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Adsorption of fluoroquinolones on calcined clays in an aqueous medium: case of ofloxacin

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Abstract

Ofloxacin (OFX) is one of the most prescribed antibiotics in the world considered an emerging contaminant of aquatic environments. The use of advanced oxidation processes for its water degradation generates by-products that are often more toxic than the parent molecule. A low-cost treatment process has been implemented to evaluate the ability of this antibiotic to completely eliminate it from aqueous media. The objective of this study is to show the ability of calcined clays to eliminate this fluoroquinolone. An experimental batch pilot was designed for ofloxacin adsorption tests of doped matrices on a bed of clay beads. The results showed a decrease in the initial concentration of ofloxacin of 95% after 45 minutes in the ultra-water matrices. For doped tap water matrices, this rate was reached after 240 minutes. In addition, ofloxacin is adsorbed in all these ionic forms. Monitoring of the total organic carbon content showed that calcined clay indicated that ofloxacin is effectively removed from the doped water matrices at the end of treatment. The clay was recalibrated after each experiment, placing this process in a perspective of sustainable remediation.

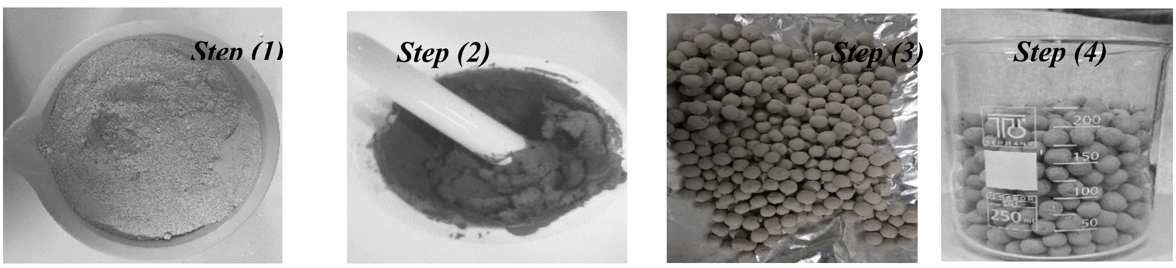
1. Introduction

Antibiotics are antimicrobial drugs that kill or reduce the growth of bacteria. They have been used in large quantities for several decades and the resistance of pathogens to antibiotics has long been at the heart of clinical research and, more recently, in environmental research. Some antibiotics such as ciprofloxacin or ofloxacin, which are among the most potent antibiotics at low concentrations (Bengtsson-Palme and Larsson, 2016) are found at relatively high concentrations in freshwater (aus der Beek *et al.*, 2016, Feitosa-Felizzola and Chiron, 2009, Ginebreda *et al.*, 2010). Antibiotics can bypass water treatment processes and end up directly in the environment. They are detected in rivers at very low and diluted concentrations (more than a million times) compared to the concentrations observed in the human body. The presence of molecules in the aquatic environments of the city of Abidjan could qualitatively affect drinking water resources in Côte d'Ivoire (Kouadio *et al.*, 2009). And in the face of all the problems that our country is experiencing in terms of sanitation and management of wastewater treatment plants, the use of other purification techniques, low-cost and simpler to manage, has become essential, if we want to protect water resources, public health and safeguard the receiving environments (N'guettia *et al.*, 2019). Efforts have been made to replace activated carbon with alternative adsorbents (Putra *et al.*, 2009; Rossner *et al.*, 2009, Kankou *et al.*, 2021). The focus is on the application of alternative adsorbents of high availability, low cost, high adsorption capacity, good removal efficiency, and high selectivity for different contaminants. It is therefore important to study adsorbents with different contaminants, in order to ensure that the material has an affinity with a wide spectrum of compounds and can therefore be considered a promising adsorbent for industrial applications (de Andrade *et al.*, 2018). Clays have a high specific surface area, mechanical and chemical stability, are abundant and have a high cation exchange capacity (Awad *et al.*, 2019), (Antonelli *et al.*, 2020). Clay plays an important role in certain fields of activity, such as the manufacture of medicines and the treatment of polluted water, for example in the adsorption of toxic organic compounds (Al-Degs *et al.*, 2008); (Wang *et al.*, 2015). Clay is a natural, ecological and recyclable adsorbent, abundant and available. This material is known for its hydrophilic character. Indeed; this property is justified by the presence of negative charges on the surface, and by the possibility of cation exchange (Ayari *et al.*, 2010), (Garmia *et al.*, 2018) Therefore, it has an advantage in water treatment. Clay plays an important role in certain fields of activity, such as the manufacture of medicines and the treatment of polluted water, for example in toxic organic decomposed adsorption (Fabryanty *et al.*, 2017). Activation is a process that consists of improving the adsorption properties of clay by subjecting it to a heat or chemical treatment. In this study, thermal activation was used for the removal of ofloxacin from water. The aim is to show that clay could be used to remove ofloxacin to treat contaminated drinking water (drinking water).

2. Methodology

2.1. Manufacture of clay balls

The clay is from the soil of the town of Daloa, in the Haut Sassandra region of west-central Côte d'Ivoire. This clay was collected from the lower horizons of water wells. This clay was transported to the laboratory where it was dried. Then it was crushed and sieved. Beads of 0.3 cm diameter were made, dried in an oven at 105 °C for 2 hours. They were then burned at 550 °C for 2 hours in a ramp of 10 °C/min. Activation is a process to improve the adsorption properties of clay by subjecting it to thermal or chemical treatment. The calcined beads were used for the removal of ofloxacin from water **(Figure 1).**



Clay powder *Clay paste* *Fresh clay beads* *Clay balls* calcined

Figure 1. steps of activation process of the clay balls

2.2. Water matrices.

The treatment tests were carried out on the water used to supply water to the Water Distribution Company of Côte d'Ivoire to the populations and that of laboratory water is ultra-pure laboratory water, and tap water: the water comes from the drinking water distribution network of Côte d'Ivoire.

2.3. Water treatment test protocol

All experiments were carried out in a horizontal reactor (*length 44 cm × width 8 cm × height 6 cm*) of laboratory batch flow **(Figure 2)**. 1000 mL of solution of pharmaceutical substances are introduced into the tank and put into circulation at a flow rate of 200 L h^{-1} using a gear pump (*Ismatec* brand). The adsorption tests on the clay bead bed were carried out in batch with in the different doped matrices ofloxacin solutions for 8 hours. After each test, the beads were calcined in the oven at 500 °C to remove ofloxacin residues adsorbed. After calcination, the same beads were used for the other experiments and until today for the adsorption tests that we carry out for the removal of various molecules in aqueous media.

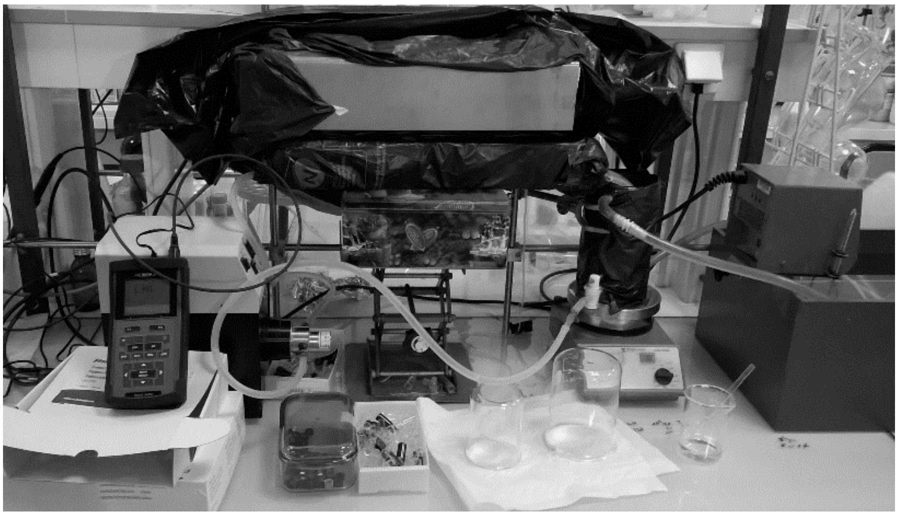
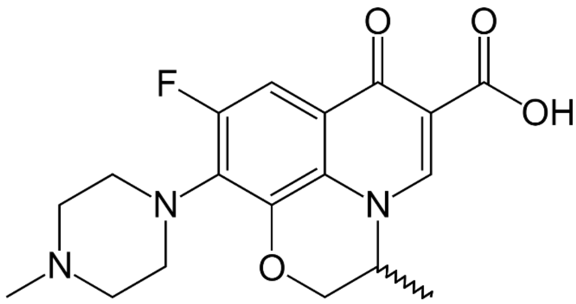


Figure 2. Adsorption reactor (length 44 cm × width 8 cm × height 6 cm)

2.4. Technical parameters

The effect of clay bead mass, initial ofloxacin concentration, pH and doped water matrices were monitored. In addition to highlighting the actual removal of ofloxacin from water matrices, the total organic carbon was measured using a SHIMADZU brand COTmeter.



Scheme 1: Molecular structure of ofloxacin

2.5. Analysis of water withdrawn

Ofloxacin residual concentrations were determined using a high-performance SHIMADZU brand liquid chromatograph. It is equipped with an injector, a column and a UV-visible detector. The mobile phase consists of ultra-pure water and acetonitrile acidified with formic acid (0.1%). The separation was carried out with a Kromasil column of type C_{18} (250 mm x 4.6 mm, 5 µm) in gradient mode for 10 minutes.

2.6. Adsorption kinetics

In this study, adsorption kinetics were established using the surface mass transfer model of a clay ball. The relationship between the adsorbed amount of ofloxacin and time is defined as :

$q_t = \frac{v}{m}(C_0 - C_r)$, q_t is the amount adsorbed (mg/g); k = $\frac{V}{m}$ is the transfer coefficient; C_0 : the initial concentration of ofloxacin (mol/L); Cr : the residual concentration of ofloxacin at time t (mol / L); m : the mass of the clay bed, v : volume of solution (0.9 L)

2.7. Reduction rate of ofloxacin

Ofloxacin removal rates were calculated as:

$Taux\ d'adsorption = \frac{(C_0 - C_r)}{C_0} x\ 100$; C_0 = Concentration of each drug at time t = 0 (mg/L) and Cr = Residual concentration of ofloxacin at time t (mg/L).

3. Results and Discussion

3.1. Clay ball mass effect

To assess the mass of clay needed in the reactor, we varied three masses of clay beads: 130 g; 170 g and 260 g **(Figure 3)**. These clay masses were chosen based on the total amount of clay beads needed to occupy the base surface of the horizontal reactor. During the experiments, the results showed that ofloxacin is eliminated for all clay masses. But the rate of adsorption is fast when we have a mass of 260 g. This reflects a greater availability of pores for an increasing mass of clay beads. We obtained similar results for ciprofloxacin under the same study conditions (Putra *et al.*, 2009), (El Azzouzi *et al.*, 2022).

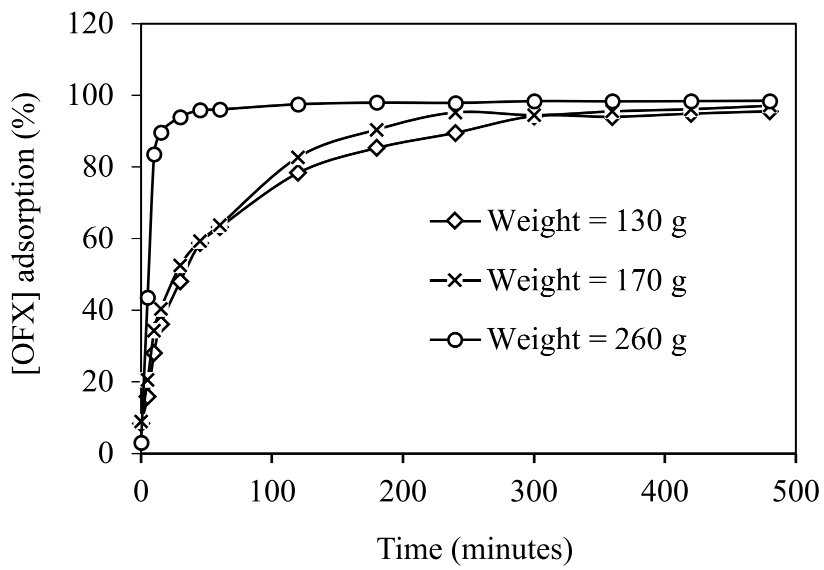


Figure 3. Effect of clay weight, [OFX] = 20 mg/L, ultra-pure water, pH = 5,3

3.2. Effect of ofloxacin concentration

The effect of the ofloxacin concentration by considering the concentrations is illustrate on figure 4. It should be noted that these concentrations ofloxacin are much higher than those found in waste water. With regard to the adsorption kinetics obtained, each ofloxacin solution doped for a given concentration is eliminated. The residual concentrations are 0.17 mg/L respectively; 0.252 mg/L; 0.23 mg/L and 0.40 mg/L respectively for 5; 10 ; 20 and 25 mg/L. These results showed the ability of calcined clay beads to remove ofloxacin from the water regardless of the concentration considered under our study conditions. This behavior may be related to the increase in motive power for mass transfer through the liquid film as well as the acceleration of the adsorption rate that leads to early saturation of the clay bed (Sotelo *et al.*, 2013; Suhas *et al.*, 2016).

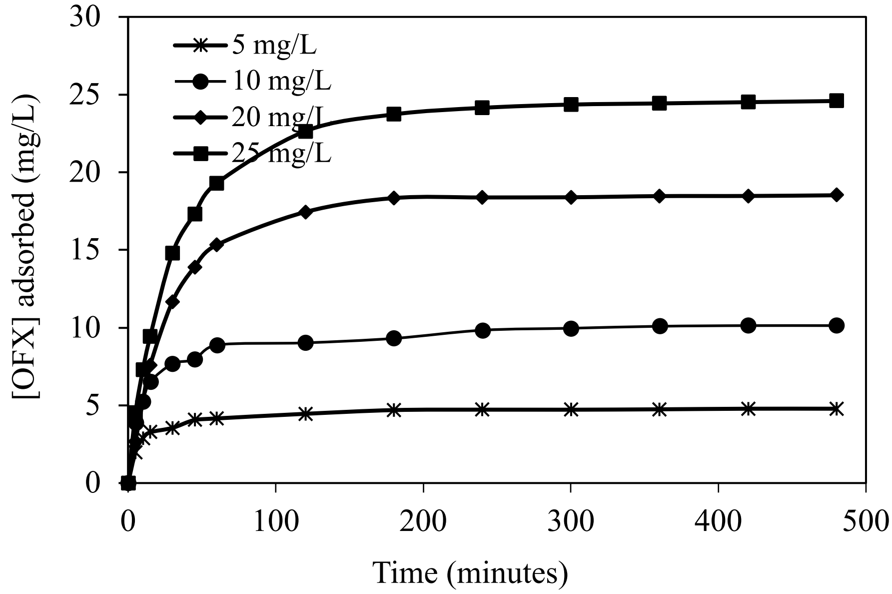


Figure 4. Effect of ofloxacin concentration, weight beads = 260 g, ultrapure water, pH = 5,3

3.3. pH effect

Treatments of acidic and basic water matrices have made it possible to monitor the evolution of pH under these conditions **(Figure 5)**. The objective is to follow the evolution of the loads on the surface of the clay balls in an aqueous medium. The pH of the aqueous medium makes it possible to know the ionic form that predominates in this water. pH values were set based on ofloxacin pKa values. Monitoring of adsorption kinetics showed all ionic forms of ofloxacin were adsorbed to the surface of the clay beads. The surface of clay beads would take is negatively charged for cationic forms and positively for anionic forms (Abdeen and Mohammad, 2013). On the other hand, the results indicated a slight decrease in the rate of adsorption of the cationic forms pH = 3 and 5 compared to the anionic forms (pH = 10). Indeed, for pH values below 2.7, the predominant species of ofloxacin ions is the cationic form (OFX^+) and the surface of the clay is positive, which leads to electrostatic repulsion between the OFX ions and the calcined beads.

For pH values above 8.25, the predominant species of ofloxacin is anionic (OFX^-) and the surface of the clay is negative, also generating electrostatic repulsion, disadvantaging the adsorption process. Indeed, clays have a surface charge that depends on the pH of the medium into which they are inserted, the pHZPC being the pH value corresponding to a zero-surface load. This data is relevant because the pH of the solution has a critical impact on the elimination of ionizable organic pollutants, which can affect the deprotonation of functional groups, the ionization of the adsorbate and the competition of ions (Antonelli *et al.,* 2020; Yang *et al.*, 2022). To show this part, the pH variations of basic and acidic doped waters were followed **(Figure 6)**. The results showed that at pH = 10, the value of the solution decreases 5.94. At initial pH equal to 3 we have a slight increase in pH values up to the value 5.03. At pH = 5, the evolution is very small. These results show that the surface of calcined clay beads has functions or fillers that allow pollutants to be fixed.

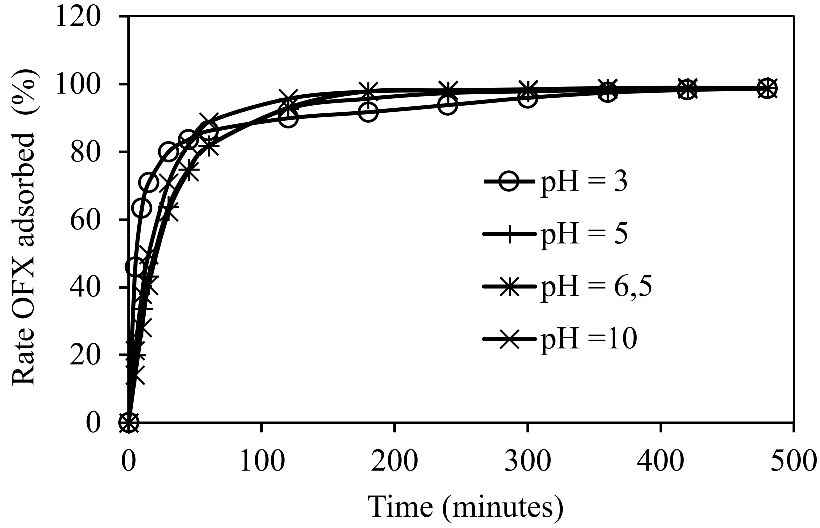


Figure 5. Effect of pH on ofloxacin adsorption on beads, weight beads = 260 g

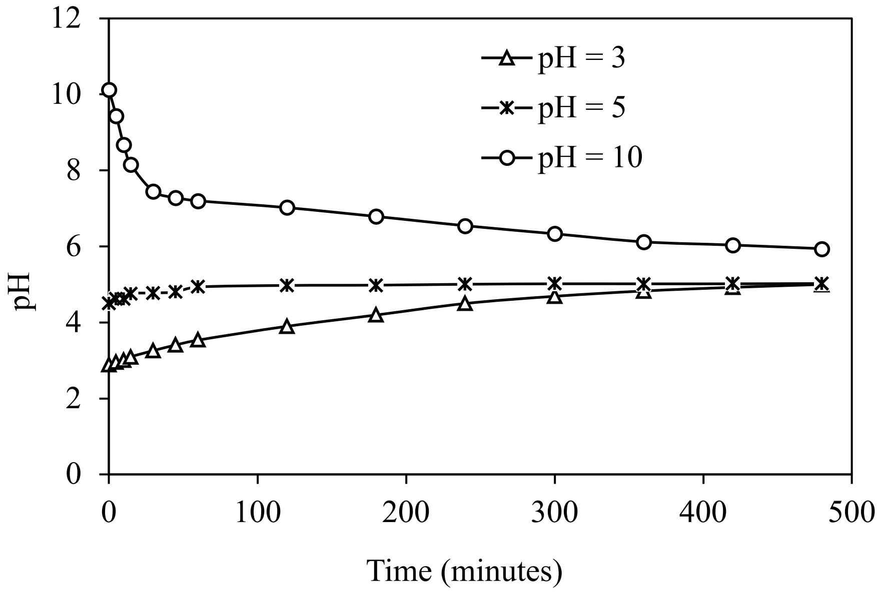


Figure 6. Monitoring the evolution of pH during the adsorption process, weight beads = 260 g

3.4. Application of the process on environmental aqueous matrices

The robustness of the process was evaluated by doping water samples from the drinking water supply network of a water distribution company in Côte d'Ivoire. It should be noted that this water is very rich in hydrogen carbonate ions ($CaCO_3^-$). **Figure 7** juxtaposes the adsorption kinetics of ofloxacin ions in drinking water and ultrapure water. The results showed that the adsorption rate of ofloxacin in ultrapure water is slightly higher than in tap water. This slight difference is thought to be due to the chemical quality of the tap water (Shamsudin *et al.,* 2022). It could reflect a competition between ofloxacin ions and calcium or hydrogen carbonate ions (CO_3^-). Indeed, by observing the rhythm of the kinetics of ultrapure water, saturation is reached after 20 minutes. On the other hand, the pace of the kinetics of the tap water shows that saturation has not been reached. This showed that an amount of ofloxacin ions (1260 µg/L) was not eliminated or 93 % elimination. The amount of molecule present in ultrapure water is 230 µg/L or 98 %. $CaCO_3^-$ ions have more affinity with the surface of calcined clays (Wang *et al.*, 2014; Ewis *et al.*, 2022).

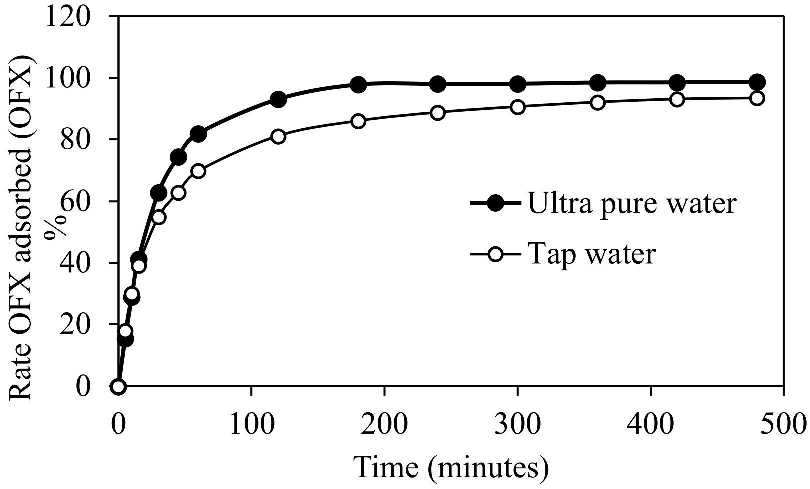


Figure 7. Adsorption kinetics of ofloxacin in ultrapure water and tap water weight beads = 260 g

3.5. Total organic carbon (TOC)

The total organic carbon level was monitored in the doped ultrapure water solutions. **Figure 8** shows the abatement rates for both adsorption and organic carbon. The results showed similar gaits to adsorption and TOC. These results would reflect a real elimination of ofloxacin from treated water. Removal rates are greater than 90 % of the initial concentration.

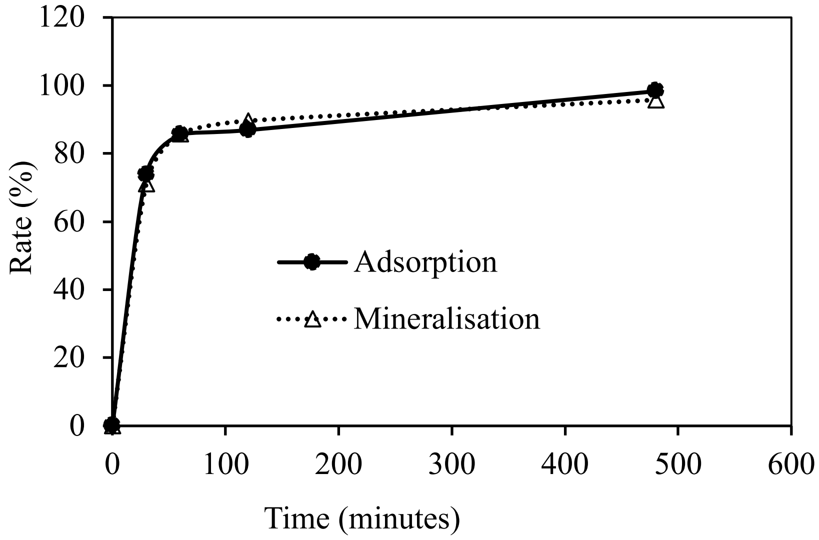


Figure 8. Adsorption and TOC adsorption rate of ofloxacin, pH = 5,3; weight beads = 260 g

Ben salem *et al.* 2015, showed that the combined processes of ionizing radiation using a BDD anode followed by microbial removal of enrofloxacin seem to be the best solution for the treatment of effluents containing enrofloxacin antibiotics. Similar results were obtained by Chen *et al.* 2022 that combining lignin biochar and perovskite materials provides a promising method for realizing high-efficiency photo-Fenton-like degradation of antibiotic water pollutions such as a ofloxacin.

Conclusion

Analysis of the parameters showed that ofloxacin is removed from doped waters. Increasing the mass of clay could improve the removal of fluoroquinolones. The initial concentration of the antibiotic has a significant effect on adsorption performance. The data obtained during adsorption are sufficient to provide accurate scaling data necessary for the design of dynamic adsorption columns.

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