ACTA CHEMICA IASI, **34_1**, 204-228 (2026)
DOI: 10.47743/achi-2026-1-0009

*Article*

# KINETICAL APPROACH OF TETRACYCLINES ADSORPTION ON BENTONITE

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**Abstract:** Adsorption of antibiotics on clays from aqueous solutions have been recently much investigated, due on one part, to their potential inclusion in topic drugs formulae, on one part, and to the convenient water cleaning strategy from trace antibiotics in a very simple and cheap approach. In our work, commercial sodium bentonite and calcium bentonite consisting mainly of montmorillonite clay, was tested as an adsorbent for three antibiotics from tetracycline family: tetracycline, doxycycline and minocycline. Parametric studies concerning the influence of analyte concentration and clay dose were performed. The adsorption kinetics were investigated by fitting the experimental data to several mathematical models: as pseudo-first and second order, Elovich and Weber-Morris and the adsorption. The role of film diffusion and internal diffusion were also highlighted. The adsorption data were fitted to Lagergren and Ho&McKay models. High adsorption capacities of hundreds of miligrams antibiotics per gram of clay were reported for all tested systems.

***Keywords*:** Adsorption, bentonite, tetracycline, doxycycline, minocycline

## Introduction

The continuous discharge of antibiotic residues into aquatic systems has emerged as a major concern in environmental chemistry, as it couples the persistence characteristic of classical micropollutants with a direct

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contribution to antimicrobial resistance. Large-scale surveys of active pharmaceutical ingredients in rivers further demonstrate that pharmaceutical contamination is geographically pervasive and analytically detectable across diverse hydrological settings.[1]

Tetracyclines are often considered almost perfect antibiotics: they are active against most common pathogens, have good oral absorption, low toxicity and incidence of allergic reactions, and have quite low prices. Therefore, they are among the most widely used as broad-spectrum antimicrobial agents. Since their discovery in the mid of 1940, the tetracycline family expanded with new compounds or modifications of natural tetracyclines.[2] The most common semisynthetic tetracyclines include the second-generation members, doxycycline and minocycline, exhibiting a broad spectrum of efficiency against various infections, as well as acne. Their antibacterial activity against both Gram-positive and Gram-negative microorganisms, combined with anti-inflammatory properties, has promoted their extensive use in human and veterinary medicine for decades. Apart from products destined to oral and parenteral administration rutes, tetracyclines are also found in the topical formulations for the treatments of skin and soft tissue infections, due to the improving of local drug delivery while minimizing systemic side effects.[3,4] Tetracycline, doxycycline, and minocycline share a common polycyclic naphthacene-carboxamide scaffold yet differ in substituent pattern, hydrophobicity, steric accessibility, acid–base behaviour, and affinity for mineral surfaces; minocycline, in particular, carries a second dimethylamino group at C-7, which appreciably alters its charge distribution and lipophilicity relative to the other two. As a consequence, the predominant species are strongly pH-dependent: cationic forms prevail under acidic conditions, zwitterionic forms dominate in

weakly acidic to near-neutral media, and anionic forms become increasingly important as the pH rises into the alkaline range.[5,6]

The extensive consumption of tetracycline antibiotics has, however, raised significant environmental concerns, since a substantial fraction of administered antibiotics is excreted and reaches soil and aquatic environments through agricultural runoff, livestock effluents and wastewater discharges[7]. The persistence of these compounds in natural waters contributes to the development of antibiotic-resistant microorganisms and may adversely affect aquatic ecosystems and human health[8]. Besides their oral administration in different therapies, tetracyclines are also employed in the treatment of skin and soft tissue infections and have attracted considerable interest for topical formulations aimed at improving local drug delivery while minimizing systemic side effects.[9,10]

These two perspectives of interest: preparation of tetracycline-containing solids for topical formulations with high amounts of embedded antibiotic and water cleansing from drug traces offer viable reasons for research the adsorption process, aiming to use cheap and available solids in the process.[11]

Adsorption has emerged as one of the most attractive approaches in the remediation technologies, because its simplicity, effectiveness and relatively low operational costs.[12] Alongside adsorption, numerous advanced oxidation methods have been employed for antibiotics removal from wastewater, as: ozone oxidation,[13] Fenton–catalyzed oxidation,[14] heterogeneous photocatalytic reactions[15] and electrocoagulation.[16,17] However, the simplicity of the approach and the easy availability of the necessary materials qualifies adsorption as a very convenient solution for tetracyclines advanced removal from aqueous solutions.[18] Natural clay

minerals have received particular attention as adsorbents owing to their abundance, low toxicity, large specific surface area and high cation-exchange capacity.[19] Montmorillonite, the principal component of bentonite clays, is a layered 2 : 1 aluminosilicate characterized by negatively charged sheets balanced by exchangeable interlayer cations.[20] These structural features confer a remarkable ability to interact with a wide range of organic and inorganic molecules through electrostatic interactions, hydrogen bonding, surface complexation and intercalation mechanisms.[21]

Recent work on hybrid adsorbents offers valuable mechanistic context for bentonite–antibiotic systems. *Adesina et al.* prepared a biomass-assisted kaolin/$TiO_2$ composite and reported more efficient removal of tetracycline than of bisphenol A, attributing tetracycline uptake primarily to favourable electrostatic interactions and to a heterogeneous distribution of adsorption sites; adsorption fell markedly at above-neutral pH, whereas ionic strength exerted little influence on uptake.[22] *Premarathna et al.* found that montmorillonite-bearing clay–biochar composites enhanced tetracycline adsorption relative to raw biochar and red-earth composites, the kinetics of the montmorillonite composite conforming to the Elovich model and the equilibrium data to the Freundlich isotherm — behaviour consistent with energetically heterogeneous surfaces and multiple uptake mechanisms.[21] Ait *Hamoudi et al.* further showed that tetracycline adsorption on clay/activated-carbon/cement/PVA geomaterials is pH-dependent, rapid in its initial stage, well described by pseudo-second-order and intraparticle-diffusion models, and substantially enhanced by the contribution of activated carbon to surface area and hydrophobic interactions.[23] Collectively, these studies confirm that clay-based materials are effective platforms for the retention of tetracycline-family antibiotics,

while also demonstrating that the adsorption mechanism depends strongly on mineral composition, carbonaceous additives, solution pH, diffusion pathways, and surface heterogeneity.

In recent years, increasing attention has been devoted to the interaction between clay minerals and tetracycline antibiotics.[24] Several studies have demonstrated that montmorillonite-based materials can effectively adsorb tetracycline and doxycycline from aqueous solutions,[25] while simultaneously offering opportunities for the development of controlled-release pharmaceutical systems.[26] A real challenge in obtaining efficient topical products containing antibiotics consists in obtaining a very fine dispersion of the antibiotic in the fat base of the product; usually, a long trituration of the drug crystals in the fat base is applied. The most challenging aspect in the cream preparation is thus the advanced dimensional fragmentation of the tetracyclines crystals, to allow their easy absorbing through the skin. Therefore, the idea of using the antibiotic adsorbed on clays is worthy to consider, since, on one part, clays are a common component in topical formulations, and on another part, the antibiotic adsorbed on clay is delivered mostly as individual molecules dispersed on the solid. Indeed, the resulting antibiotic-loaded composites retained antibacterial activity against skin-associated microorganisms, in proportion to the antibiotic loading,[27] comparable antimicrobial activity has likewise been reported for tetracycline- and minocycline-montmorillonite systems, underlining the pharmaceutical potential of clay-bound tetracyclines.[28]

The adsorption process is strongly influenced by the physicochemical properties of both the clay mineral and the antibiotic molecules, including pH-dependent speciation, surface charge distribution

and swelling behavior of the clay structure[10]. Despite the growing body of literature concerning tetracycline adsorption on clay minerals, comparative investigations involving different members of the tetracycline family and different bentonite types remain limited. In particular, information regarding the adsorption behavior of tetracycline, doxycycline and minocycline on sodium and calcium bentonites under comparable experimental conditions is still scarce. A better understanding of adsorption capacities, kinetic mechanisms and mass-transfer phenomena is essential both for the optimization of clay-based drug delivery systems and for the design of efficient adsorbents for environmental remediation. Such a comparison is valuable because sodium and calcium bentonites differ in swelling, hydration, interlayer accessibility, and cation-mediated binding, while tetracycline, doxycycline, and minocycline differ in molecular size, substituent chemistry, hydrophilicity/lipophilicity, and protonation profile. The study pursues two complementary objectives: to develop a simple and inexpensive clay-based strategy for collecting dissolved antibiotics from water, and to advance the mechanistic understanding of clay–antibiotic interactions relevant to topical clay-based drug formulations. The effects of the initial antibiotic clay dose were examined, and the adsorption kinetics were fitted with the pseudo-first-order, pseudo-second-order, Elovich, and Weber–Morris models. The Lagergren pseudo-first-order model assumes that the adsorption rate is proportional to the number of unoccupied sites, that is, to the difference between the equilibrium and instantaneous uptakes, $(q_e - q_t)$, whereas the Ho–McKay pseudo-second-order model assumes that the rate is proportional to the square of that quantity, $(q_e - q_t)^2$.[29,30] The pseudo-second-order model is frequently equated with chemisorption, although this mechanistic interpretation has been questioned and should be treated with caution.[31] The Elovich model is particularly suited to energetically heterogeneous surfaces, on which the activation energy of

adsorption varies with surface coverage, while the Weber–Morris model resolves the relative contributions of external film diffusion, intraparticle diffusion, and possible multistage mass transfer[32]. Kinetic models should not, however, be read as direct proof of a single molecular mechanism; they are best regarded as comparative descriptors, to be evaluated alongside the experimental design, the adsorption capacity, the clay dose, and the concentration-dependent trends.[33]

The contributions of film diffusion and intraparticle diffusion were further assessed in order to distinguish rapid external uptake from slower transport into aggregates and interlayer-accessible domains. By comparing two bentonite forms and three related tetracycline antibiotics, the study helps to identify how the type of exchangeable cation, the antibiotic structure, the adsorbent dose, and the concentration gradient govern adsorption efficiency. The high adsorption capacities obtained—reaching several hundred milligrams of antibiotic per gram of clay—underscore the potential of commercial bentonites both as low-cost adsorbents for antibiotic-contaminated waters and as promising matrices for further investigation in clay-based topical pharmaceutical systems.

A systematic investigation of all three antibiotics on both Na- and Ca-bentonite can therefore establish whether adsorption is governed chiefly by the form of the clay mineral, by the antibiotic structure, by dose-dependent surface availability, or by diffusion limitations.

## Materials and methods

The bentonite used in the series of experiments was provided by the Research Center of Oenology Iasi, Romania. Two ionic forms, sodium (B_Na) and calcium bentonite (B_Ca) were tested. The solids before and after adsorption were characterized by XRD performed on a Shimadzu

D6000 apparatus and by FT-IR spectroscopy, on a Jasco 660+ machine, by using the KBr technique for sample preparation.

Tetracycline (T), doxycycline (D) and minocycline (M) were purchased as capsules filled with powder from pharmacy. The powder was used without previous purification. The high drugs purities were proved by HPLC analysis. Distilled water was used for all preparations to obtain solutions of antibiotics of 500 ppm. The concentration values of the antibiotics were determined by spectrophotometric measurements performed on a Shimadzu UV- 2401 PC machine, assisted by dedicated software allowing stocking the calibration curves and deducing directly the samples solutions concentrations. The analyzed solutions were diluted at ratios of 1 / 9 with distilled water, to fit inside the linear Lambert-Beer equation range, before measuring.

The adsorption experiments were run in beakers hosting 200 mL of antibiotic solutions, under magnetic stirring (500 rpm). Doses of 0.5, 1.0, 1.5 and 2.0 g/L bentonite were employed in four series of experiments. When the clay was dropped in the solution, a timer was started. Suspension samples were withdrawn after 5, 10, 15, 20, 25, 30, 45, 60, 120, 180, 240 and 360 minutes using a 10 ml syringe. The clear solutions of antibiotic were collected after filtration through 0.45 μm Teflon syringe filters and stocked until measurements. The adsorption experiment was let to continue for 24 h under parafilm foil, to allow the determination of the complete clay capacity of adsorption at saturation. The clay samples after adsorption were denoted as B_Na or B_Ca, followed by the capital initial of the antibiotic name precised above.

The amount of adsorbed antibiotic was expressed as the retention degree, calculated with the relation:

$$\text{Retention, \%} = 100*(C_o-C_t)/C_o,$$

where $C_o$ and $C_t$ are the initial and time t concentration values, respectively.

The amount (mg) of antibiotic adsorbed per gram of bentonite was calculated as:

$$\text{Drug/clay, mg/g} = V*(C_o-C_t)/m$$

where V = drug solution volume (0.2 L) and m is the weight of bentonite used in a certain experiment.

Several adsorption models were chosen to fit our data for describing the adsorption kinetics: Lagergren (pseudo-first degree), Ho&McKay (pseudo-second degree), Elovich, and Weber-Moritz (Table 1), aiming to investigate both the raw interaction between the solid and the antibiotic during its immobilization on the clay surface, and the influence of the diffusion processes occurring in time, due to the porous structure of the solid and the chemisorption in pores.

**Table 1.** Adsorption kinetic models selected for bentonite-tetracyclines system characterization.

| Model | Equation | Reference |
|---|---|---|
| Lagergren | $\ln (qe - qt) = \ln qe - K_1 \text{ x } t$ | (29,33) |
| Ho&McKay | $\frac{t}{qt} = \frac{1}{K_2 \text{ x } qe^2} + \frac{1}{qe} \text{ x } t$ | (30) |
| Elovich | $qt = 1/\beta (\ln \alpha\beta) + 1/\beta \ln t$ | (34) |
| Weber-Moriss | $qt = K_3 t^{1/2} + C$ | (34, 35) |

where: qe and qt – amounts adsorbed at equilibrium and time t; $K_1$ – rate constant of pseudo-first degree ($min^{-1}$); $K_2$ - rate constant of pseudo-second degree (g/mg $min^{-1}$); $\alpha$ – initial adsorption rate; $\beta$ – desorption constant; $K_3$ - intraparticle diffusion rate constant (mg/(g $min^{1/2}$)); C - value related to the thickness of the diffusion boundary layer (higher the C value, more intense boundary layer effect).

## Results and discussions

### 1. Structural investigations of the adsorbent

The crystalline structure of bentonite and of the antibiotic-clay composites was investigated by XRD (Figure 1).

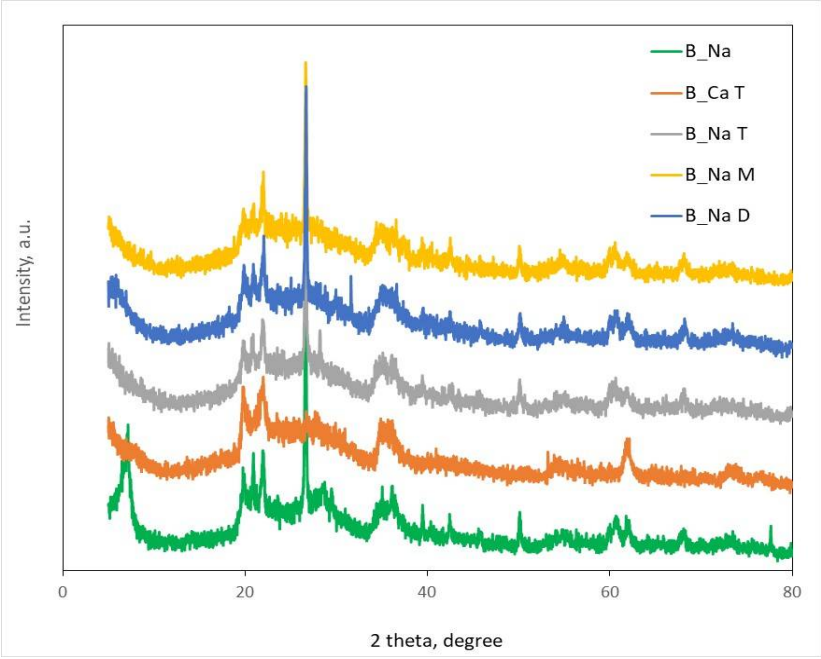



**Figure 1.** XRD patterns of bentonite and bentonite-antibiotic composites.

The experimental data indicate the presence of montmorillonite phase, as proved by the maxima from 2θ of 7.16; 19.76; 20.92; 22.44; 34.64; 54.04 and 61.78º, assigned, respectively to the plans defined by Miller indexes (100); (020); (110); (040, 220); (150, 240, 310) and (060, 330), respectively. The very sharp and intense peak from 26.62º is due to quartz phase impurity, in excellent fit with literature data.[37] The crystalline structure is well preserved after the antibiotics adsorption, as shown by the presence of the same signals after the adsorption, excepting the maximum from 7.16º. The (100) plan in clays is associated with the interlayer between two consecutive cationic sheets. After the adsorption, this signal disappears and another signal is well observed mainly for sample B_Na-D around 5.6º. The

interlayer space value calculated using Bragg equation indicated a decrease from 12.34 Å in B_Na sample to 15.88 Å in sample B_Na-D, suggesting that the initial sodium ions acting as layer charge compensators were replaced by doxycycline molecule. Similar structure changes were reported by Wang et al.,when using bentonite at lower dose (0.2 g/L) and tetracycline solution of 100 ppm[38]. Indeed, the investigations of acidity performed on this drug indicate two basic sites established between cycles B, C and D (having the pKa value of 7.97) and to the tertiary amino group from cycle A (having the pKa value of 9.15).[38] It is highly probable that the cationic exchange also occurs in the tetracycline and doxycycline, but the normal range of angles in XRD does not allow registering signals below 2 theta of 5$^{o}$.

The presence of chemisorbed tetracycline, doxycycline and minocycline on B_Na and of tetracycline on B_Ca, respectively were also proved by the FT-IR transmission spectra (Figure 2). The literature data[39,40] assign the signals from tetracycline and minocycline spectra as shown in Table 2.

**Table 2.** FT-IR spectra bands assignment ($cm^{-1}$) in T and M.

| **Tetracycline** | **Minocycline** | **Bands assignment** |
|---|---|---|
| 3341–3329 | 3480–3355 | N-H and O-H stretching |
| 3085–3024 | 3089–2879 (wide) | aromatic C-H vibrations |
| 2995–2863 | | $CH_3$ stretching vibrations |
| 1669–1650 | 1664 | amidic C=O stretching |
| 1648–1582 | 1617, 1583 | C=C stretching |
| 1458 and 1357 | 1460 | aromatic C-H and $CH_3$ bending |
| 1247–1000 and 567–501 | 1291 | aromatic ring deformation in plan and above |
| 965 | 1000-500 (multiple bands) | C-N stretching band |

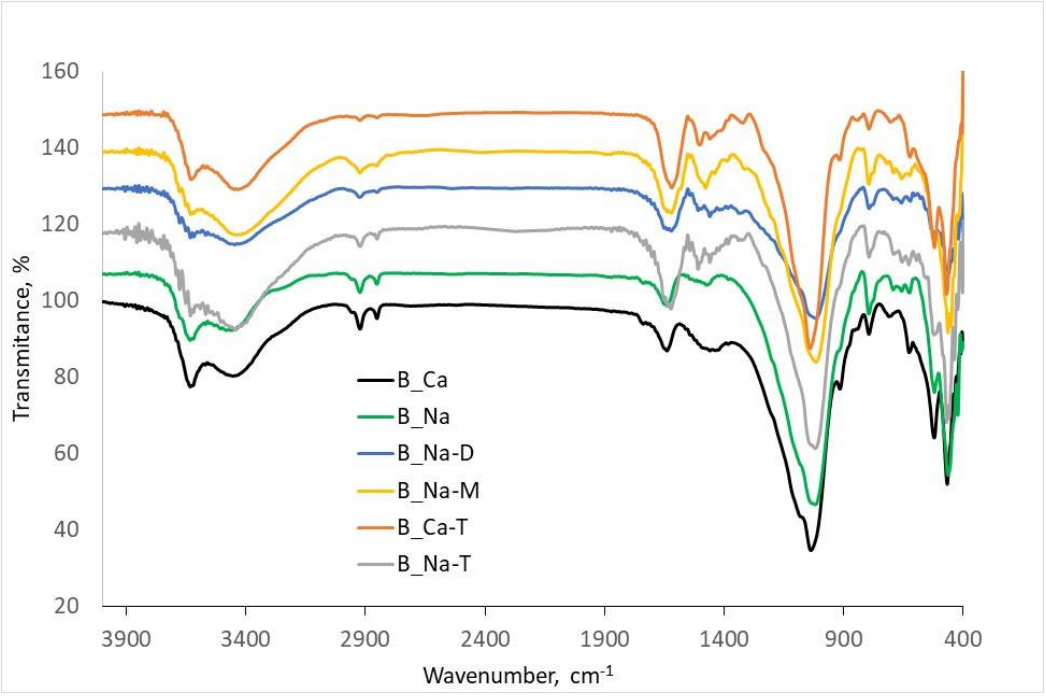



**Figure 2**. FT-IR spectra of initial bentonites and selected adsorption products

In the bentonites spectra, the hydroxyl groups and adsorbed water give wide bands between 3800-3400 cm $^{-1}$, while the signals in the range of 1000 – 500 cm $^{-1}$ are due to the bonds in the clay network, identified as from Al-O and Si-O bonds as well as to Al-O-Si and Si-O-Si bonds from quartz impurity.

Although the signals from the range between 4000 – 2800 cm$^{-1}$ overlap between the clay and the drugs, the inclusion of tetracyclines in the solids causes significant changes in the relative intensities of the bands. The significant intensity decrease of the bands between 3800 – 3550 cm $^{-1}$ due to hydroxyl groups from pure clay and an increase and broadening of the band between 3500 – 3300 cm $^{-1}$, due to antibiotic hosting between the layers. Also, the intensification of the band from 1617 cm $^{-1}$ suggests an important input of antibiotic in the clay structure.

## 2. Investigation of clay performances in adsorbing tetracyclines

The overall achievement of the adsorption process was expressed as the retention yield on the clays and depended in a high extent on the solid dose. The results are displayed in Figure 3. As expected, the both type of solid and dose value had a high influence on the process performance. The superiority of sodium bentonite in comparison with calcium form revealed for tetracycline adsorption led to selecting this solid for detailing the further studies. This behavior is quite expected, since the compensation of the charge of the layered structure by divalent cations decreases the ionic exchange rate and yield, since the positioning of the multivalent ions occurs in the nearby of one anionic site from the layer and somehow afar from another, therefore, this first site will be disadvantaged in the ionic exchange process.[22]

This is further supported by the slower rate for equilibrium settling, as the data in figure 3 a and b show. It is worthy to note that there are significant differences in the adsorption yields for the three drugs. The best uptake level for tetracycline reaches a maximum of 83% on B_Na at the highest clay dose after 180 minute, while the retention of minocycline was above 95% after 60 minutes at doses of 1.5 and 2 g/L, and that of doxycycline was over 82% after 30 minutes and reached values of 89% and 93%, respectively, for the same two doses.

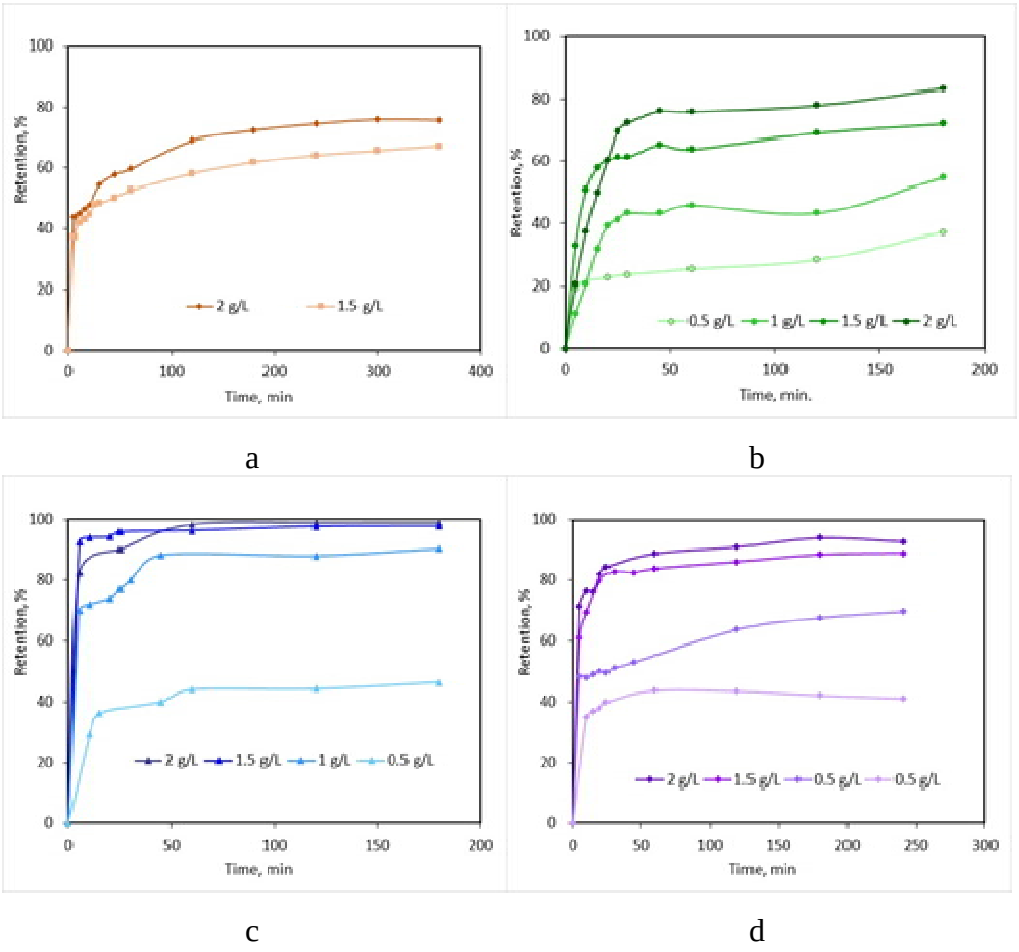



**Figure 3**. Tetracyclines retention degree evolution in time at different adsorbent doses
T series - B_Na-T system; D series - B_Na-D system, M series - B_Na-M system.

These high capacities of bentonite to adsorb tetracyclines could qualify them as excellent agents for water cleaning from pollutants, but also support the idea that the obtained composites provide valuable alternatives for including the antibiotic in topical preparations (figure 4).

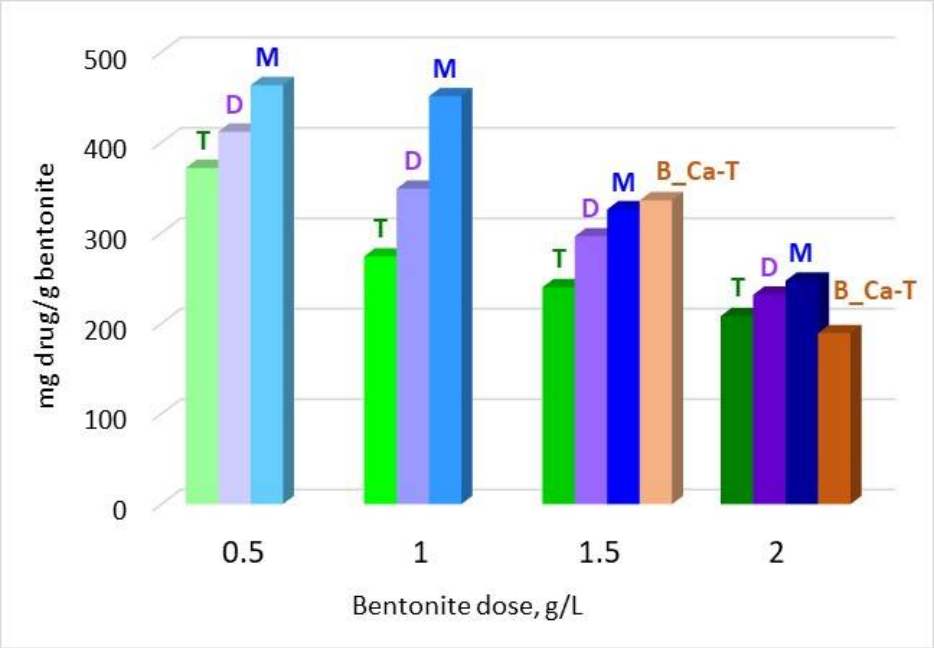



**Figure 4.** Bentonites adsorption capacities of tetracyclines adsorption (B_Na-T, B_Na-D and B_Na-M series labeled with T, D and M for each dose; B_Ca-M series labeled distinctively).

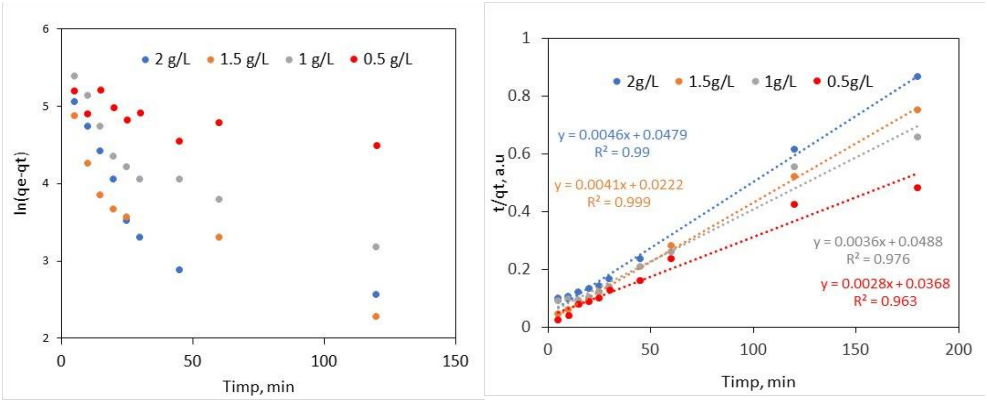
The values of the uptake of drug per gram of adsorbent is in the same range as literature reported data, as comprehensively gathered by Gopal et al. in their review[18]. The highest amounts of antibiotic per gram of bentonite were obtained at the lowest clay doses, suggesting that the process efficiency depends very much on the adsorbate concentration; when the dose of solid is high, the strong adsorption eliminates most of the available amount for further process continuation and the overall uptake remains lower. In a perspective of a practical application for obtaining composites for topical preparations, the optimum conditions are reached at low bentonite doses. In the case of B_Ca, the situation is opposite, suggesting the observation that divalent ions of calcium behave in a different manner from sodium, rendering the cationic exchange more difficult. These results

indicate that the performance of bentonites in terms of adsorption capacity is similar with those of polymeric resins[41]. Also, the bentonite price is much lower and its greenness is very high[42,43].

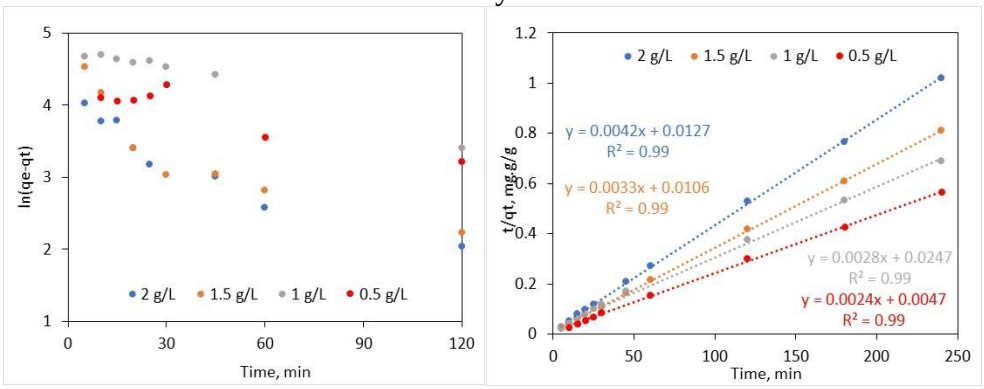
## 3. Kinetic approaches

The time dependence of the adsorbed amounts of tetracycline, doxycycline and minocycline were processed according to Lagergren (pseudo-first degree) and Ho&McKay (pseudo-second degree) models. The data are organized in Figure 5.

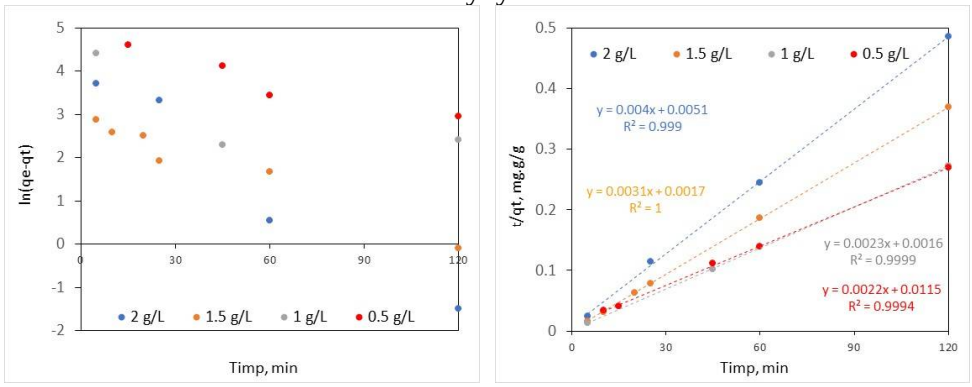
In all the experiments, the data fitted excellently on the second order model, while the first order model fit was improper on the whole experiment range of time values. Since clay wetting could influence the adsorption process, we have further fitted the data on the pseudo-first kinetics for 30 minutes. The data indicate an interesting aspect (Figure 6): the good fit of the pseudo-first order model for tetracycline and doxycycline at the higher doses (1, 1.5 and 2 g/L). This result indicates that the insertion of the drug between the layer suggested by the XRD results is the mechanism happening in the incipient stage of the adsorption.




Tetracycline




Doxycycline




Minocycline

a b

**Figure 5.** Experimental data fit on Lagergren (pseudo-first order) (a) and Ho&McKay (pseudo-second order) (b) for tetracyclines adsorption on B_Na.

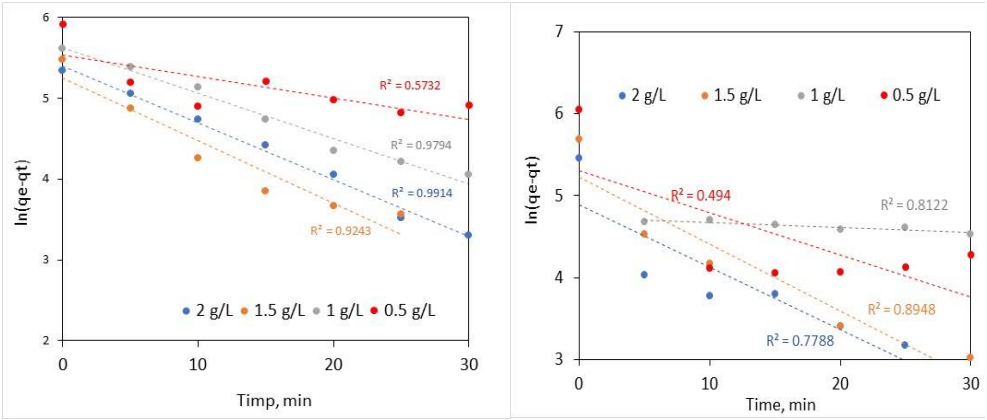



**Figure 6.** Pseudo-first order kinetic model applied in the first 30 minutes of adsorption of tetracycline and doxycycline on B_Na.

## 4. Influence of intraparticle diffusion

Since important differences in the adsorption kinetics were observed in correlation with the drug nature and the dose used, two kinetic models describing the adsorption evolution were tested for our data fitting to investigate the influence of the intraparticle diffusion. In this respect, two models were used, Elovich[33,47] and Weber-Morris.[32] When the data fit the Elovich model, this is an indication that a chemical reaction is very probable to occur. The Weber-Morris model allows concluding if the intraparticle adsorption occurs, when in the representation of qt versus the square root of the time value presents two linear distinctive ranges with different slopes. The data fit on Elovich and Weber-Morris models for B_Na and B_Ca clays and adsorption of tetracycline are displayed in Figure 7. Similar findings were reported by Ocampo-Pérez et al. on activated carbon[44] and by Chang et al. on shrimp shell-derived adsorbent.[45]

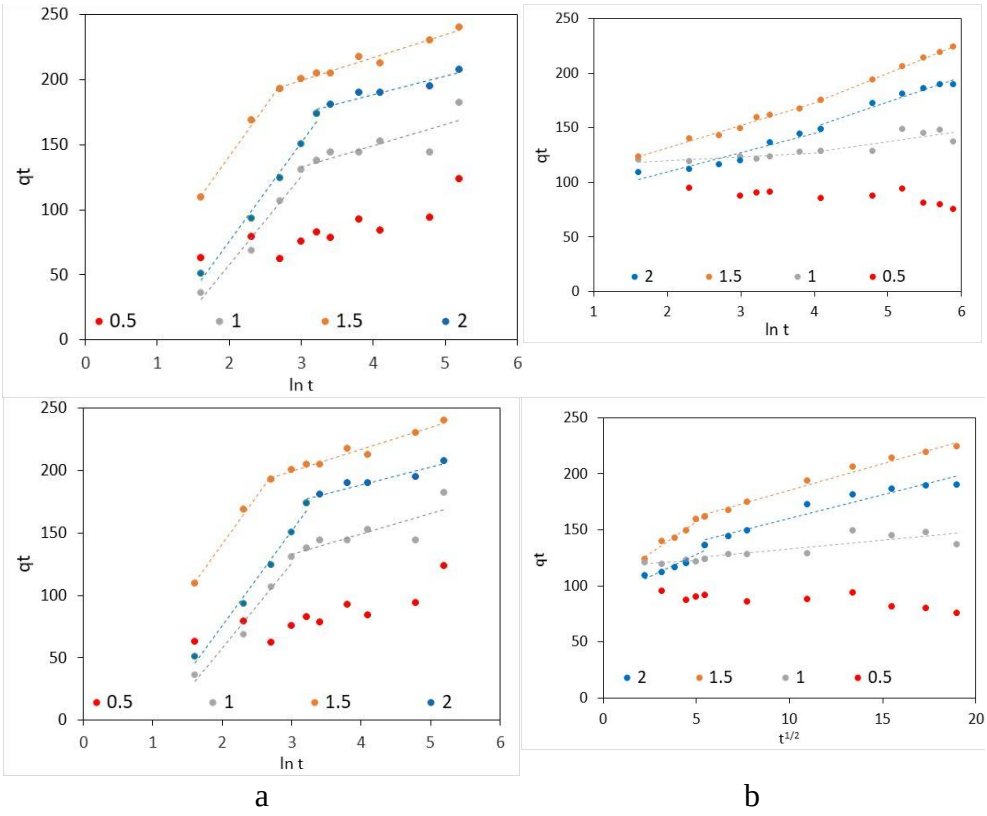



**Figure 7.** Representation of Elovich (a) and Weber-Morris (b) kinetic models for tetracycline adsorption of B_Na and B_Ca clays.

This behavior shows that initially the clay offers a large number of adsorption centers on the surface or in very easily accessible pores. Over time, the diffusion of the antibiotic inside the solid structure causes changes in its structure (as also highlighted by XRD analysis), i.e. the increase in the free space between the clay layers, by the insertion of drugs instead of some of the initial cations (Na or Ca). The increase in the space between the layers compensated by tetracyclines instead the initial sodium or calcium ions is due to their larger size. For this reason, the adsorption of tetracycline proceeds slower, as the layers with adsorption potential allow the access of

the new ions by changing their orientation, either by exfoliation or slide past each other.

**Conclusions**

This study presents information about adsorbing three tetracyclines: tetracycline (T), doxycycline (D) and minocycline (M) on Na and Ca bentonites (B_Na and B_Ca). All the experiments were performed at drug concentrations of 500 mg/L and clay doses of 0.5, 1, 1.5 and 2 g/L.

The experimental results indicated that the solids provided excellent adsorption capacities, allowing the uptake of hundreds of milligrams of drugs immobilized on the clays: the best results regarding the incorporation of the drug into the clay were obtained at a dose of 0.5 g/L B_Na (371.94 mg T/g; 411.8 mg D/g; 463.4 mg M/g). Thus, our findings confirm that this very simple and cheap method is an excellent alternative for obtaining composites ready to use in medicinal topical products. It provides especially a valuable alternative important in the case of minocycline, which is very much used in the treatment of acne, and clays are also a common component of topical products. A release study of tetracyclines from these clay-drug composites is a future research direction found in the close attention of the authors. Also, a collaboration with specialists from semisolid drugs preparation could bring interesting results for clay--tetracyclines composites healing effects.

The structural changes upon tetracyclines adsorption performed by X-ray diffraction indicates that the adsorption was partly followed by cationic exchange, partially replacing Na and Ca by drug molecules.

The kinetic investigations revealed that the pseudo-second order model (Ho&McKay) describe well all three tetracyclines adsorption processes on both solids. The investigation of the possible influence of the

chemical reaction and the internal diffusion of tetracyclines in the clay was confirmed by the Elovich and Weber-Morris models. The hypothesis of the adsorption accompanied by both chemical reaction (ionic exchange) and intraparticle diffusion were confirmed to occur by experimental data fit on these models.

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