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**Adsorption behavior and mechanisms of the emerging antibiotic pollutant norfloxacin on eco-friendly and low-cost hydroxyapatite: Integrated experimental and response surface methodology optimized adsorption process**

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**Highlights**

* •

nat-HAp produced by thermal [calcination](https://www.sciencedirect.com/topics/chemistry/calcination) of bovine bone was used to remove [NOR](https://www.sciencedirect.com/topics/chemistry/norfloxacin) from aqueous phase.

* •

Optimization of process parameters using Box-Behnken design in [response surface methodology](https://www.sciencedirect.com/topics/physics-and-astronomy/response-surface-methodology).

* •

Adsorption of [NOR](https://www.sciencedirect.com/topics/chemistry/norfloxacin) onto nat-HAp takes place as monolayer adsorption.

* •

Adsorption of NOR onto nat-HAp was controlled by [physisorption](https://www.sciencedirect.com/topics/chemistry/physisorption" \o "Learn more about physisorption from ScienceDirect's AI-generated Topic Pages).

* •

[Electrostatic](https://www.sciencedirect.com/topics/physics-and-astronomy/electrostatics), hydrophobic, H-bond and n-π electron donor–acceptor interactions were the main mechanisms.

* •

nat-HAp was still stable after four cycling runs.

**Abstract**

In this study, hydroxyapatite derived from bovine bone (nat-HAp) was used to remove norfloxacin antibiotic (NOR) from an aqueous solution. The nat-HAp properties were interpreted by analysis of the structure, specific surface area, functional groups, morphology, and composition. The pseudo-second-order kinetic and Langmuir isotherm suit the experimental data on NOR adsorption very well. Maximum absorption was shown to be 166.01 mg g−1. Using a [response surface methodology](https://www.sciencedirect.com/topics/physics-and-astronomy/response-surface-methodology" \o "Learn more about response surface methodology from ScienceDirect's AI-generated Topic Pages) (RSM), the highest NOR elimination of 96.20 % was obtained under optimum conditions: NOR of 132.57 mg L–1, pH of 7.88, nat-HAp dose of 0.99 g L–1, and temperature of 25.06 °C. Thermodynamic studies demonstrated that the adsorption process was favorable, spontaneous, and exothermic. The value of standard enthalpy change (ΔH0) shows that [physisorption](https://www.sciencedirect.com/topics/chemistry/physisorption) controlled the adsorption, and for this purpose, a viable mechanism for the adsorption of NOR onto nat-HAp was suggested. Based on the reusability experiment, the nat-HAp remained stable after four cycling runs. These results show that nat-HAp effectively absorbed NOR and might be a cost-effective alternative adsorbent to eliminate fluoroquinolone antibiotics during wastewater treatment.

**Graphical abstract**

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**Introduction**

The widespread usage of antibiotics has increased the presence of these substances in aquatic environments, which may negatively impact human and environmental health [1]. Antibiotics are often detected in surface water and wastewater [2]. Their toxicological effects on aquatic species and the resistance they can create in some bacterial strains, even at low doses, are becoming a growing concern [3]. Numerous antibiotics have properties of limited biodegradability and environmental persistence [4]; fluoroquinolone (FQ) antibiotics are an essential family of regularly used antibiotics. Norfloxacin (NOR,1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-carboxylic acid) is a fluoroquinolone antibiotic, broad-spectrum antibacterial compound with high antibacterial activity against both Gram-negative and Gram-positive bacteria through inhibition of DNA gyrase [5]. It is widely used in human and veterinary medicines [6]. However, norfloxacin had a slow rate of metabolism in both humans and animals, which led to the release of 40–90 % of the drug's active metabolites into the environment via domestic sewage and farming wastewater [7]. In recent years, norfloxacin has been found in various aquatic environments, including drinking water [6], [7], [8]. As a broad-spectrum antibiotic, trace levels of norfloxacin in the environment may produce selection pressure on microbes, thereby increasing their antibiotic resistance [9], [10], causing genotoxicity and teratogenesis, posing a threat to aquatic organisms and ecosystems [7], [10], and finally posing a threat to public health. Considering the hazards of norfloxacin contamination in the aquatic environment, it was imperative to remove norfloxacin from the aquatic environment using a practical and efficient method.

Until now, various methods have been used to remove NOR from aqueous solution, such as adsorption [11], photocatalysis [12], Fenton oxidation [13], and electrochemical oxidation [14]. The most promising of these methods is adsorption owing to its environmental friendliness, low cost, simplicity, high efficiency, simple recovery, and reusability of the adsorbent [15], [16]. Traditional adsorbents, such as biochar [17], activated carbon [18], alumina [19], zeolite [20], and others, are ineffective, have limited adsorption capabilities, and are challenging to renew for the removal of antibiotics [21]. Therefore, creating adsorbents with simple regeneration, high efficiency, and high adsorption capacity is crucial.

Hydroxyapatite [Ca10(PO4)6(OH)2] is a widely used inorganic material in the fields of biology and medicine [22], [23]. Due to its non-toxicity, bioactivity, biocompatibility, osteoconductivity, and non-immunogenic and non-inflammatory properties, it is the most promising biomaterial [24]. Due to its particular structure bestowing ionic exchange characteristics, low solubility in water, high stability in reducing and oxidizing conditions, and adsorption affinity towards several contaminants [25], it has been discovered to be an efficient adsorbent for environmental processes. This biomaterial has been used to remove potentially hazardous metal ions and chemical molecules from water [25], [26]. It has been widely applied in chromatography to separate and purify nucleic acids and proteins [27]. Hydroxyapatite as a medication carrier has been the topic of extensive research [28].

Traditionally, one variable is changed simultaneously during experimental optimization while the others remain unchanged. Due to the large number of required trials, it is also difficult to conduct tests using every possible combination of study variables. By maximizing all influencing parameters collectively using a statistical experimental design, such as RSM [29], these limitations of a conventional technique can be overcome. RSM is a combination of statistical and mathematical approaches for constructing models, organizing experimentation, evaluating the impacts of variables, and determining the optimal conditions for factors to predict desired responses [30]. When developing an adsorption process, employing statistical experimental design techniques can lead to a reduction in process variability, an increase in product yields, a more precise confirmation of the output response to target requirements, as well as a reduction in both the amount of time required for development and the total cost of the project. Multiple researchers have described using RSM to optimize batch adsorption techniques [30], [31]. Box-Behnken design (BBD) is RSM’s most prevalent and efficient design. BBD has several benefits over the Doehelrt and Central Composite designs, including the need for fewer experimental points and greater efficiency [32].

Therefore, the present study demonstrates that hydroxyapatite derived from bovine bone (nat-HAp) can effectively remove the antibiotic norfloxacin. The specific objectives of our investigation were as follows: (i) to prepare the low-cost hydroxyapatite material by pyrolysis (calcination) technique and to study its characteristics using X-ray diffraction (XRD), Nitrogen-Brunauer Emmett–Teller surface area analysis (N2-BET), Fourier transform infrared spectroscopy (FTIR), and field emission scanning electron microscopy coupled with energy dispersive spectroscopy (FESEM/EDX); (ii) to examine the applicability of different isotherm models (such as Langmuir, Freundlich, and Temkin) in order to determine the best-fit isotherm equation; (iii) To determine the utility of various kinetic models (such as pseudo-first-order and pseudo-second-order models); (iv) to study the feasibility of nat-HAp as an adsorbent for NOR antibiotic and optimize the adsorption using a Box–Behnken design-based (BBD) response surface methodology (RSM) with the Design Expert software (DES, Version 12, Stat-Ease, USA) under four independent variables including initial concentration, pH, adsorbent dosage, and temperature; (v) to discuss the mechanism through which NOR adsorbs to nat-HAp; (vi) to study the thermodynamic properties (such as free Gibbs energy, enthalpy, and entropy); and (vii) to study the reusability of the nat-HAp.

**Section snippets**

**Materials**

NOR was purchased from Sigma-Aldrich (Chem. Co., USA). The structure and relevant physicochemical properties of Norfloxacin are shown in Table 1. pH was adjusted using 0.1 mol/L NaOH and 0.1 mol/L HCl. All solutions were prepared using ultrapure water (Adrona, Millipore Milli-Q UV Plus, R = 18.25 MΩm).

**Preparation of adsorbent nat-HAp**

The nat-HAp was prepared as reported in [34]. The fresh cortical bone of mature bovine (2–4 years old) was collected from the local slaughterhouse of Bouira (Algeria) and kept at − 20 °C. The

**Characterization of the adsorbent material**

The XRD pattern of natural hydroxyapatite before norfloxacin adsorption was presented in Fig. 1a. The components of the crystalline phase were identified using standard JCPDS cards accessible through the system software. The peaks at 2 Θ = 25.9°, 29.01°, 31.72°, 32.20°, 33°, 34.15°, 39.82°, 46.87° and 49.51° confirm the phase and purity of derived nat-HAp crystals.

The textural properties of the nat-HAp material were assessed using N2 adsorption–desorption isotherms at T = 77 K. As depicted in

**Conclusion**

This work studied the adsorption of NOR from aqueous solutions using natural hydroxyapatite derived from bovine bone by calcination at 800 °C. Response surface methodology was utilized to maximize the removal of norfloxacin by the nat-HAp adsorbent. Experiments were conducted using a statistical design based on the Box–Behnken surface with four input variables: initial concentration, pH, adsorbent dose, and temperature. Contact time (180 min) was considered a constant input parameter. With a

**CRediT authorship contribution statement**

**Sabrina CHEIKH:** Conceptualization, Investigation, Software, Writing – original draft, Methodology, Data curation, Formal analysis. **Ali IMESSAOUDENE:** Software, Data curation, Methodology, Writing – review & editing, Visualization, Validation. **Jean-Claude BOLLINGER:** Validation, Methodology, Supervision, Visualization, Writing – review & editing. **Amar MANSERI:** Resources, Data curation, Visualization. **Abdelkrim BOUZAZA:** Resources, Supervision, Validation, Writing – review & editing. **Amina HADADI:**

**Declaration of Competing Interest**

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

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