systems (Egbo et al., 2021; Goñez-Rodríguez et al., 2021; Muller et al., 2019).

To understand the mechanisms governing the adsorption process, the temporal evolution of antibiotic removal was analyzed using kinetic experiments. Analysis of the adsorption kinetics revealed two distinct behaviours among the antibiotics studied (Fig. 2). AMX, TMP, SMZ, and CLDM exhibited a biphasic uptake pattern, characterized by a rapid initial phase followed by a slower approach to equilibrium. This behaviour is consistent with multi-step mass transfer processes, in which an initial fast adsorption stage, mainly governed by external surface interactions, is followed by a slower stage controlled by intraparticle diffusion within the porous structure of the adsorbent (Wang and Guo, 2022).

This indicates that intraparticle diffusion contributes to the overall adsorption process, but it is not the only rate-limiting step. The best fit obtained with the PFO + PSO mixed model suggests that the overall kinetics result from the simultaneous contribution of two adsorption mechanisms operating at different rates: a fast initial component associated with the occupation of easily accessible external surface sites, and a slower component reflecting progressive diffusion toward higher-energy internal sites within the adsorbent's porous structure (Rudzinski and Plazinski, 2006). This biphasic kinetic behaviour is consistent with that described for SMZ and TMP in biochar-enriched media, where the rate constant for rapid adsorption was up to two orders of magnitude higher than that for slow adsorption (Liu et al., 2022).

In contrast, AZM, CIP, OFL, and TCN reached adsorption equilibrium in a considerably shorter time, with kinetic curves that plateaued within the first few minutes of contact, a behaviour that is adequately described by a simple PFO model. This behaviour suggests a mechanism dominated by the rapid occupation of high-affinity surface sites, in which diffusion processes, if any, occur on timescales that cannot be resolved under the experimental conditions applied. This contrasts with the findings of Wu et al. (2019), who reported that equilibrium for TCN and CIP on natural montmorillonite was reached within approximately 0.5 h and was better described by a PSO model, with both surface diffusion and intraparticle diffusion contributing to the overall rate-controlling mechanism. The organic modification of the clay in the present system may explain this difference, by favouring greater accessibility of active sites and broadening the range of interaction mechanisms — including hydrophobic interactions, π - π stacking, and Van der Waals forces — compared to unmodified clay (De Oliveira et al., 2020). With respect to equilibrium data, in individual isotherms the excellent fit to the Freundlich model ($R^2 = 0.992$ – 0.999) (Fig. 3) is consistent with the nature of the soil/PM199 system and suggests that adsorption occurs on an energetically heterogeneous surface with multiple types of active sites. The values of the heterogeneity parameter n for each of the evaluated antibiotics ranged between 0.69 and 0.83, indicating a favourable adsorption process in which higher-energy sites are preferentially occupied at low concentrations. This behaviour is characteristic of complex adsorbent systems such as modified soils and clay materials, where the coexistence of different mineral and organic phases generates a wide distribution of adsorption energies and multiple interaction mechanisms between antibiotics and the solid matrix (Cela-Dablanca et al., 2025; Franklin et al., 2022; Míguez-González et al., 2023). In contrast, the Langmuir and Sips models did not provide a physically meaningful interpretation of the system, since the estimated maximum adsorption capacities ($q_{\max}$) were higher than the experimentally observed values. This result suggests that saturation of the active sites was not reached within the evaluated concentration range, a situation frequently observed in heterogeneous adsorbent systems such as soils and amended materials, where the diversity of adsorption sites makes it difficult to define a clearly delimited maximum capacity (De Vargas Brião et al., 2023; Li et al., 2020; Perelomov et al., 2025).

The differences observed in adsorption affinity in this study, where the K_F values followed the order SMZ > CLDM > TMP > AMX, can be explained by the physicochemical properties of each antibiotic and their ionization state under the experimental conditions, factors that play a key role in adsorption processes in soil-solution systems (Alhalabi et al., 2024). SMZ showed the highest adsorption affinity in the mixture. Although this antibiotic often exhibits relatively high mobility in natural soils due to the predominance of its anionic form at near-neutral pH (De Mastro et al., 2022), its retention can significantly increase in amended systems, where modified surfaces and additional organic domains enhance adsorption processes (López-Cabeza et al., 2024). In the soil/PM199 system, the incorporation of the organoclay likely introduces additional organic domains associated with the presence of organic modifiers within the clay structure, as supported by FTIR analysis (Figure S1). These domains can promote hydrophobic interactions and van der Waals dispersion forces with organic compounds present in solution, resulting in a heterogeneous surface combining mineral and organic phases and enabling multiple interaction mechanisms. Consequently, SMZ, due to its aromatic structure, may also participate in π - π interactions and hydrogen bonding, whereas CLDM predominantly interacts through hydrogen bonding, hydrophobic interactions, and electrostatic forces depending on its speciation. This is consistent with adsorption mechanisms reported for SMZ in organoclay-based systems, where electrostatic interactions (including cation exchange), ion-dipole interactions, and hydrophobic forces have been identified as the main driving mechanisms (De Oliveira et al., 2018), as well as with early studies on clay minerals showing

that adsorption of ionizable pharmaceuticals is strongly governed by electrostatic interactions and speciation-dependent processes (Porubcan et al., 1978). These features explain the higher affinity observed for SMZ and CLDM, which can be attributed to the combined influence of aromaticity, functional groups, and, in the case of CLDM, the presence of protonable amine groups that favour electrostatic interactions. TMP showed intermediate affinity, whereas more polar compounds with multiple ionizable groups, such as AMX, exhibited lower affinity, likely due to reduced interaction with the hydrophobic domains of the adsorbent.

Multicomponent modelling indicates that adsorption in the soil/PM199 system is only weakly affected by competitive interactions among the antibiotics. The interaction coefficients close to unity (Fig. 4D) suggest that, despite the structural and physicochemical diversity of the four antibiotics, their simultaneous presence in solution results in limited mutual interference for sorption sites. Similar behaviour has been reported in soils with high organic content or complex mineralogy, where structural diversity among sorbates favours partitioning into distinct microenvironments rather than direct competition for shared sites (Kočárek et al., 2016; Schmidová et al., 2020). From an environmental perspective, the limited competitive effects observed suggest that the soil/PM199 system can effectively retain multiple antibiotics simultaneously without a substantial loss of adsorption efficiency for individual compounds under the studied conditions. This behaviour is particularly relevant in co-contamination scenarios, which are the rule rather than the exception in agricultural soils receiving treated wastewater or manure (Alhalabi et al., 2024).

The systematic reduction of $K_{F,comp}$ relative to $K_{F,ind}$ (29–35%) reflects an overall competitive effect in the quaternary system, whereby the simultaneous presence of the four sorbates reduces the apparent adsorption affinity of each individual compound. This behaviour is consistent with the theoretical framework of Sheindorf et al. (1891), in which interspecies competition is reflected through interaction terms and apparent affinity changes quantified by the competitive coefficients α_{ij} . The near-unity values of the α_{ij} matrix observed in the present study indicate weak and largely non-selective competition among the four antibiotics, with no single compound exerting dominant displacement over the others. Notably, the Freundlich heterogeneity parameter n showed negligible variation between individual and competitive conditions ($\Delta n < 4\%$), indicating that the energy distribution of active sites in the adsorbent is not significantly altered by the simultaneous presence of the four antibiotics. This behaviour suggests that each compound preferentially interacts with distinct energetic domains of the heterogeneous adsorbent surface, consistent with the multisite adsorption framework described by Koopal et al. (2020).

However, other studies have reported more pronounced competitive effects in multicomponent systems, where the simultaneous presence of different pollutants can alter individual adsorption due to competition for active sites and potential interactions between solutes on the adsorbent surface. This behaviour has been observed in systems based on agricultural waste materials, such as sugarcane bagasse, where decreases of 5–28% in adsorption capacity have been reported in multicomponent mixtures (Peñafiel et al., 2023), as well as in natural soil aggregate fractions, where reductions of 9–25% were detected in binary systems and even greater decreases in ternary systems (Lv et al., 2023). Additionally, global Freundlich-type approaches have been successfully applied to describe the overall behaviour of multicomponent systems, suggesting that total adsorption can be interpreted as the combined contribution of individual adsorption processes occurring on energetically heterogeneous surfaces (Cela-Dablanca et al., 2025). Overall, these results support the potential of soils enriched with organoclays as effective multi-component retention systems for antibiotic mixtures, offering a promising strategy for mitigating the environmental risk associated with antibiotic cross-contamination in agricultural soils irrigated with treated wastewater or enriched with organic waste.

5 Conclusions

The incorporation of the organoclay PM199 into the soil significantly increased the retention of antibiotics exhibiting a biphasic adsorption mechanism (AMX, TMP, SMZ, and CLDM), with statistically significant improvements relative to the unamended soil. The organomineral nature of the adsorbent broadens the range of available interaction mechanisms, which explains both the kinetic differences observed among the antibiotics and the order of affinity identified in the multicomponent system. The organomineral nature of the adsorbent broadens the range of available interaction mechanisms, accounting for both the kinetic differences observed among antibiotics and the affinity order identified in the multicomponent system. Modelling using the Freundlich isotherm, under both single-component and multicomponent conditions, demonstrated that adsorption in the soil/PM199 system occurs on an energetically heterogeneous surface with multiple active sites, where each antibiotic preferentially interacts with different sites, resulting in limited competitive interactions. Overall, these results highlight the potential of the soil/PM199 system as an effective strategy for the simultaneous retention of antibiotic mixtures, with important implications for mitigating environmental risks associated with antibiotic co-contamination in agricultural soils.

Declarations

Declaration of Competing Interest

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

Statement on generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of the present work, Google's Gemini AI (v.3.5), ChatGPT (v.5.5 Pro), DeepL, and DeepLWrite was used to assist with text translation, as well as to improve grammar and stylistic fluency for greater clarity. The Graphical Abstract was initially generated using the generative artificial intelligence features within BioRender.com. This visual element was subsequently post-processed, edited, and refined by the author using GIMP (GNU Image

Manipulation Program, 2.10.12) to ensure its accuracy with the central concepts of the manuscript. After using these tools and services, the author reviewed, verified, and edited the content as necessary and assumes full responsibility for the content of the published article.

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Author Contribution

U.G.-G.: Conceptualization, data curation, formal analysis, investigation, methodology, writing – original draft. C.M.: Conceptualization, formal analysis, investigation. J.M.: Conceptualization, supervision, validation. A.Z.-G.: Conceptualization, data curation, methodology, funding acquisition, project administration, supervision, writing – review & editing. All authors reviewed and agree with the content of this manuscript.

Data availability

Data will be made available on request.

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Figures

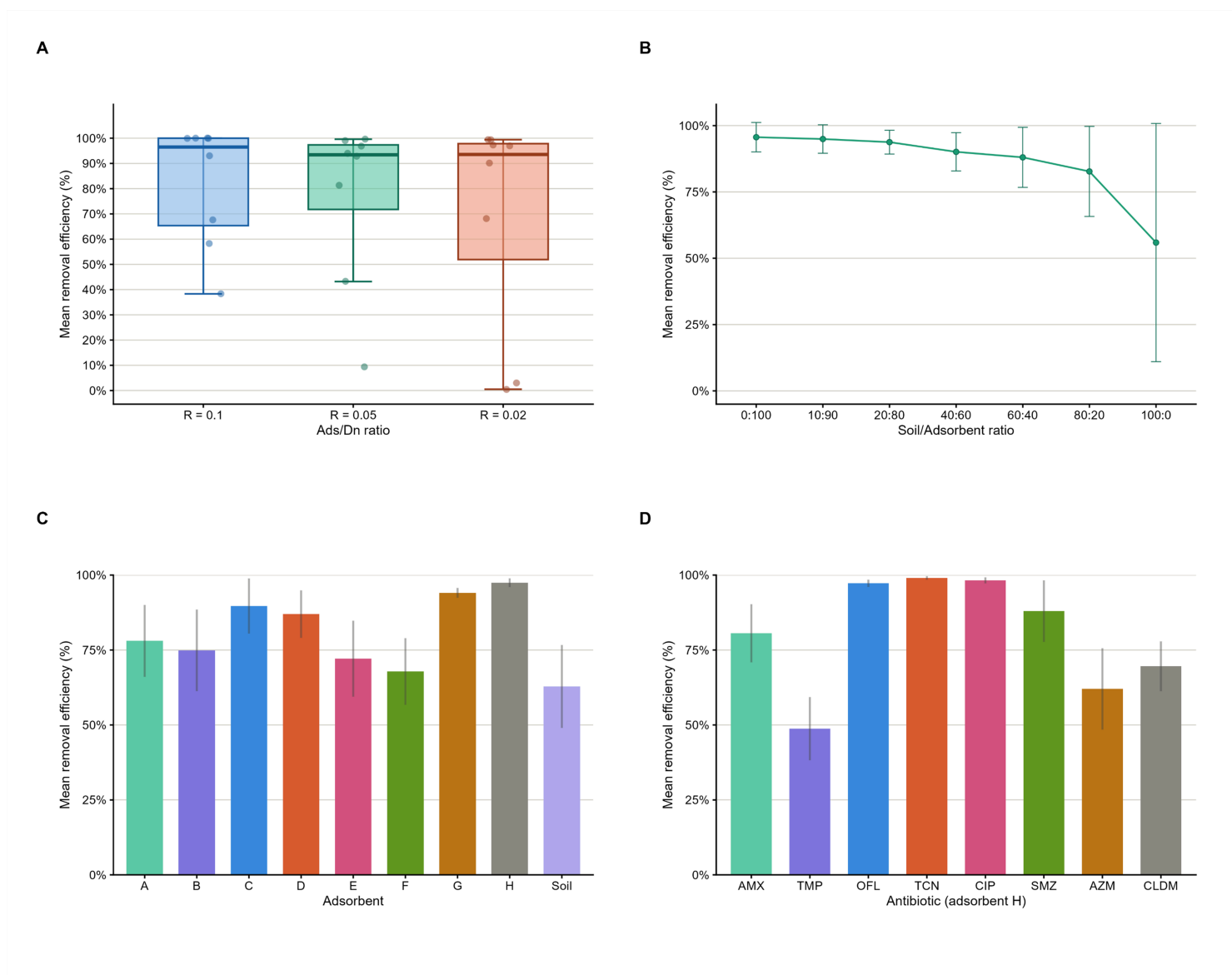


Figure 1

Removal efficiency of antibiotics under different experimental conditions: (A) preliminary screening of sorbent-to-solution ratio (Ads/Dn) using sorbent A as a representative material at an initial concentration of 2.5 mg L^{-1} for all antibiotics, (B) influence of soil/sorbent ratio on removal efficiency using sorbent H, at initial concentrations of 10 mg L^{-1} (AMX) and 5 mg L^{-1} (TMP, SMZ, CLDM), (C) comparison of removal performance among adsorbents (A–H) and soil, and (D) antibiotic-specific removal efficiencies using adsorbent H.

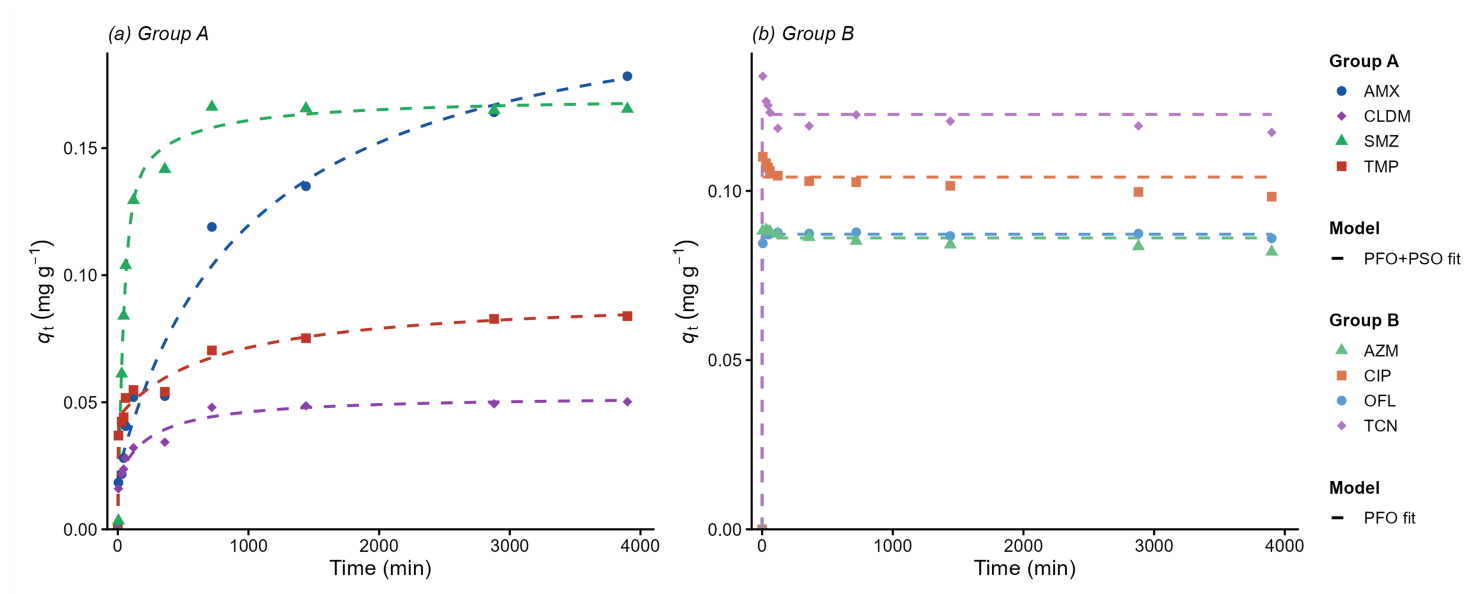


Figure 2
Adsorption kinetics of antibiotics in the soil/PM199 system over time: (A) Group A showing biphasic behaviour fitted with the PFO+PSO model and (B) Group B showing rapid equilibrium behaviour fitted with the PFO model.

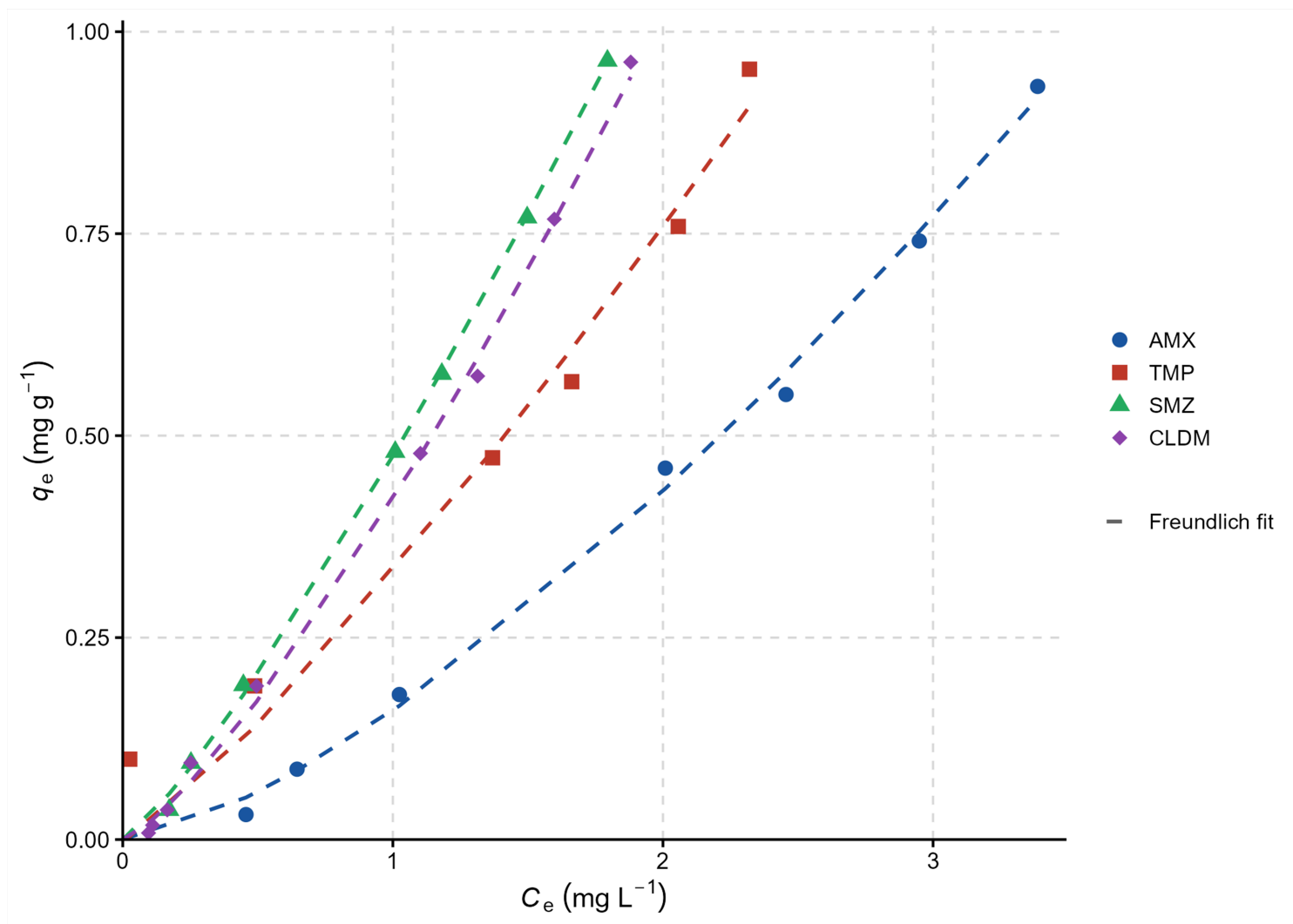


Figure 3

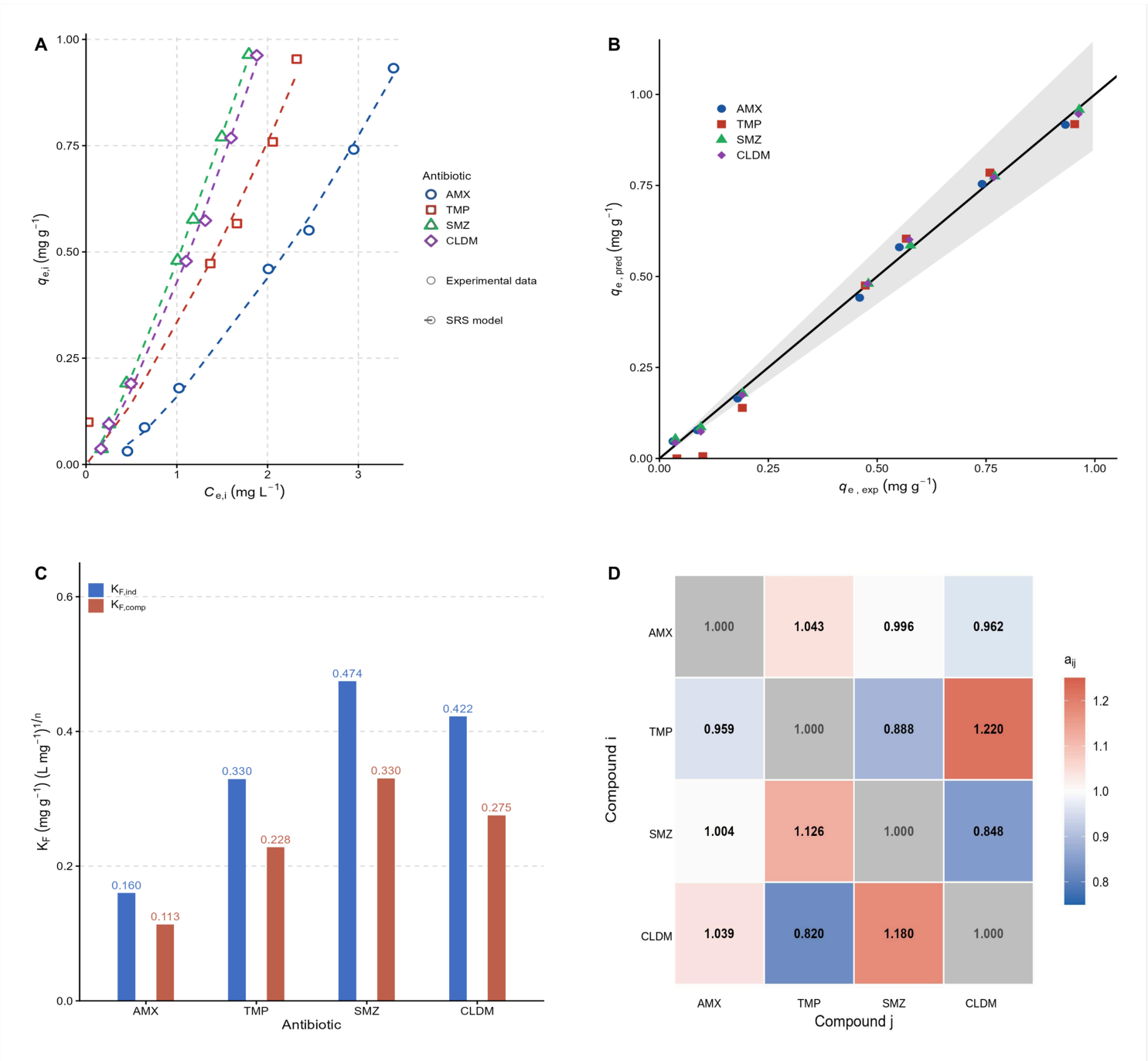


Figure 4

Multicomponent adsorption behaviour in the soil/PM199 system: (A) adsorption isotherms fitted with the SRS model, (B) model validation (predicted vs. experimental values), (C) comparison of Freundlich coefficients under individual and competitive conditions, and (D) interaction coefficients (α_{ij}).

Supplementary Files

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