



Research article

Natural and modified clays as low-cost and ecofriendly materials to remove salinomycin from environmental compartments

Samiha Hamdi^{a,b,c}, Ainoa Míguez-González^b, Raquel Cela-Dablanca^b, Ana Barreiro^{b,*}, María J. Fernández-Sanjurjo^b, Avelino Núñez-Delgado^b, Esperanza Álvarez-Rodríguez^b

^a Department of Biotechnology, Faculty of Science and Technology of Sidi Bouzid, University of Kairouan, 9100, Sidi Bouzid, Tunisia

^b Department Soil Science and Agricultural Chemistry, Engineering Polytechnic School, University of Santiago de Compostela, 27002, Lugo, Spain

^c Laboratory of Nutrition – Functional Foods and Health (NAFS)-LR12ES05, Faculty of Medicine, University of Monastir, Avenue Avicenne 5019, Monastir, Tunisia



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ABSTRACT

Antibiotics in the environment represent a substantial pollution threat. Among these emerging pollutants, ionophore anticoccidials are of special concern due to their potential ecological impact, persistence in the environment, and role in promoting antimicrobial resistance. To investigate the adsorption/desorption of the ionophore antibiotic salinomycin (SAL) on/from raw and modified clay adsorbents, batch-type experiments were performed using 0.5 g of clay adsorbent mixed with 10 mL of increasing doses of SAL solutions for each sample, at room temperature, with a contact time of 24 h. All measurements were conducted in triplicate employing HPLC-UV equipment. Three different natural (raw) and modified clay samples were investigated, which were denominated as follows: AM (with 51% calcite), HJ1 (with 32% kaolinite), and HJ2 (with 32% microcline). The experiments were carried out using three pH ranges: between 3.33 and 4.49 for acid-activated clays, 8.39–9.08 for natural clays, and 9.99–10.18 for base-activated clays. The results indicated that, when low concentrations of the antibiotic were added (from 5 to 20 $\mu\text{mol L}^{-1}$), more than 98% of SAL was strongly adsorbed by almost all clays, irrespective of the physicochemical and mineralogical composition of the clays or their pH values. When higher SAL concentrations were added (40 and 100 $\mu\text{mol L}^{-1}$), the adsorption of the antibiotic showed pH-dependent ligand adsorption mechanisms: (i) highly decreased as the pH raised (for the raw and base-activated AM and HJ1 clays), while (ii) slightly decreased as the pH decreased (on the acid-activated clays). Among the adsorption equations tested (Freundlich, Langmuir, and Linear), the Freundlich model was identified as the most suitable for fitting the data corresponding to SAL adsorption onto the studied clays. SAL desorption from clays was consistently below 10% for all the clay samples, especially for the acid-activated clays, due to cation bridging adsorption mechanisms, when the lowest concentration of the antibiotic was added. Additionally, it should be stressed that the desorption values can increase with rising SAL concentrations, but they always remain below 20%. Overall, the clays here investigated (both raw and modified) provide a cost-effective and efficient alternative for the removal of the veterinary anticoccidial antibiotic SAL, with potential positive and practical implications in environmental remediation and antibiotic pollution management, particularly by serving as amendments for contaminated soils to enhance their adsorption capacities against SAL. Additionally, using these clays in water treatment processes could improve the efficiency of mitigating antibiotic contamination in aquatic systems.

1. Introduction

Despite several issues related to the worldwide use of a substantial volume of antibiotics, notably the development of antibiotic resistance, these compounds currently play a pivotal role in the prevention, diagnosis, mitigation, and cure of infectious diseases in both humans and

animals (Banin et al., 2017). In this regard, therapeutic, prophylactic, and growth-promoting applications are attributed to veterinary antibiotics (Park et al., 2016; Rahman et al., 2022; Tabashsum et al., 2023). With the increasing prevalence of antibiotic use, there is a growing apprehension about their widespread environmental emergence and impact (Díaz-Cruz and Barceló, 2005; Kemper, 2008; Kulik et al., 2023).

* Corresponding author.

E-mail address: ana.barreiro.bujan@usc.es (A. Barreiro).

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Part of these pharmaceutical products are excreted after ingestion, with excretion being the major route through which these products reach the environment as pollutants (Chaturvedi et al., 2021). For example, Qiu et al. (2016) estimated that pigs excreted between 36 % and 87 % of administered sulfonamides.

In addition, these contaminants can accumulate extensively in municipal wastewater treatment plants (WWTPs) effluents since they are inefficiently removed from most of these treatment facilities. Consequently, using WWTP-purified water to irrigate crops can lead to the transfer of antibiotics into water systems and agricultural soils (Piña et al., 2020). In fact, the advancement of analytical techniques has revealed the widespread presence of pharmaceuticals in water environments, as evidenced by numerous studies (Yang et al., 2011; Uslu et al., 2013; Tahiri et al., 2023; Khan and Barros, 2023; Paiga et al., 2024). Similarly, veterinary antibiotics can reach soils through sewage sludge, animal manures, and slurries widely applied as fertilizers in agricultural crops (Gros et al., 2019; Kominko et al., 2024). Subsequently, this contamination can enter the food chain, raising several health concerns (Wu et al., 2021). In fact, the emergence and spread of antimicrobial resistance in bacteria due to the high consumption of these pharmaceutical products in veterinary and agricultural sectors represent a threat to both human and animal health and result in high financial costs (EFSA, 2005; Ahmed et al., 2024).

These concerns have prompted investigations into the sources, behavior, fate, risks, and control measures associated with these emerging pollutants (Manaia, 2022; Hansima et al., 2023; Kamilya et al., 2023; Nguyen et al., 2023; Zhang et al., 2023), including anticoccidial molecules (Furtula et al., 2012).

Among anticoccidial antibiotics, polyether ionophores like Lasalocid A, Salinomycin, and Semduramicin, widely employed in veterinary medicine, show high toxicity (Ekinci et al., 2023) compared to other antibiotics. Taking Lasalocid as an example, its lethal dose to 50% of study population (LD50) in adult rats is much lower (100 mg/kg) than the LD50 for chlortetracycline (10,800 mg/kg) or sulfamethazine (1600 mg/kg) (Hardmann et al., 1997).

Specifically, salinomycin (SAL) is a polyether antibiotic that acts as an ionophore. This antibiotic has been proved to have efficacy against gram-positive bacteria (Antoszczak and Huczyński, 2019), mycobacteria, and certain fungi, and is commonly used in veterinary medicine as an antiprotozoal agent in treating coccidial infections in poultry, caused by coccidia parasites (Chapman, 2018; Spišáková et al., 2024). In fact, manure from animals treated with ionophore antibiotics like SAL may be applied to soils as a fertilizer (Schlüsener et al., 2006; Cha and Carlson, 2018). When SAL is applied to soil, it may exhibit varying degrees of adsorption, depending on soil properties (such as pH, organic matter content, clay content, and cation exchange capacity). Soil pH can impact SAL adsorption in a variable degree, as indicated by Hussain and Prasher (2011) and by Jayashree et al. (2021, 2024). Some of these authors observed an inverse effect of pH on the sorption potential of SAL in soil samples, consistent with trends reported for monensin and lasalocid (Sassman and Lee, 2007; Hafner and Parikh, 2020). Specifically, at higher pH levels, a decrease in sorption kinetics was observed, contradicting the typical trend expected for acidic chemicals beyond their pK_a values (Hussain and Prasher, 2011; Jayashree et al., 2024).

Also relevant, a substantial amount of these compounds presents in the soil solution because of its high persistence (Ramaswamy et al., 2012), can pass into water resources. This contamination has the potential to propagate to animals and humans through drinking water, posing relevant challenges (Van Assen, 2006; Holliman et al., 2011; Markiewicz et al., 2014; Pietruk et al., 2018).

Currently, there is insufficient data available regarding the toxicity of SAL (Scherzad et al., 2015; Ekinci et al., 2023), with some studies reporting effects on humans due to accidental ingestion (Story and Doube, 2004; Li et al., 2010), and other dealing with animals (Radko and Olejnik, 2018), such as calves (Omidi et al., 2010), and pigs (De Carvalho et al., 2021; Wang et al., 2023). Recent studies indicate that it is

highly probable that moderate human exposure to SAL occurs through the consumption of animal products (Scherzad et al., 2016; Chiodowska et al., 2024; Spišáková et al., 2024).

Consequently, the presence of SAL in water bodies (Kim and Carlson, 2006; Hussain et al., 2012; Chauhan and Punia, 2023) and different soils (Ramaswamy et al., 2012; Jayashree and Prasher, 2017; Jayashree et al., 2024) has raised questions about its adsorption behavior, mobility, and the potential risks it poses to ecological balance. Furthermore, its complex molecular structure and chemical properties make it a challenging pollutant to manage and remove from environmental matrices, leading to significant interest and concern among researchers.

In response to these concerns, research based on various eco-friendly strategies, such as adsorption, oxidation, filtration, and photodegradation, has been directed to remove antibiotics, particularly from contaminated water and wastewater (Zhang et al., 2008; Verlicchi et al., 2012; Li et al., 2023a, 2023b). Among these strategies, the adsorption process, using low-cost and eco-friendly materials, emerged as one of the most promising approaches for addressing this ecological issue (Anastopoulos et al., 2020; Liu et al., 2022; Vinayagam et al., 2022; Míguez-González et al., 2023), also related to the promotion of recycling, sustainability and circular economy (Biava et al., 2024; Núñez-Delgado et al., 2023; Roy et al., 2021). One of the most developed low-cost adsorbents are clay-based materials, which demonstrate significant potential for adsorbing concentrated emerging pollutants present in water (Eniola et al., 2023) and wastewater (Gharbi-Khelifi et al., 2023), and have been widely used as efficient adsorbents for pharmaceuticals (Kryuchkova et al., 2021), particularly antibiotics (Septian et al., 2018; Hacıosmanoğlu et al., 2022; Adhikary et al., 2023), both as raw material or activated.

Despite the continuous development of new sorbents for water remediation, particularly those employed in the removal of antibiotics, clays are still considered efficient adsorbents. This is attributed to their abundance in nature, low-cost, simple application, and, most importantly, high adsorption capacities. In this field, Tunisia benefits from abundant clay resources, with deposits widely distributed across the country (Lafi et al., 2016; Mosbahi et al., 2017), positioning them as valuable resources with widespread utility across various industries (Baccour et al., 2008; Bousset et al., 2016). Additionally, these clays can be applied in environmental remediation, serving as effective agents in the removal of contaminants (like antibiotics) from water and wastewater through adsorption processes (Gharbi-Khelifi et al., 2023).

Previous studies indicated that Tunisian clays have remarkable efficiency in antibiotics removal, specifically for tetracycline (TC) (Hamdi et al., 2024a) and sulfadiazine (SDZ) (Hamdi et al., 2024b), surpassing other low-cost adsorbents (Aslan and Şirazi, 2020; Islam et al., 2023; Said et al., 2024). Their unique porous structure and high surface area provide abundant binding sites for antibiotics, enhancing adsorption capacities (Hamdi et al., 2024a). Additionally, the ion exchange properties of clay minerals contribute to their efficiency in removing antibiotics from aqueous solutions (Hacıosmanoğlu et al., 2022). In general, the adsorption of antibiotics such as SAL onto clays could be a promising solution for effectively removing these contaminants from various environmental compartments.

Taking this background into account, the present study was designed with the following objectives: i) analyze the SAL adsorption capacity of three different Tunisian clays (both natural and modified) from an artificially contaminated aqueous solutions under experimental conditions; ii) shed further light on the adsorption mechanism affecting SAL retention onto these materials; and iii) explore the effects of the activation processes applied to raw clays to eventually increase the adsorption capacity of this ionophore antibiotic.

2. Material and methods

2.1. Clays

The Maknessy-Mazzouna basin (Sidi Bouzid, Central Tunisia), is a geologically significant region that has garnered attention for its diverse

and complex geological features (Mosbahi et al., 2017; Jaballi et al., 2019) (Fig. 1).

For the current research, three different raw clays were sampled in a variety of geographic areas in the Maknessy-Mazzouna basin (Center-western Tunisia), with some basic details about their physicochemical and mineralogical properties presented in Supplementary Material

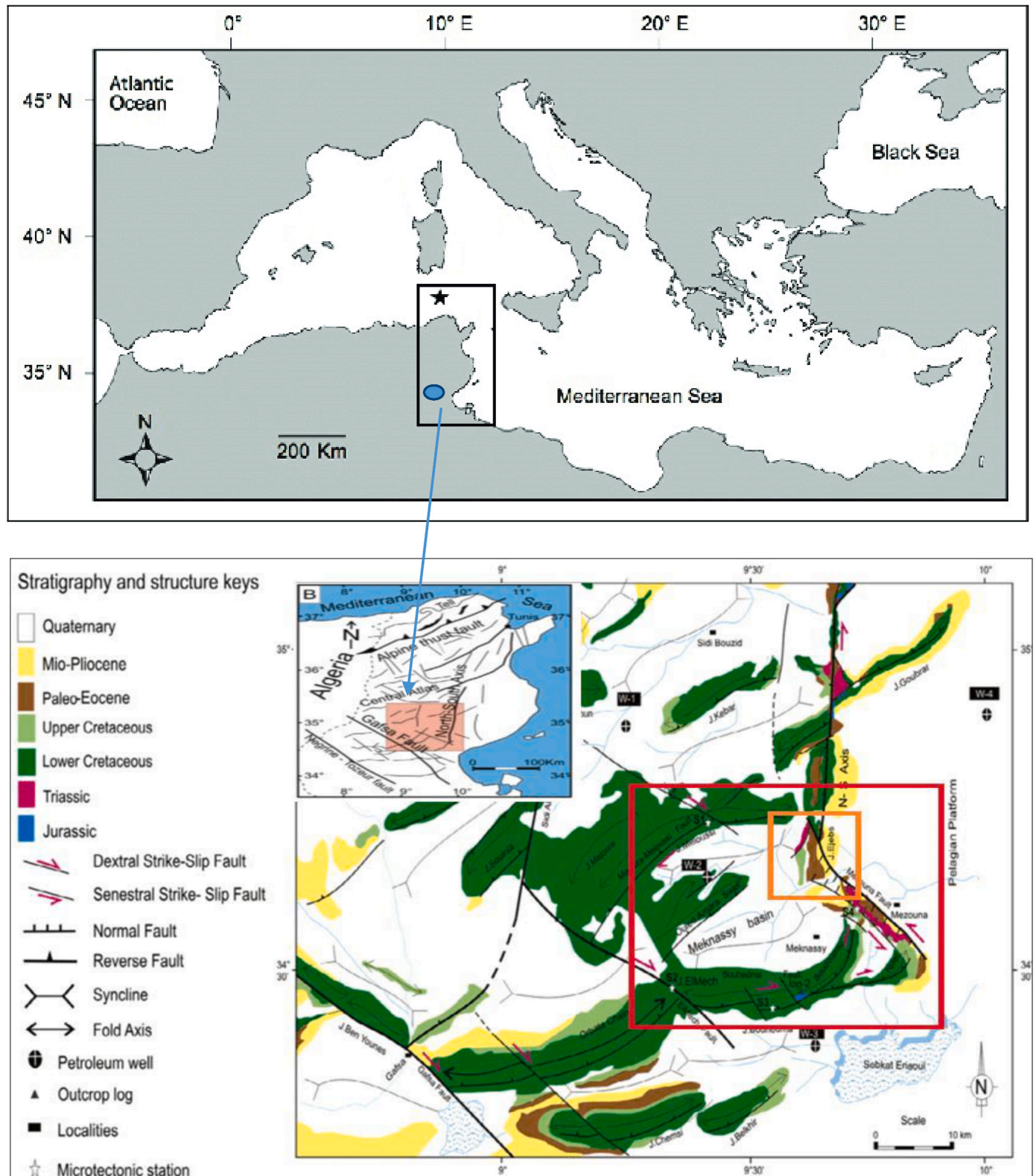


Fig. 1. Geological maps of the study area showing the location of the Mekkassy-Mezzouna basin in Sidi Bouzid, Center-Western of Tunisia (Lafi et al., 2016).

(Tables S1 and S2), and previously described by Hamdi et al. (2024a, b). Among the three clays used, two were from Jbel Jebess, Maknessy: i) HJ1, which was taken at the top of the El Haria formation, located on the West of Jebel Jebbes El Meheri (Maknessy); ii) HJ2, sampled from the Chouabine formation (lower Eocene), located in the lithological section situated in Oued Errizgui (Jebel Meheri El Jebbes-Maknessy); and iii) AM, which is derived from Jbel Mazzouna, specifically from the Aleg formation. The sampling method was previously described by Hamdi et al. (2024a). Samples were taken in summer to avoid the impact of humidity on the clay materials.

Once at the laboratory, and previously to be stored for further study, all clay samples were washed to eliminate impurities, dried (at 60 °C) and then sieved through a 50 µm mesh (Hamdi et al., 2024a, 2024b).

2.2. Chemicals and reagents

Salinomycin (SAL) is synthesized by *Streptomyces albus* (ATCC 21838). It is weakly acidic (Miyazaki et al., 1974; Scherzad et al., 2013; Lu et al., 2016; Li et al., 2021) and has a specific chemical structure (Fig. S1, Supplementary Material). It has a molecular formula of C₄₂H₇₀O₁₁, with Table 1 showing its physicochemical characteristics (EFSA, 2004; Schlüsener et al., 2006; Sassman and Lee, 2007; Hussain et al., 2012; Zhu et al., 2017).

SAL was provided as PX-Salinomycin, 35 g/kg, a mixture commercialized for being added to animal feed/treatment. Additionally, analytical reagent grade or high purity chemicals, methanol, CaCl₂, acetic acid, Trichloroacetic (TCA) and 2,4-Dinitrophenol (DNP), were purchased from Sigma- Aldrich (Madrid, Spain).

2.3. Basic and acid activation of the clays

The basic and acid activation procedures used for the chemical modification of the studied clay samples were detailed in a previous publication (Hamdi et al., 2024a).

Briefly, for the basic activation process, 1.5 g of solid sodium carbonate (Na₂CO₃) was mixed with 30 g of clay sample. Subsequently, the mixture of clay and Na₂CO₃ was soaked in 300 mL of distilled water and then, stirred for 1 h at 75 °C (Mosbahi et al., 2017; Gharbi-Khelifi et al., 2023; Hamdi et al., 2024a, 2024b).

A similar procedure was followed for acid activation, with slight differences, notably the time of agitation, which was 4 h for acid activated instead of 1 h for basic activation. As for the acid activation, 24.84 mL of hydrochloric acid (HCl) were added to 100 mL of distilled water. Subsequently, 33.3 mL of this solution were added (separately) to 30 g of the purified powder for each type of clay and stirred continuously for 4 h at 75 °C (Hamdi et al., 2024a).

2.4. Analysis of the clay adsorbents

The following physicochemical characteristics were measured in all natural (raw) clay samples: pH (in H₂O); Electric Conductivity (EC, dS m⁻¹); total C, O, Na, Mg, Al, Si, P, Cl, K, Ca, Cu, Ti, and Fe contents;

effective cation exchange capacity (eCEC) and exchangeable Ca, Mg, Na, and K cations (in cmol_c kg⁻¹). The results obtained are detailed in Tables 2 and 3 as well as in Table S1 (Supplementary). All the methods are detailed in Supplementary Material.

Furthermore, scanning electron microscopy (SEM) (Oxford instruments, UK) characterization was carried out for the current research to reveal the surface morphology, porous structure, and geometric shapes of the clay particles (Fig. 2). This analysis was performed at medium magnification levels, with scale bars of 250 µm for HJ2 clay and 500 µm for AM and HJ1 clays. For the modified clays, pH_w, and EC values, as well as the exchangeable Al, Ca, K, Mg, and Na contents (expressed in cmol_c kg⁻¹) were determined. Relevant characteristics of the modified clays used in the present work are provided in Tables 2 and 4. It is important to note that all these analyses were conducted at room temperature (25 ± 2 °C) without adjusting the pH. More details regarding the methodology are provided in Supplementary Material.

The mineral contents in the three raw clays were quantified by means of X-ray diffraction (Philips PW1710 diffractometer, The Netherlands) and the results (shown in Table S2, Supplementary Material) were previously described by Hamdi et al. (2024a).

2.5. Adsorption-desorption experiments

To investigate adsorption, batch-type experiments were conducted as described in a previous study (Hamdi et al., 2024a). This methodology is considered a part of the first steps in a wider and extended protocol to be implemented in future complementary phases (Núñez-Delgado, 2024a). Briefly, aliquots of 0.5 g of clay were weighed in 50 mL centrifuge tubes (Deltalab, Spain) and suspended in 10 mL of solution of the studied ionophore antibiotic (SAL), at 6 different concentrations (between 5 and 100 µmol L⁻¹), all of these containing 0.005 M CaCl₂ as the ionic background electrolyte.

Subsequently, the resulting suspensions were agitated for 48 h in the dark, using a rotary shaker (SIR EM-SA, motor: 220V, N1: 2700 rpm, N2: 48 rpm), at 50 rpm, and at room temperature (25 ± 2 °C), without pH adjustment, working at "natural" (unmodified) values. Previous kinetic studies had indicated that 48 h were sufficient to achieve equilibrium for other ionophore antibiotics such as monensin and lasalocid (Sassman and Lee, 2007) and was reported as well as the time used to reach equilibrium for the antibiotic amoxicillin when adsorbed into soils and various biosorbents (Cela-Dablanca et al., 2022a). Preliminary unpublished data from our laboratory showed that it is time enough to reach equilibrium for this and other ionophore antibiotics (such as monensin), with the adsorbent materials under study.

Hence, the adsorption samples were then centrifuged for 15 min at 4000 rpm. Following centrifugation (performed using a Rotina 35R centrifuge, Hettich Zentrifugen, Tuttlingen, Germany), the samples were filtered through 0.45 µm nylon syringe filters (Fisher Scientific, Madrid, Spain). The pH of the studied samples was also determined via combined glass micro-electrode (Crison, Barcelona, Spain). The concentrations of SAL in the equilibrium solution were determined by means of HPLC-UV, using 2 mL capacity Eppendorf propylene vials (Fisherbrand, Madrid,

Table 1

Main physicochemical characteristics of the antibiotic SAL. K_{oc}: organic carbon partition coefficient; K_{ow}: octanol-water coefficient of partition.

Molar weight (g mol ⁻¹)	Molecular Formula	Solubility in water (mg L ⁻¹)	pK _a	Stability	Produced by	Log K _{oc}	Log K _{ow}	Melting point
751 ^c	C ₄₂ H ₇₀ O ₁₁ ^c	57 to 905 ^a	4.4 ^{d,e}	Unstable in Acidic condition, stable in alkaline condition ^c	<i>Streptomyces albus</i> ^c	2.2 to 2.8 ^a	5.15 ^a >6.2 ^b	112.5–113.5 °C

^a [Anonymous, 2004].

^b [EFSA, 2004].

^c [Hussain et al., 2012].

^d [Sassman and Lee, 2007].

^e [Schlüsener et al., 2006].

Table 2

pH in water (pH_w) and electrical conductivity (EC) values for the different raw and activated clays (AM, HJ1, and HJ2). Average values (n = 3), with coefficients of variation always <5%.

	AM	HJ1	HJ2	AM + base	HJ1+base	HJ2+base	AM + HCl	HJ1+HCl	HJ2+HCl
pH _w	9.08	8.7	8.39	10.00	9.99	10.18	4.49	4.21	3.33
EC (dS m ⁻¹)	495	459	446	42.4	30.1	44.4	3.62	3.03	4.17

Table 3

Results of the EDXS analyses for the three raw clays in two different zones (methodological details provided in Supplementary Material).

Samples	Statistics	C (%)	O (%)	Na (%)	Mg (%)	Al (%)	Si (%)	P (%)	S (%)	Cl (%)	K (%)	Ca (%)	Ti (%)	Fe (%)	Cu (%)
AM raw	Max (spectrum 6)	50.71	50.18	1.44	0.83	7.36	14.58	0.05	0.22	0.41	0.51	5.19	0.44	2.96	0.07
	Min (spectrum 5)	15.88	33.97	0.66	0.32	2.98	5.85	0.05	0.12	0.17	0.24	2.90	0.21	1.69	0.06
	Average	33.29	42.08	1.05	0.58	5.17	10.21	0.05	0.17	0.29	0.38	4.05	0.32	2.32	0.07
	Standard Deviation	24.63	11.46	0.56	0.36	3.09	6.17	–	0.07	0.17	0.19	1.61	0.16	0.89	0.01
HJ1 raw	Max (spectrum 8)	25.14	50.37	0.98	1.82	8.51	20.53	0.09	0.20	0.18	1.10	2.13	0.47	4.09	0.13
	Min (spectrum 7)	10.24	44.34	0.72	1.22	6.40	14.43	0.09	0.16	0.14	0.92	1.37	0.35	3.87	0.10
	Average	17.69	47.35	0.85	1.52	7.45	17.48	0.09	0.18	0.16	1.01	1.75	0.41	3.98	0.12
	Standard Deviation	10.53	4.26	0.18	0.43	1.49	4.31	–	0.03	0.03	0.13	0.54	0.08	0.15	0.02
HJ2 raw	Max (spectrum 10)	17.24	46.51	0.61	1.68	7.18	18.49	1.58	0.29	0.15	0.99	5.56	0.49	4.44	0.13
	Min (spectrum 9)	16.52	46.40	0.61	1.45	5.94	15.80	0.15	0.22	0.13	0.83	2.56	0.38	3.56	0.11
	Average	16.88	46.46	0.61	1.57	6.56	17.14	0.87	0.26	0.14	0.91	4.06	0.43	4.00	0.12
	Standard Deviation	0.51	0.07	0.00	0.17	0.87	1.91	1.01	0.05	0.02	0.11	2.12	0.08	0.62	0.02

Spain). The amount of antibiotic adsorbed in the clays was calculated by subtracting the initially added antibiotic concentration from the concentration remaining in the solution after reaching equilibrium (48 h).

For the desorption study, the same clay samples which were initially employed in the adsorption tests were weighed to determine the remaining solution content in the clay. Subsequently, the clay was re-suspended in 10 mL of 0.005 M CaCl₂. These clay samples underwent shaking, centrifugation, filtration, and analysis following the same procedure outlined for the adsorption phase (Hamdi et al., 2024a, 2024b). All the determinations were performed in triplicate.

2.6. Quantification of SAL

Prior to the quantification analysis, a derivatization process was performed to enhance the detectability of the SAL antibiotic by the UV detector (Dusi and Gamba, 1999). Firstly, 100 µL of trichloroacetic acid (TCA) was added to 700 µL of each adsorption/desorption sample, and the mixtures were rapidly agitated. Secondly, after a 10-min incubation period, a volume of 200 µL of 2,4-dinitrophenol (DNP) acid was added, and the samples were agitated once again before being placed in an oven at 50 °C for 20 min. Finally, SAL was quantified in the filtered and previously prepared supernatants (0.45 µm), employing a HPLC-UV Thermo Scientific Ultimate 3000 equipment (model LPG 3400 SD, Thermo-Scientific, USA). More details about this equipment are include in the Supplementary Material. During these measurements, the samples were run with an isocratic method, with a single phase composed of methanol (88.5%), water (10%), and acetic acid (1.5%), with a flow rate set at 1 mL/min. The injection volume was 200 µL with a total time of analysis of 25 min and the retention time for SAL was 11.25 min, using 392 nm as wavelength. The syringe was rinsed with the running solution between each measurement. All these determinations were conducted at room temperature (25 ± 2 °C) and in triplicate.

2.7. Modeling and statistics

Data from the adsorption-desorption experiments were fitted to various models: Freundlich, Langmuir, and Linear. More details are shown in Supplementary Material.

After performing adsorption and desorption calculations, the hysteresis index (HI) was determined using Eq. (1), a formula previously described by Liang et al. (2022):

$$HI = (q_a^D - q_a^S) / q_a^S \quad (1)$$

where q_a^S (in µmol kg⁻¹) represents the concentration of SAL retained in the clay adsorption experiments, and q_a^D (in µmol kg⁻¹) is defined as the final SAL concentration after the desorption experiments.

SPSS 21 was the software used for models fitting and for statistical analyses, specifically one-way ANOVA ($p < 0.05$; $n = 9$), followed post-hoc tests (Tukey and Duncan) to examine the

pH effect on adsorption-desorption behavior of SAL on the studied clays.

3. Results and discussion

3.1. Clays characteristics

Scanning electron microscopy (SEM) analyses followed by Energy Dispersive X-ray Spectroscopy (EDXS) were performed for each raw clay sample, as illustrated in photographs included in Fig. 2. The surface of the AM sample (Fig. 2 (A)) appeared to be highly compact and with irregularly shaped particles. However, the surface of the HJ1 and HJ2 samples (Fig. 2 (B and C, respectively)) had larger size pores between the particles compared to AM. Moreover, the surface of the AM clay appeared to be formed by several flaky particles accumulated together in form of agglomerates.

Additionally, the chemical composition of these materials is represented in Table 3. The analyses provided an estimation of the clay's porosity, particularly for HJ1 clay ($P = 36.4\%$) (Fig. 2), and the richness of clays in total carbon (average values between 16.88 and 33.29%), particularly for AM clay. Also, shown are the values for total oxygen (42.08–47.3%), silicon (10.21–17.48 %, with the highest value for HJ1 raw clay), and the values for Al (5.17–7.45 %), with slight variability among the three raw clay samples.

Furthermore, as shown in Table 4, the chemical composition of the activated clays (not previously described) indicates that acid-activated clays had a higher content of exchangeable Ca, with the highest value noted for HJ2+HCl (55.221 cmol_c kg⁻¹). In contrast, base-activated clays and HJ2+HCl clays predominantly contained exchangeable Na. As indicated in a previous study (Hamdi et al., 2024a), the raw clays have Ca contents ranging from 6.91 to 25.85 cmol_c kg⁻¹, with the highest value noted for the AM raw clay (Table S1, Supplementary). These values were lower than those obtained for acid-activated clays (38.373–55.221 cmol_c kg⁻¹) and higher compared to those observed for the base activated clays (8.359–8.980 cmol_c kg⁻¹). Concerning Na contents in the raw clays, they were higher for AM (61.34 cmol_c kg⁻¹)

AM raw

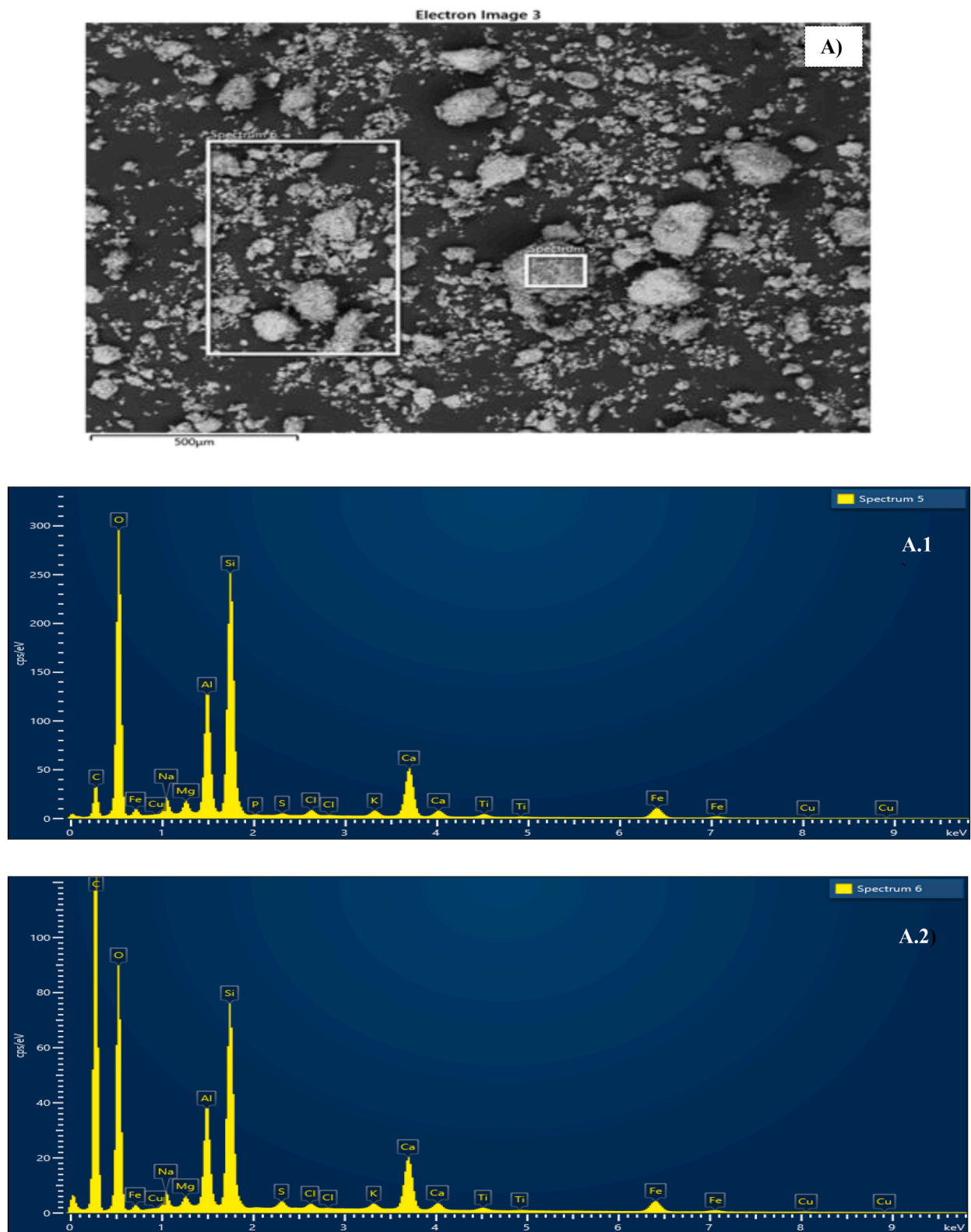


Fig. 2. Scanning electron microscopy images corresponding to the natural (raw) clay samples (A, B, C) and examples of their elemental compositions (A.1, A.2; B.1, B.2; C.1, C.2) determined by EDXS (methodological details provided in Supplementary Material)

HJ1 raw

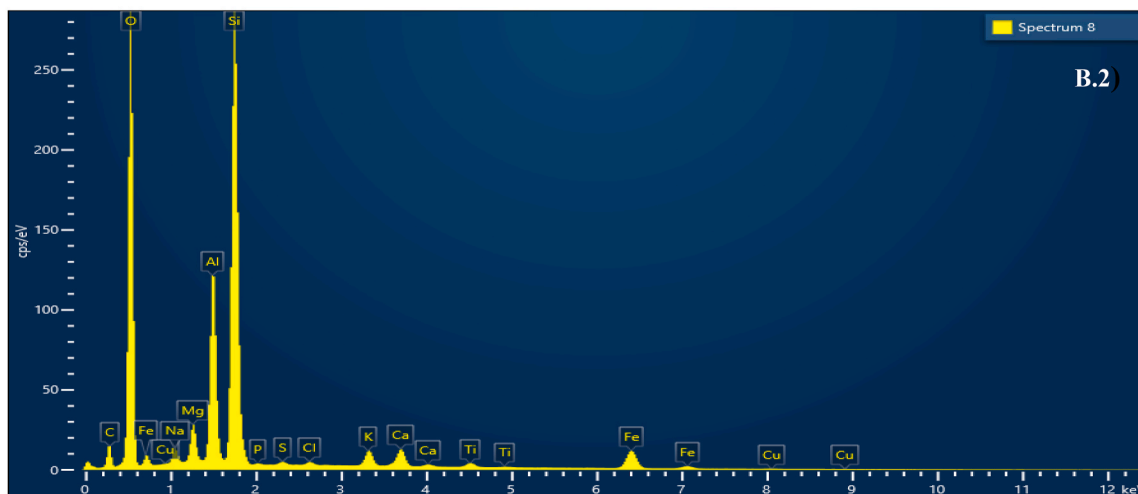
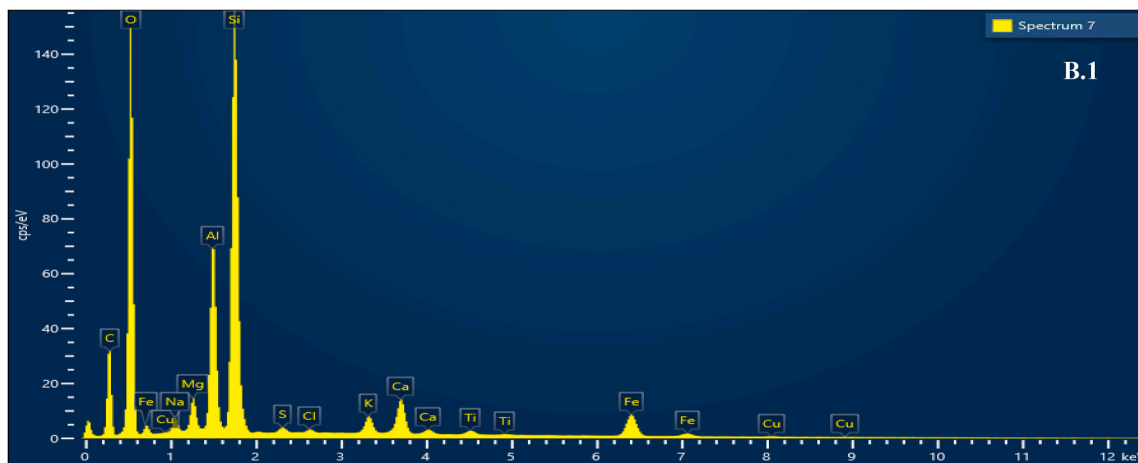
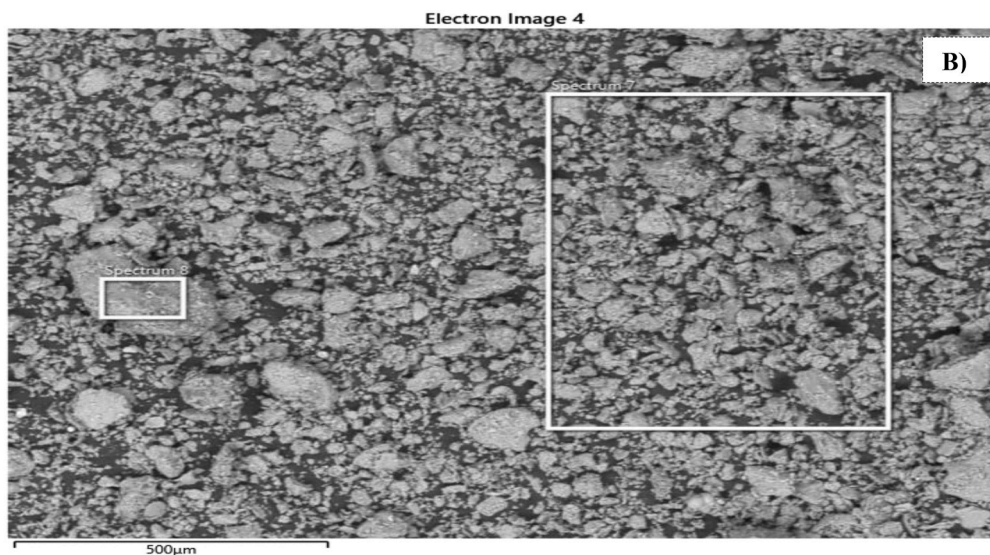


Fig. 2. (continued).

compared to modified clays, while both HJ1 and HJ2 raw clays were considered poorer in Na (35.75 and $19.74 \text{ cmol}_c \text{ kg}^{-1}$, respectively), as it was the case for the acid-activated clays (15.213 – $28.737 \text{ cmol}_c \text{ kg}^{-1}$).

Notably, all the modified clays were poorer in Mg contents (9.223 – $15.154 \text{ cmol}_c \text{ kg}^{-1}$, with the lowest Mg value observed for the HJ2+HCl clay) compared to HJ1 and HJ2 raw clays (Table S1,

HJ2 raw

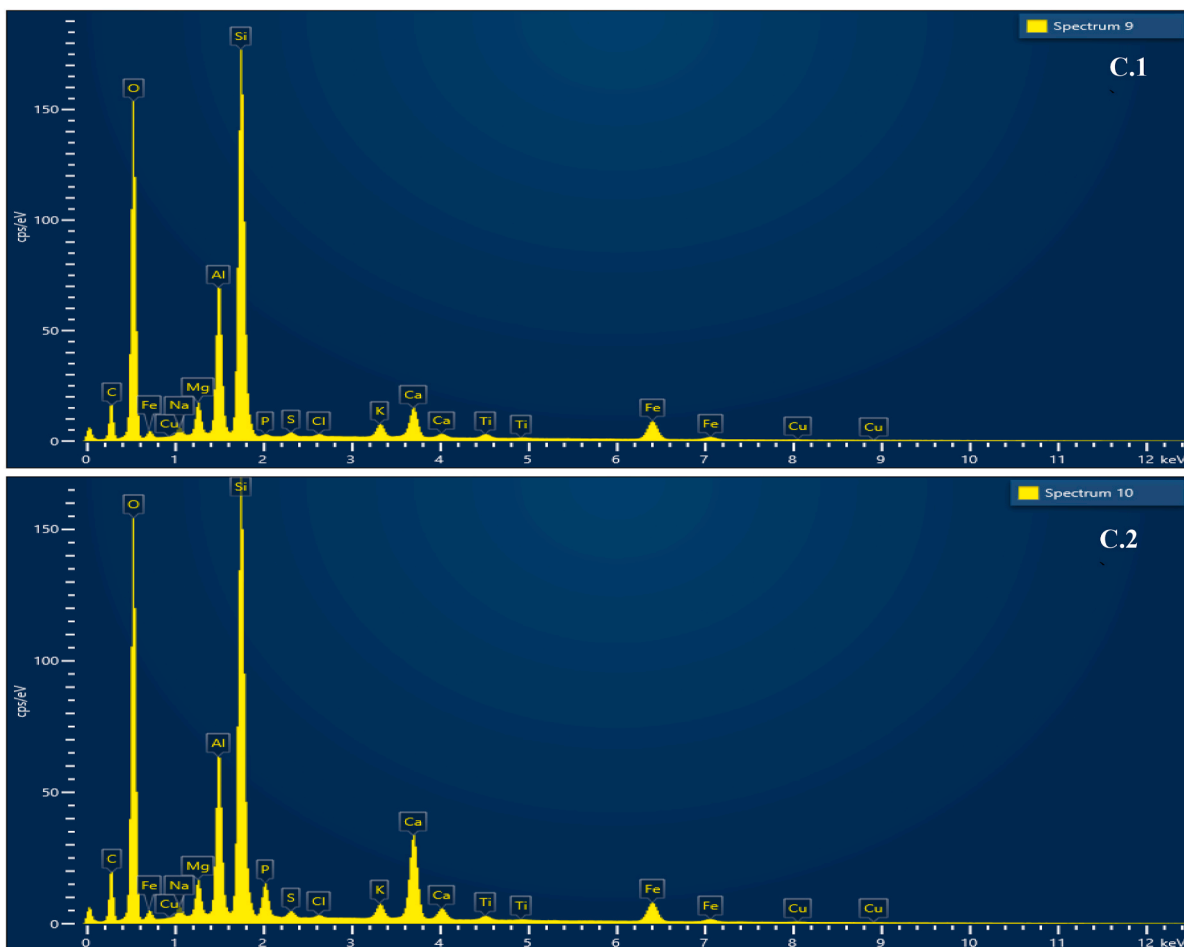
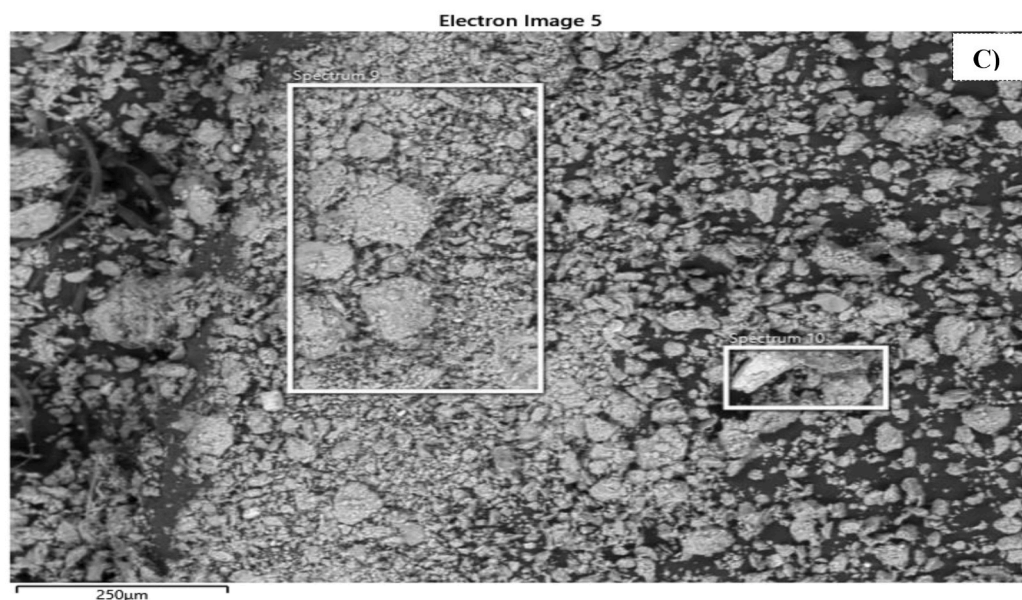


Fig. 2. (continued).

Supplementary; Table 4). Similarly to the raw clays, both acid- and base-activated clays exhibited low Al contents, ranging from 0.003 to 0.182 $\text{cmol}_c \text{kg}^{-1}$, with the highest values noted for HJ2+base clay

(Table 4). However, these values were still lower than those of the raw clays listed in Table S1 (Supplementary). Furthermore, the potassium (K) contents, ranging from 1.515 to 11.238 $\text{cmol}_c \text{kg}^{-1}$, with the lowest

Table 4

Chemical characteristics of the activated clays. Average values (n = 3) with standard deviation between brackets.

Clay samples	Al	Ca	K	Mg	Na	eCEC
	(cmolc kg ⁻¹)					
AM + base	0.005 (0.011)	8.980 (0.972)	3.099 (1.075)	12.224 (0.923)	37.712 (18.458)	62.021
AM + HCl	0.0095 (0.003)	48.04 (12.535)	1.515 (0.813)	13.193 (1.817)	15.213 (4.844)	77.97
HJ1+base	0.003 (0.001)	8.359 (1.418)	9.517 (2.754)	14.195 (1.656)	40.601 (10.232)	72.677
HJ1+HCl	0.115 (0.001)	38.373 (16.452)	10.881 (0.499)	13.54 (3.084)	17.823 (2.964)	80.732
HJ2+base	0.182 (0.00)	8.721 (1.023)	11.238 (3.006)	15.154 (1.299)	42.02 (9.106)	78.316
HJ2+HCl	0.0035 (0.001)	55.221 (4.418)	5.779 (2.214)	9.223 (3.635)	28.737 (5.105)	98.308

value noted for AM + HCl, were generally higher compared to those obtained for the natural (raw) clays (2.21–5.62 cmolc kg⁻¹). Similarly, the highest effective cation exchange capacity (eCEC) values were observed for the acid-activated clays (77.970–98.308 cmolc kg⁻¹), compared to the base-activated clays (62.021–78.316 cmolc kg⁻¹), with the HJ2+HCl clay exhibiting the highest eCEC value (Table 4).

3.2. Potential of the studied clays to adsorb SAL

Adsorption curves (adsorbed amounts of SAL in $\mu\text{mol kg}^{-1}$ as a function of equilibrium concentration in SAL solutions, in $\mu\text{mol L}^{-1}$) for the three raw and modified clays are shown in Fig. 3. Most of the clay samples exhibit a L-type curve, not linear, with a concave shape (Giles et al., 1974), indicating that SAL has a high affinity for the adsorption sites at low initial concentrations added, while adsorption (in $\mu\text{mol kg}^{-1}$) decreases with the rise in the antibiotic concentration added, due to the lower availability of vacant sorption sites (Rangabhashiyam et al., 2014).

The adsorption capacity differs depending on the type of clay. The adsorption curves for base-activated clays tend to be more linear (Fig. 3), though they can also be considered type L, but with a much lower slope compared to those of the other clay samples. These curves align with those obtained previously for the adsorption of the antibiotic tetracycline onto these same clays (Hamdi et al., 2024a). However, they differ to the linear curves corresponding to the adsorption of sulfadiazine also using the same clay samples (Hamdi et al., 2024b).

Figures S2a and S2b (Supplementary Material) show SAL adsorption (expressed in $\mu\text{mol kg}^{-1}$, and as percentage) onto the three raw and modified clays versus the initial concentrations of the ionophore antibiotic added (expressed in $\mu\text{mol L}^{-1}$). Specifically, as observed in Figure S2a, the amount adsorbed generally increases with the rise in the concentration of SAL added, while the total percentage adsorbed decreases. This is attributed to the progressive saturation of the adsorption sites in the clays as higher concentrations of antibiotics are added, as happens for other antibiotics such as some in the group of tetracycline (Avisar et al., 2010). This study was performed under pH = 7.2 using montmorillonite clay as adsorbent, and showed the high capacity if this clay to adsorb tetracycline antibiotics but a very low capacity to adsorb sulfonamide antibiotics.

The maximum SAL adsorption values in our study are in the range 48.83–1180.9 $\mu\text{mol kg}^{-1}$ in natural (raw) clays, between 45.76 and 922.9 $\mu\text{mol kg}^{-1}$ in base-activated clays, and between 50 and 1621.91 $\mu\text{mol kg}^{-1}$ in acid-activated clays. In the acid-activated clays, particularly in the case of HJ2+HCl and HJ1+HCl, the adsorption values are higher, reaching 1280.99 and 1621.91 $\mu\text{mol kg}^{-1}$, respectively, especially when the highest SAL concentrations are added (from 40 to 100 $\mu\text{mol L}^{-1}$) (Fig. S2a, Supplementary). In fact, the adsorption data (in $\mu\text{mol kg}^{-1}$) indicates that the acid-activation of clays can enhance their

adsorptive capacities for SAL, especially in case of HJ2+HCl. This clay has a pH ≤ 5.5 (specifically, a pH value of 3.33), an EC value above 4, and high Ca and Na contents (55.221 and 28.737 cmolc kg⁻¹, respectively), with the highest value of eCEC reaching 98.308 cmolc kg⁻¹.

The adsorption percentages of SAL consistently remain high, ranging between 71.80 and 100% for the lowest concentrations of antibiotic added (from 5 to 20 $\mu\text{mol L}^{-1}$) in natural clays, between 37.47 and 100 % in base-activated clays, and between 92.2 and 100 % in acid-activated clays (Fig. S2b, Supplementary). According to Figure S2b, for the highest antibiotic concentration added, the highest adsorption percentages were observed for natural and acid-activated HJ2 clays (around 68.33 and 93.1%, respectively), revealing a decrease in SAL adsorption as the added concentrations increased. It should be noted that raw and acid/base activated HJ2 clays were the most efficient in removing SAL in all cases, compared to raw and modified AM and HJ1 clays. This became more evident when the highest concentrations of the added antibiotic were used (ranging from 40 to 100 $\mu\text{mol L}^{-1}$).

This can be explained essentially by the predominance of microcline (32%) in this clay, a mineral absent in the other two clays. The high surface area characterizing the HJ2 clay (approximately 158 m² g⁻¹), its high eCEC value (80.65 cmolc kg⁻¹) (Table S1, Supplementary), and its high kaolinite and sepiolite contents (25% and 13 %) (Table S2, Supplementary) may also play a crucial role in the improving of its adsorptive characteristics (Hamdi et al., 2024a, 2024b). Essington et al. (2010) reached maximum adsorption values of 1770–4200 $\mu\text{mol kg}^{-1}$, depending on the pH, for the antibiotic chlortetracycline on pure kaolinite, meanwhile our results showed maximum SAL adsorption for the clay with high kaolinite content (HJ2) with a value of 1180.9 $\mu\text{mol kg}^{-1}$. The acid-activation of this clay can lead to the increase of porosity and its surface area, as showed by Panda et al. (2010) with kaolinite treated with sulfuric acid.

Additionally, for the natural AM and HJ1 clays, acid-activation played a significant role in enhancing their capacity to adsorb contaminants, since it could further expand the interlayer distance of clays by leaching of cations and subsequently weakening interlayer forces (Zhou et al., 2021). In general, the acid activation process can generate additional acidic sites on the surface of clay materials while maintaining their layered structure. This leads to a gradual evolution of the structural properties of clays (Zhou et al., 2021; Hamdi et al., 2024b), including an increase in their specific surface area and the optimization of pore size within these materials.

In this context, recent findings emphasize the significant role of cation exchange in antibiotic adsorption, providing insights into the intricate interactions between these pharmaceutical compounds and clays (Hamdi et al., 2024a), since different clay types adsorb antibiotics through a wide array of interactions such as van der Waals forces, competitive adsorption, H-bonding, electrostatic force or ion-exchange mechanisms (Mangla et al., 2022).

It is relevant to note that base-activated clays consistently exhibited the lowest adsorption capacities across the SAL concentrations, likely due to its basic pH values, which were equal to 9.99, 10.00, and 10.18, respectively, for HJ1+base, AM + base, and HJ2+base clays (Table 2). In the present study, adsorption data for SAL reveal that cation bridging could be a predominant mechanism for sorption onto acid-modified clays, this confirmed by the stronger adsorption capacities observed in acid-activated clays compared to raw and base modified clays, due to their high cation contents, especially for Ca (in the case of the HJ2+HCl clay reaching 55.221 cmolc kg⁻¹), which can function as a chelating agent.

Specifically, it has been suggested that the adsorption of ionophore antibiotics such as SAL onto mineral and solid substrates like soils, and particularly clay soils, could undergo pH-dependent ligand exchange mechanisms and the formation of surface complexes (Sassman and Lee, 2007; Jayashree et al., 2011). During the adsorption process, the interplay between the pH values of the equilibrium solution (Table S3, Supplementary) and the cation exchange capacities of clays (Table S1,

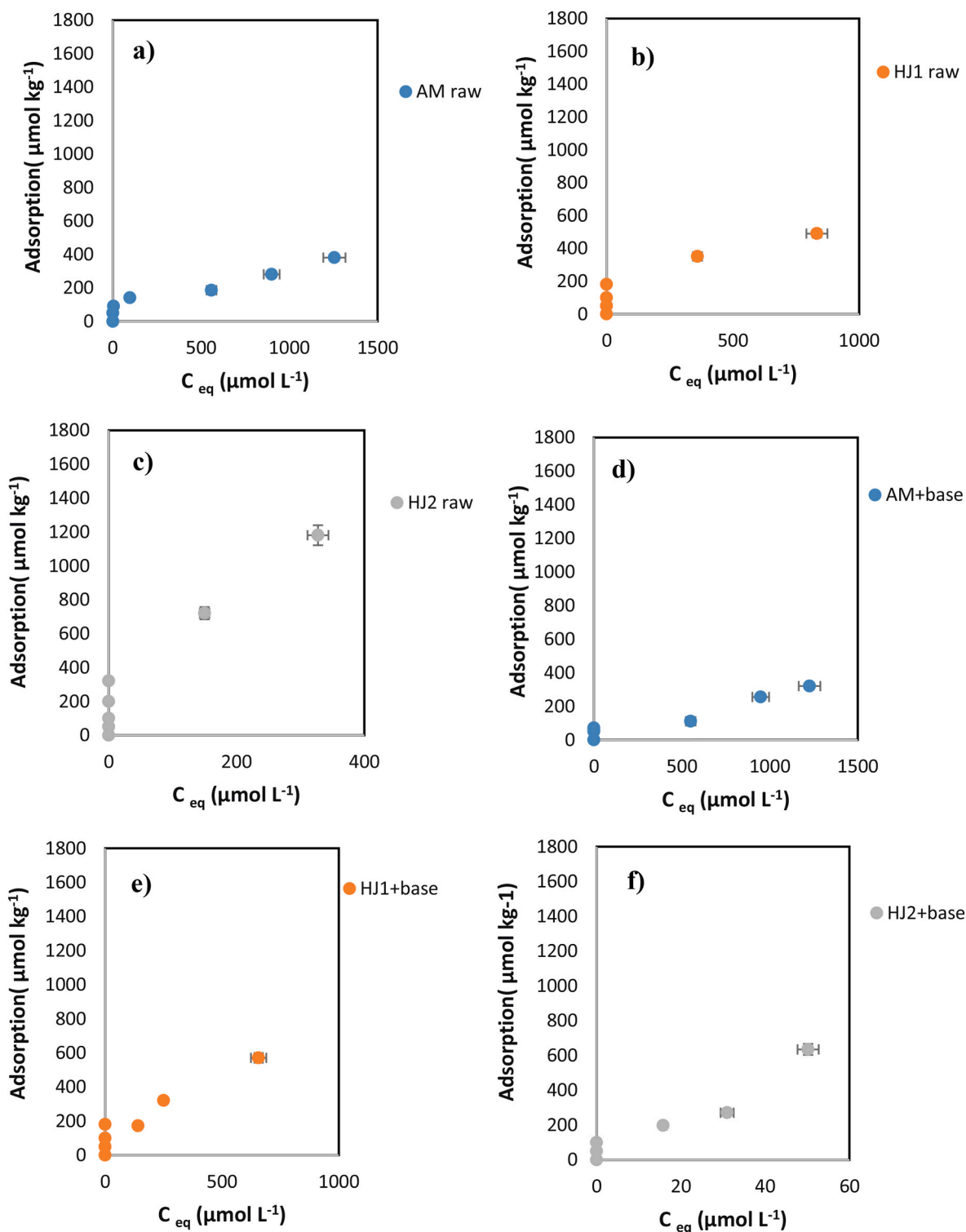


Fig. 3. Adsorption curves for SAL corresponding to the different raw (a,b,c), base activated (d, e, f) and acid activated (g, h, i) clays under study. Average values ($n = 3$), with coefficients of variation always $<5\%$. Adsorption tests conditions: 0.5 g of clay with 10 mL of 0.005 M CaCl_2 solutions containing from 0 to 100 $\mu\text{mol L}^{-1}$ of SAL, shaking for 48 h in the dark and at $25 \pm 2^\circ\text{C}$ at 50 rpm, then centrifuging ($4000\times g$) and filtering by 0.45 μm before HPLC quantification.

Supplementary) can be seen as influential in the adsorption of SAL onto the studied clays, as previously indicated by Jayashree et al. (2011) for SAL retention onto clay soils. When evaluating the impact of the pH of the adsorption solution, it was observed that it had a significant effect on the adsorption behavior of SAL as regards the studied clays, indicated by one-way ANOVA analyses ($p = 0.02$) and further confirmed by Tukey

and Duncan tests ($p = 0.022$ and $p = 0.026$, respectively).

In the present study, the investigated ionophore antibiotic, SAL, is characterized by a $\text{pK}_a < 7$ (Table 1) (Sassman and Lee, 2007; Schlüsener et al., 2006). This indicates that each molecule carries positive charge in a neutral medium ($\text{pH} = 7$), where SAL molecules exist in a protonated form (Sun et al., 2016). When the pH of the equilibrium solution is acidic

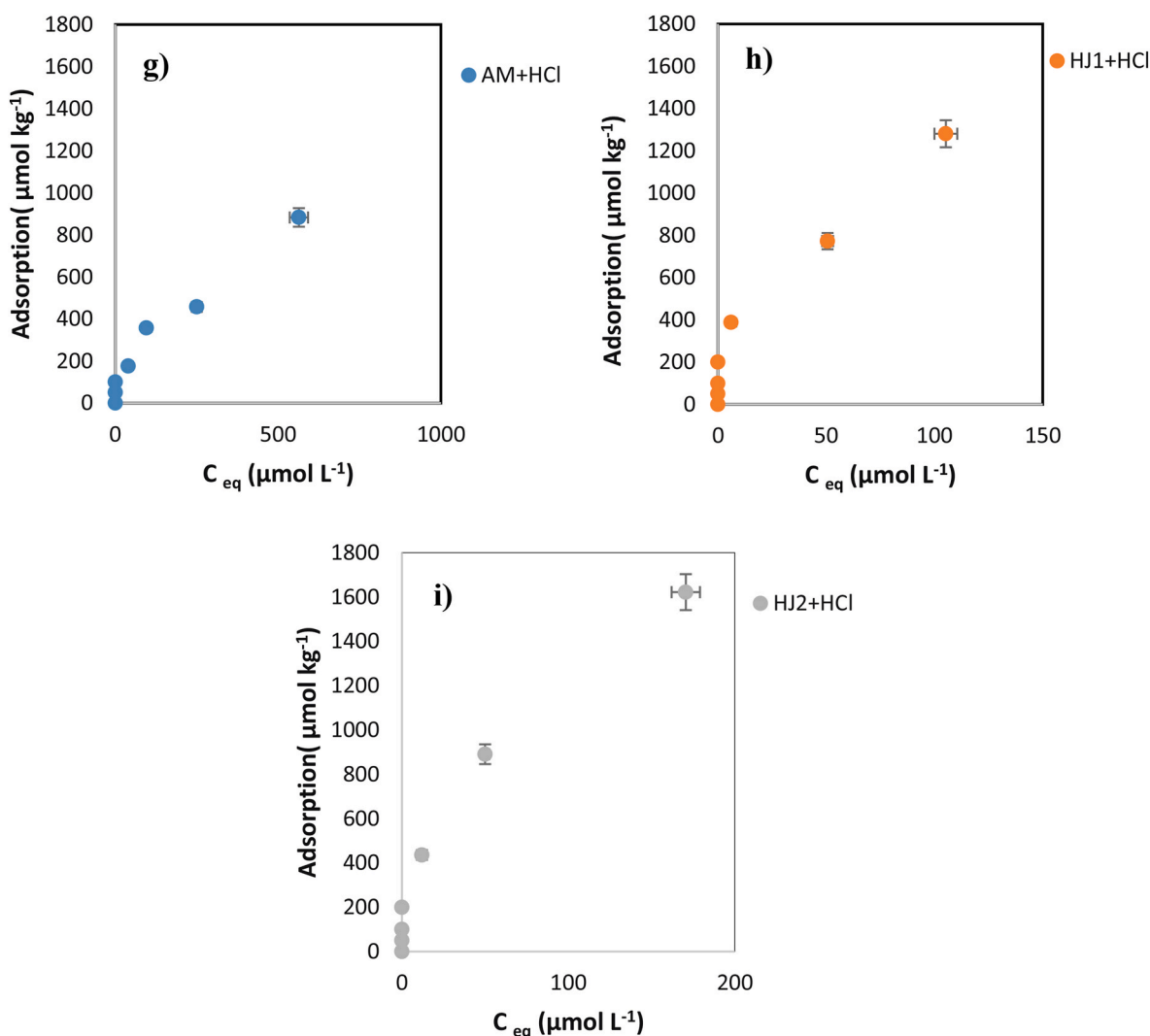


Fig. 3. (continued).

(so, for SAL, $\text{pH} < \text{pK}_a$) as observed in case of acid-activated clays, with pH values ranging from 5.99 to 6.8 (Table S3, Supplementary), molecules like SAL would primarily exist in a protonated form (Kinashi et al., 1975; Miao et al., 2003) due to the gained proton (H^+) (Miao et al., 2003; Jędrzejczyk et al., 2022). Notably, clay surfaces consistently exhibit a negative charge which highly interact with SAL molecules in their protonated forms, facilitating the adsorption process and leading to the formation of the adsorptive layer (mono or multilayer). Therefore, these findings can explain the high adsorption capacities of acid-activated clays compared to those noted for natural and base activated clays at the highest concentrations of SAL used, due to the increment in the external surface area of the clay and introduction of permanent mesoporosity (Hart and Brown, 2004) and the fact that acid activated clays have amorphous, porous, protonated and hydrated silica with a three-dimensional cross-linked structure (Komadel, 2016).

During adsorption, various functional groups present in the SAL molecule have the potential to interact with clay surfaces. Specially, i) Hydroxyl (-OH) and carboxyl (-COOH) groups, participate, respectively, in hydrogen bindings and electrostatic forces, facilitating the progress of adsorption (Mitani et al., 1975); ii) the lactone and polyether cycles (Rutkowski and Brzezinski, 2013), crucial for the ionophoric properties, contribute by interacting with clay particles; iii) carbonyl groups engage in specific interactions with clay surfaces, thereby enhancing adsorption; and finally, iv) alkyl chains influence the solubility of SAL and its interaction with solid surfaces, but their contribution to adsorption may

be less pronounced compared to the functional groups previously mentioned. Globally, the ionophoric nature of SAL, involved in transporting its molecules through clay layers, notably influences their adsorption behavior onto clays, with interactions between these ionophoric regions and the active sites on clay surfaces.

In summary, it can be affirmed that the acid activated clays here studied can be seen as suitable for helping in SAL remediation, especially in water systems, as they efficiently adsorb moderate concentrations of SAL, widely present in the aquatic environment, in both their natural and activated forms. Municipal, hospital animal feedlots, or rural wastewater serve as the primary route for pharmaceutical compounds entering fresh water or marine environment (Focazio et al., 2008; Matamoros et al., 2008; Anderson et al., 2013; Carvalho et al., 2013; Li et al., 2014). A previous study conducted by Gharbi-Khelifi et al. (2023) focused on the adsorption potential of the same clay samples used here for wastewater treatment, and the results found showed that these clays are capable of simultaneously removing a variety of pollutants, including microbes (such as *Staphylococci*, *E. coli*, *Salmonella* and fungi) and physicochemical contaminants (such as suspended solids, chloride, and phosphorus). However, there are no studies on the adsorption of salinomycin from wastewater using these Tunisian clays and the current work can be considered as a first step for further experiments to evaluate SAL adsorption in competing systems. Furthermore, future work would be needed to shed light on in-depth mechanisms governing the retention (and release) processes taking place. Additionally, the adsorption results

from this research suggest that scaling up the acid activation procedure for these clays is feasible for removing SAL from wastewaters and livestock effluents on a larger scale.

3.3. Modeling SAL adsorption

Table 5> presents the fitting of the experimental adsorption data to the Freundlich, Langmuir, and Linear models. Considering the coefficient of determination (R^2) values and the errors associated, SAL adsorption shows a better fit to the Freundlich model in most clay samples. Even though the R^2 values for the Langmuir model are not low (≥ 0.601) the errors associated are too high to allow the adjustment in several cases. The Linear model has higher coefficients of determination (≥ 0.714) compared to the Langmuir model, and show errors values not too high in any case. In all the samples that fit the Freundlich model, the R^2 values are higher than 0.923.

In a previous study, Hamdi et al. (2024a) obtained the best fit for the adsorption of tetracycline onto the same clays with the Sips model (with R^2 values > 0.844), compared with the Freundlich and Langmuir models, but the adjustment was not satisfactory for the samples of the present study.

In the current study, as regards the Freundlich model, the calculated K_F values range between 10.352 and 145.333 $L^n \mu mol^{1-n} kg^{-1}$, with a mean value of 62.874 $L^n \mu mol^{1-n} kg^{-1}$. For base-activated clays (with pH range of 9.99–10.18), K_F values were lower (10.352–30.849 $L^n \mu mol^{1-n} kg^{-1}$) than those of natural (17.153–128.367 $L^n \mu mol^{1-n} kg^{-1}$) and acid-activated clays (57.593–145.333 $L^n \mu mol^{1-n} kg^{-1}$), showing lower adsorption, which can also be influenced by factors such as the type of clay.

Other authors have noted that adsorption of some ionophore antibiotics, like lasalocid (LAS) and monensin (MON), onto soil samples adjusted well with the Freundlich model, with K_F ranges of 7.75–237 and 0.94–42.7 $L^n \mu mol^{1-n} kg^{-1}$ respectively for LAS and MON (Sassman and Lee, 2007). Concerning the values of n parameter in the Freundlich model, they were consistently below 1 (ranging between 0.271 and 0.792), indicating a high degree of concavity in the adsorption curves.

Considering the fittings to the Langmuir model, it was not the most appropriate to explain SAL adsorption. The q_m parameter, related to the adsorption capacity (Foo and Hameed, 2010; Cela-Dablanca et al., 2022b), was higher for the acid-activated clays (1449.038–2225.360 $\mu mol kg^{-1}$) than for natural (425.373–963.086 $\mu mol kg^{-1}$) and base-activated clays (229.167–652.945 $\mu mol kg^{-1}$), with a mean value of 958.766 $\mu mol kg^{-1}$ (Table 5). The K_L parameter (related to the adsorption energy, Khezami and Capart, 2005), ranged between 0.01 and 0.119 $L \mu mol^{-1}$, and was higher for the acid-activated clays than for the natural and base-modified clays (Table 5), indicating that the adsorption of SAL onto the acid-modified clays is stronger and therefore its mobility and desorption behavior will be lower than that of the other clay samples. Globally, for all the studied clay samples, the obtained K_L

values suggest strong interactions between the SAL molecules and the clay surfaces. This could be indicative of strong chemical bonds or forces, contributing to the adsorption process (Kern et al., 2022; Fu and Gray, 2023). Comparing the K_L values found for SAL in the current study with those mentioned in the literature, the results also show lower scores for the adsorption of MON and LAS (0.01–0.09 $L kg^{-1}$, respectively) onto other clays based on kaolinite, illite and montmorillonite (Swan, 2012), suggesting a greater affinity and adsorption capacity for SAL on the here studied clays.

In addition, clay pH and the type of activation process used had influence on the differences in K_L values found for the clay samples. At pH range of 3.33–4.49 (acid-activated clays), K_L was slightly higher than in the case of the clays having superior pH levels: natural clays (pH 8.39–9.08) and base activated clays (pH 9.99–10.18).

Previous investigations (Hamdi et al., 2024a, b) found that the Langmuir model was not appropriate for describing the adsorption of tetracycline and sulfadiazine onto the same clay samples. However, Gao et al. (2012) utilized graphene oxide for tetracycline adsorption, demonstrating a good fit to the Langmuir model.

The Linear model was also applied to SAL (Table 5), resulting in K_d values that were relatively low for both natural and base-activated AM and HJ1 clays (oscillating between 2.358 and 6.814 $L kg^{-1}$), indicating lower adsorption capacities of these clays. However, the K_d values registered for the acid activated clays were significantly higher than those of both natural and base-activated clays, ranging from 5.630 $L kg^{-1}$ (AM + HCl) to 12.283 $L kg^{-1}$ (HJ2+HCl). These findings align with those reported by Hamdi et al. (2024a) for tetracycline adsorption onto the same clay samples, where the acid-activated HJ2 clay was found to have a higher K_d value (1829.0 $L kg^{-1}$) compared to natural (947.011 $L kg^{-1}$) and base activated HJ2 clay (975.6 $L kg^{-1}$). Overall, the obtained K_d values in all clay samples (2.358–12.283 $L kg^{-1}$) were consistently lower than those mentioned for tetracycline adsorption onto the same clay samples, which ranged between 105.59 and 1829.0 $L kg^{-1}$ (Hamdi et al., 2024a). However, they were notably higher than the corresponding values observed for sulfadiazine adsorption with these same clays, which oscillated between 3.484 and 7.061 $L kg^{-1}$ (Hamdi et al., 2024b).

Additionally, it is important to note that the K_d values observed for both natural and modified HJ2 clays were generally higher than those resulting for the other clay samples.

Essentially, the K_d values observed for the acid-activated clays suggest that a substantial amount of SAL will be strongly adsorbed onto active sites of the acid-activated clay surfaces, as previously shown for tetracycline and sulfonamide (Figuroa et al., 2004; Shikuku et al., 2018; Dolatabadi et al., 2020).

When comparing the K_d values of SAL with those previously obtained by Hussain and Prasher (2011) for other ionophore antibiotics such as monensin (MON) and narasin (NAR), it is noted that, in the current study, the K_d scores obtained for the acid-activated clays (5.630–12.283

Table 5

Fitting of the SAL adsorption experimental data to the parameters of the Freundlich model (K_F and n), the Langmuir model (K_L and q_m), and the Linear model (K_d). K_F is expressed in $L^n \mu mol^{1-n} kg^{-1}$; K_L in $L kg^{-1}$; q_m in $\mu mol kg^{-1}$; K_d in $L kg^{-1}$; R^2 : coefficient of determination; -: error too high for fitting.

	Units	AM raw	AM + base	AM + HCl	HJ1 raw	HJ1+base	HJ1+HCl	HJ2 raw	HJ2+base	HJ2+HCl
Freundlich model	K_F	17.153	10.352	57.593	26.721	–	129.78	128.37	30.849	145.33
	Error	1.797	1.602	2.971	9.61	–	31.873	2.503	16.368	25.543
	n	0.353	0.271	0.597	0.414	–	0.673	0.532	0.307	0.792
	Error	0.116	0.097	0.094	0.089	–	0.122	0.367	0.076	0.074
	R^2	0.935	0.983	0.962	0.924	–	0.948	0.982	0.992	0.975
Langmuir model	K_L	–	–	0.1	0.04	0.02	0.115	0.09	–	0.119
	Error	–	–	0.03	0	0.001	0.091	0.003	–	0.062
	q_m	–	–	–	609.1	354.9	1719.9	–	–	2225.4
	Error	–	–	–	200.9	149.4	602.6	–	–	1355.4
	R^2	–	–	0.945	0.661	0.601	0.971	0.862	–	–
Linear model	K_d	4.314	2.358	5.63	5.946	3.633	10.887	6.814	5.493	12.283
	Error	0.038	0.027	0.171	0.047	0.035	0.431	0.284	0.196	0.775
	R^2	0.785	0.861	0.881	0.843	0.752	0.873	0.838	0.714	0.903

$L\ kg^{-1}$) are lower than those found by these authors for NAR ($38.24\text{--}98.8\ L\ kg^{-1}$), but they are close to those of MON (ranging from 8.52 to $17.65\ L\ kg^{-1}$) at pH 6.8 (Hussain and Prasher, 2011). Furthermore, it is noteworthy that, according to Hussain and Prasher (2011), sandy clay loam soil samples showed higher K_d values ($98.8\text{--}17.65\ L\ kg^{-1}$) than sandy soil samples ($5.03\text{--}4.28\ L\ kg^{-1}$) for these two ionophore antibiotics (MON and NAR). This suggests that the clay content in soils can improve their adsorption capacities for these antibiotics.

In view of the fitting results, the high K_F values, related to the multilayers adsorption capacity (with n values always below 1, ranging between 0.271 and 0.792), suggest the existence of heterogeneity and exponential distribution of the active sites and their energy during the adsorption process (Saadi et al., 2015). This implies that the stronger binding sites are initially occupied, followed by an exponential decrease in the adsorption energy (when the concentration of pollutant added increases) until the completion of the adsorption process (Saadi et al., 2015).

The results of the data fitting indicated that physical interactions would be relevant in the adsorption of SAL onto the studied clays and suggested the spontaneous and feasible nature of the adsorption of SAL

on the clay-based adsorbents with the used concentrations, especially in the case of the acid-activated clays. Moreover, the experimental data show the efficiency of the activation process in enhancing the adsorption capacities of the raw clays.

3.4. SAL desorption

Fig. 4 shows desorption for SAL, expressed in percentage, corresponding to the natural (raw) and modified clay samples under study, plotted against the concentration of SAL added. According to Fig. 4, as the concentration of SAL added increased, desorption percentages also increased. In addition, when the highest concentration of SAL was added ($100\ \mu\text{mol}\ L^{-1}$), the maximum desorption percentage of SAL (19.5 %) was reached for the HJ2 raw clay, whereas the minimum desorption value was observed for the acid-activated AM clay (6.2%) (Fig. 4). The desorption percentages were generally lower than 10% (in the range of 0.0–9.9%, with an average value of 4.95%) with SAL concentrations added varying from 5 to $20\ \mu\text{mol}\ L^{-1}$, while, when the SAL concentrations added oscillated between 40 and $100\ \mu\text{mol}\ L^{-1}$ desorption never exceeded 20% (in the range of 3.8–19.5%, with an average value of

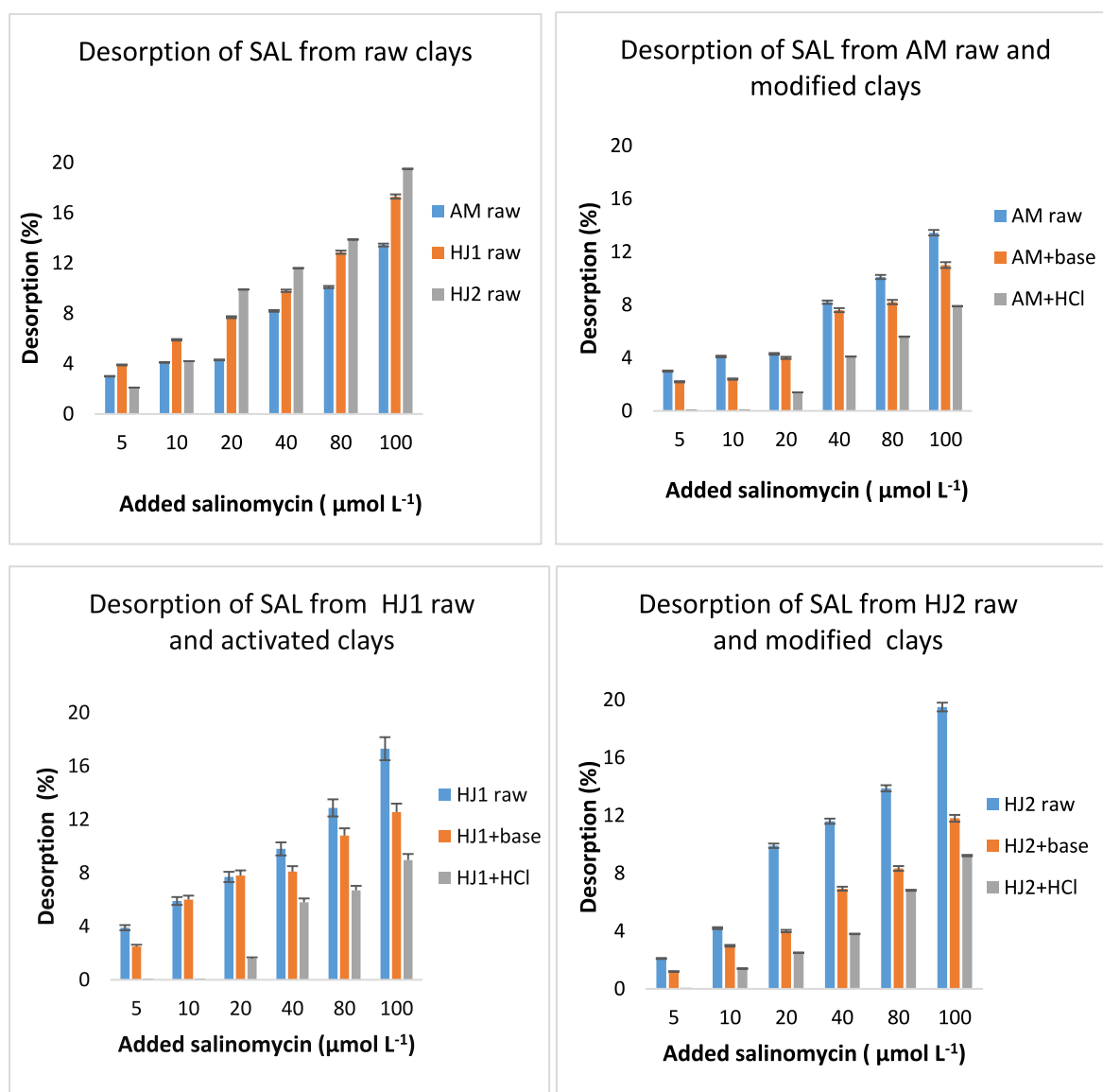


Fig. 4. Percentage desorption for salinomycin (SAL) from raw and activated clays as a function of the concentration of the antibiotic added ($\mu\text{mol}\ L^{-1}$). Average values ($n = 3$), with coefficients of variation always $<5\%$.

11.65%) for all clay samples (Fig. 4). Compared to this, El Sayed and Prasher (2014) found a high mobility for the ionophore antibiotic monensin (MON) in soils.

Furthermore, it is stressed to note that the acid-activation of the studied clays shows a good efficiency in reducing their release, with desorption percentages for acid-activated clays not exceeding 8.22% across all the SAL concentrations added. Additionally, desorption percentages for base-activated clays were slightly lower than those observed for natural (raw) clays, with maximum desorption percentage of 12.56 (reached for AM + base clay at 100 $\mu\text{mol L}^{-1}$ of SAL added). The effect of pH on SAL desorption was previously described by Jayashree et al. (2011) who observed that the desorption of the antibiotic from sandy, clay, and loamy soils marginally varied when methanol was used as desorption solution, however, desorption increased 70% when a phosphate buffer with pH = 7 was used.

In the current study, regarding the desorption data and considering the R^2 values, the highest compatibility corresponded to the Freundlich model (values ranging between 0.890 and 1, Table 6), although in some cases errors were too high for fitting, as for the Langmuir model, while this did not happen for the Linear model.

Discussing the desorption parameters for SAL, it will be noted that they were relatively high, indicating a rather low desorption of the used ionophore antibiotic from all the clay samples under study. Specially, the K_F (des) values (Freundlich model), which varied in the range 3.601–31.26 $\text{L}^n \mu\text{mol}^{1-n} \text{kg}^{-1}$, suggest a low or moderate (depending on the clay sample) degree of irreversibility in SAL adsorption onto the clay samples (Table 6). Desorption results reported by Swan (2012) for monensin as regards manure, soils and montmorillonite clays indicated to be moderate in all bio-adsorbents used for MON in individual system, but it could be notably elevated in competitive studies with other ionophore antibiotics like lasalocid (LAS).

Furthermore, the K_L (des) values found for SAL were generally close to zero (ranging from 0.015 to 0.082 L kg^{-1}) as listed in Table 6, suggesting a slow desorption process and therefore a marked affinity between the antibiotic and the used clay adsorbents.

It should be noted that the studied clays previously showed higher K_L (des) values for tetracycline (oscillating from 0.028 to 0.941 L kg^{-1}) than those obtained for SAL, as reported by Hamdi et al. (2024a). Additionally, the q_m (des) values (ranging from 50.435 to 697.582 $\mu\text{mol kg}^{-1}$) (Table 6) were considered high when compared to those noted for AM, HJ1 and HJ2 clays as regards tetracycline (with q_m (des) oscillated between 25.357 and 38.981 $\mu\text{mol kg}^{-1}$) (Hamdi et al., 2024a).

Concerning the Linear model, K_d (des) values were generally low in all clay samples, with higher value observed for the base-activated HJ2 clay (around 6.643 L kg^{-1}) (Table 6). Higher K_d (des) values (ranging between 16.835 and 168.751 L kg^{-1}) were reported for tetracycline with these based-clay materials in Hamdi et al. (2024a).

It is important to note that the low desorption percentages found for the acid activated clays, compared to those noted for raw and base-

activated clays, suggest that the desorption process can be clearly reduced/inhibited under acidic pH experimental conditions.

In the present study, a statistical analysis was conducted using one-way ANOVA and followed by post-hoc tests (Tukey and Duncan), aimed to evaluate the effect of pH on the desorption behavior of SAL from the studied clays ($n = 9$). The tests revealed a significant effect of pH on the desorption process ($p = 0.035$), confirmed by the Tukey and Duncan tests ($p = 0.038$ and $p = 0.042$, respectively). These results differed from those obtained by Jayashree et al. (2011), which indicated that SAL desorption from sandy soil samples marginally increased as the pH decreased, whereas the desorption from clay soils significantly increased with the rise in pH.

In the current work, the hysteresis index (HI) was generally higher than 0.694 for all clay samples, as listed in Table 7, specially, for the lowest concentrations of SAL (ranging between 5 and 40 $\mu\text{mol L}^{-1}$), indicating the slow desorption of SAL from the studied clays (Li et al., 2015). However, when the initial concentrations of the added antibiotic increased, the HI values clearly decreased, with the minimum value achieved by the AM raw clay (0.110), with 100 $\mu\text{mol L}^{-1}$ of SAL added.

These HI values are higher than those obtained for tetracycline with the same clays, which did not fall below 0.96 when tetracycline concentrations up to 1000 $\mu\text{mol L}^{-1}$ were added (Hamdi et al., 2024a). Moreover, it is important to note that the hysteresis index calculated for the clay samples at different SAL concentrations added ($\mu\text{mol L}^{-1}$) was consistently lower for the highest concentrations applied (80 and 100 $\mu\text{mol L}^{-1}$). This could reflect a higher desorption tendency or a faster release of the SAL antibiotic from the clay surfaces, according to Ramaswamy et al. (2012). All these findings may suggest that the desorption performance of these clays was dependent on the SAL concentrations added, with desorption capacities increasing as this operating variable increased, as shown in Fig. 4. Additionally, under acidic conditions, the reduction of the surface charge and, consequently, of the effective cation exchange capacity (eCEC) can occur, leading to lower percentages of antibiotic desorbing from clay surfaces, especially at lower concentrations of the antibiotic added (Ortiz-Ramos et al., 2022). Furthermore, high calcium (Ca) content combined with low magnesium (Mg) content in acid-activated clays and AM raw clays can reinforce their binding to SAL molecules, leading to enhanced adsorption capacities and, consequently, reduced desorption rates (Table 4 and S1, Supplementary). In this context, the high presence of calcite in the AM raw clay could be the reason of showing a slightly slower SAL, desorption compared to the other raw clays, where calcite is either weakly present (HJ1 raw clay) or totally absent (HJ2 raw clay) (Table S2, Supplementary Material).

In summary, the low reversibility of SAL adsorption on the here studied clay-based adsorbents, as demonstrated by their low desorption percentages (not surpassing 20% for any of the clay samples) and HI values (with average scores always above 0.693 in all clay samples), contributes to the heightened stability of SAL adsorption onto the adsorbent surfaces.

Table 6

Values of the SAL desorption parameters for the Freundlich model (K_F and n), for the Langmuir model (K_L and q_m), and for the Linear model (K_d). K_F ($\text{L}^n \mu\text{mol}^{1-n} \text{kg}^{-1}$); K_L (L kg^{-1}); q_m ($\mu\text{mol kg}^{-1}$); K_d (L kg^{-1}); R^2 : coefficient of determination; -: error too high for fitting.

	Units	AM raw	AM + base	AM + HCl	HJ1 raw	HJ1+base	HJ1+HCl	HJ2 raw	HJ2+base	HJ2+HCl
Freundlich model	K_F	5.010	3.610	7.068	9.018	4.062	–	31.260	11.577	9.092
	Error	0.000	0.561	2.819	3.385	0.000	–	0.000	0.000	0.219
	n	0.742	–	0.712	0.447	1.196	0.520	5.925	0.089	0.235
	Error	0.325	–	0.055	0.192	0.412	0.120	1.061	0.000	0.062
	R^2	0.890	0.956	0.875	0.888	1.000	0.929	0.957	1.000	0.997
Langmuir model	K_L	0.021	0.042	–	0.039	0.082	0.022	0.046	0.022	0.015
	Error	0.010	0.000	–	0.001	0.000	0.000	0.030	0.000	0.000
	q_m	471.84	414.09	–	384.60	320.91	360.00	697.58	542.79	312.31
	Error	185.79	283.07	–	121.58	83.83	0.00	334.68	253.20	10.08
	R^2	0.716	0.677	–	0.889	0.618	1.000	0.768	0.881	0.998
Linear model	K_d	6.643	2.045	0.491	4.635	5.220	1.000	1.000	3.646	1.000
	Error	1.807	0.809	0.042	0.679	1.332	0.000	0.000	8.528	0.000
	R^2	0.816	0.775	0.654	0.796	0.813	0.982	0.768	0.637	0.998

Table 7

The hysteresis index for the desorption of SAL.

SAL concentration ($\mu\text{mol L}^{-1}$)	Hysteresis index (HI)								
	AM raw	HJ1 raw	HJ2 raw	AM + base	HJ1+base	HJ2+base	AM + HCl	HJ1+HCl	HJ2+HCl
5	0.970	0.961	0.975	0.978	0.975	0.988	1.000	1.000	1.000
10	0.955	0.941	0.940	0.972	0.940	0.970	1.000	1.000	0.986
20	0.940	0.922	0.918	0.893	0.918	0.958	0.985	0.984	0.975
40	0.764	0.827	0.836	0.710	0.836	0.912	0.940	0.934	0.962
80	0.425	0.614	0.579	0.467	0.579	0.856	0.865	0.911	0.917
100	0.110	0.227	0.305	0.260	0.305	0.760	0.840	0.895	0.922
Min	0.110	0.227	0.305	0.260	0.305	0.760	0.840	0.895	0.917
Max	0.970	0.961	0.975	0.978	0.975	0.988	1.000	1.000	1.000
Average values	0.694	0.748	0.867	0.713	0.759	0.908	0.938	0.954	0.960

Both SAL adsorption and desorption processes on/from the studied sorbent materials will need further additional in-depth research, to elucidate details like the specific mechanisms taking place in each case, which is programmed to be developed in the coming future. To do that, complementary analytical procedures (such as FTIR analysis for the samples before and after adsorption and desorption, and also other specific analyses under implementation and refining) will be used, as well as supercomputational work focused on the pollutants and their interactions with the sorbents, which will be considered in a variety of environmental situations (Núñez-Delgado, 2024b).

4. Conclusions

The clays tested in this research show a clearly differentiated adsorption/desorption behavior for the antibiotic salinomycin (SAL). Among the natural and modified clay samples, acid-activated clays and especially the acid-activated HJ2 clay showed higher affinity for SAL than the natural (raw) and base-activated clays at high concentrations of the antibiotic added. The acid activation plays a crucial role in increasing the surface area and the porosity of the HJ2 clay, which in turn enhances its adsorption capacities, especially at higher SAL concentrations added. However, when low concentrations of SAL were added, the acid activated HJ1 and HJ2 clays also showed efficiency in removing SAL. This may be due to the generation of additional binding sites on the surface of clay materials, an increase in their specific surface area, and the optimization of their porosity resulting from the acid activation of these clays. The low pH values in the acid-activated clays ($\text{pH} < 5$) are also decisive in this strong and continuous adsorption process, even as the SAL concentration increases. It was evidenced that the decrease in the adsorption capacities of the sorbents at high concentrations of the antibiotic added, especially for raw and base-activated clays, was a result of the saturation of the active sites present on the clay surfaces. Furthermore, the Freundlich model, was the one that best explains the adsorption of SAL in these clays, indicating that it is a heterogeneous adsorption system. Additionally, desorption percentages did not exceed 10% at low concentrations added ($5\text{--}20 \mu\text{mol L}^{-1}$), or 20% for the highest SAL concentrations added ($40\text{--}100 \mu\text{mol L}^{-1}$). This suggests a rather low reversibility of SAL adsorption, interesting for the assessment of the whole removal process. It helps to prevent the release of the previously retained contaminants into the environment, ensures sustainable SAL removal, and minimizes secondary pollution risks.

For future studies, it would be interesting to evaluate the adsorption-desorption behavior of other ionophore antibiotics widely used, like monensin, lasalocid or naransin, on/from these clays (and other low-cost sorbents, such as plant fibers and natural barks) from contaminated aqueous solutions and different environmental compartments, and eventually considering other experimental conditions to those used in the current research (particularly examining a wide range of modified pH values in adsorption-desorption equilibrium solutions), to broaden the range of any relevant variable affecting these process with marked environmental and public health impact. In addition, complementary experiments focusing on elucidating in-depth mechanisms taking place

during the retention/release process, for a variety of environmental conditions, and using a wide range of laboratory and computational tools could give crucial details.

CRedit authorship contribution statement

Samiha Hamdi: Writing – original draft, Visualization, Software, Investigation, Data curation. **Ainoa Míguez-González:** Visualization, Software, Investigation. **Raquel Cela-Dablanca:** Visualization, Software, Investigation, Data curation. **Ana Barreiro:** Writing – original draft, Visualization, Validation, Supervision, Software, Data curation. **María J. Fernández-Sanjurjo:** Writing – original draft, Visualization, Validation, Supervision, Methodology, Conceptualization. **Avelino Núñez-Delgado:** Writing – review & editing, Visualization, Validation, Supervision. **Esperanza Álvarez-Rodríguez:** Writing – original draft, Visualization, Validation, Supervision, Methodology, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Given his role as editor, Dr. Avelino Núñez-Delgado was not involved in the peer-review of this article and has no access to information regarding its peer-review. Full responsibility for the editorial process for this article was delegated to Professor Raf Dewil.

Data availability

Data will be made available on request.

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Appendix A Supplementary data

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