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# Studies on adsorption of oxytetracycline from aqueous solutions onto hydroxyapatite

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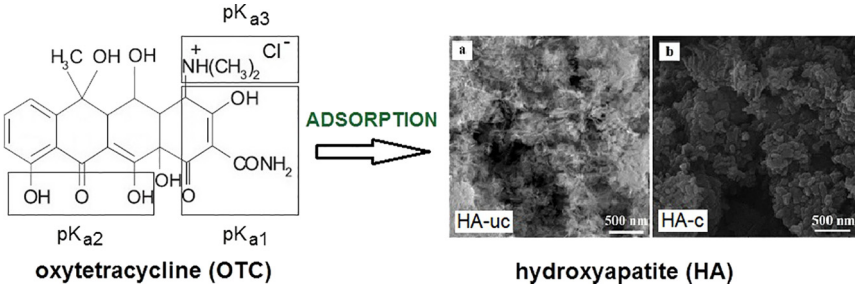
## HIGHLIGHTS

- Results obtained support the use of hydroxyapatite (HA) as adsorbent for removal of oxytetracycline (OTC).
- Maximum OTC removal rate of 97.58% was obtained.
- OTC follows the pseudo-second order kinetic model for adsorption on HA.
- Surface complexation is the main adsorption mechanism of OTC to HA.
- Zwitterions are the most adsorbed OTC species on HA, adsorption being pH-dependent.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The presence of antibiotics in the water and wastewater has raised problems due to potential impacts on the environment and consequently their removal is of great importance. For this reason, this article aims to perform a study on the possibility of oxytetracycline (OTC) adsorption from aqueous medium by using the hydroxyapatite (HA) nanopowders as adsorbent materials. The hydroxyapatite nanopowders were synthesized by wet precipitation method by using orthophosphoric acid and calcium hydroxide as raw materials and investigated by XRD, SEM-EDX, FTIR and BET methods. The uncalcined and calcined hydroxyapatite samples have hexagonal crystal structure with crystal sizes smaller than 100 nm and a specific surface area of 316 $m^2$/g and 139 $m^2$/g, respectively. The adsorption behavior of oxytetracycline, a zwitterionic antibiotic, on nanohydroxyapatite was investigated as a function of pH, contact time, adsorbent dosage and drug concentration by means of batch adsorption experiments. High oxytetracycline removal rates of about 97.58% and 89.95% for the uncalcined and calcined nanohydroxyapatites, respectively, were obtained at pH 8 and ambient temperature. The adsorption process of oxytetracycline onto nanohydroxyapatite samples was found to follow a pseudo-second order and intraparticle diffusion kinetic models. The maximum adsorption capacities of 291.32 mg/g and 278.27 mg/g for uncalcined and calcined nanohydroxyapatite samples, respectively, have been found. The adsorption mechanism of OTC on the hydroxyapatite surface at pH 8 can be established via surface complexation. The obtained results are indicative of good hydroxyapatite adsorption ability towards oxytetracycline drug.



## 1. Introduction

In recent years, soil and water pollution by the antibiotic residues is a matter of growing interest (Bound and Voulvoulis, 2004). The antibiotics can enter the environment in many ways, such as the production of active pharmaceutical ingredients, removal of the pharmaceutical

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residues, the discarding of unused medicines, etc. Some antibiotics are easily degraded (such as penicillins), while others are much more persistent (such as tetracyclines), allowing them to exist more time in the environment, to further spread and accumulate in higher concentrations. In surface waters receiving municipal wastewaters, concentrations of antibiotics rarely exceed 1 mg/L, being usually within a low μg/L range (Larsson, 2014). The antibiotics occurrence in the water environment exposes human beings and animals to constant low concentrations of antibiotics through drinking water contamination.

Among different groups of antibiotics, tetracyclines receive a special attention because large quantities are applied in the therapy of human and animal infections and also in animal feed as growth promoters. But, only a small amount of tetracyclines can be metabolized or absorbed by humans and animals. Residues of these antibiotics are accumulated in environmental waters and soil and they may lead to occurrence of resistant species (Gao et al., 2012b).

Oxytetracycline (OTC), a prominent member of tetracyclines, is a broad-spectrum antibiotic, active against a wide variety of bacteria. Oxytetracycline is widely used in human and veterinarian medicine to treat many infections, both common and rare. As a drug, it undergoes minimal metabolism being mainly excreted as such via urine (CVMP, 1995). A soil sorption study indicated that oxytetracycline is strongly adsorbed in soil regardless soil type (Rabølle and Spliid, 2000). Broad scale monitoring studies have found oxytetracycline in concentrations as high as 300 μg/kg in some soils, and up to 15 μg/L in some ground and surface waters (Fatta-Kassinos et al., 2011). The World Health Organization (WHO) recommends a guideline value of <1 ppb of antibiotic residues in the aquatic environment and <100 ppb in the soil (WHO (World Health Organization) Library, 2012).

Therefore, efficient and inexpensive treatment methods for removing the antibiotics from the environment were developed. A low-cost strategy to remove such compounds from the effluents of sewage treatment plants consists in including a solid phase adsorption step after a traditional treatment. The adsorption of the tetracyclines on isolated clays, organic clays, soils, organic matters and marine sediment has been previously investigated (Kulshrestha et al., 2004; MacKay and Canterbury, 2005; Rabølle and Spliid, 2000).

The apatites are the most commonly occurring phosphate minerals on the Earth's crust, and consequently the primary natural sources of phosphorous in the biosphere (Oelkers and Valsami-Jones, 2008). The apatites are important in a great variety of natural and industrial processes. They are used as raw material in the fertiliser production and remediation of contaminated soils (Manning, 2008). The hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA), a compound similar to the biological apatite which is the main constituent of mammalian bone and teeth, is a promising material for bone and tooth implants (Ciobanu et al., 2008; Ciobanu et al., 2012; Dorozhkin, 2015). Due to its high adsorption capacity and low water solubility, hydroxyapatite is a good adsorbent for heavy metals, dyes and other contaminants in wastewaters (Ciobanu et al., 2009; Nishiyama et al., 2016; Wang et al., 2016).

The present work involved a study of the OTC adsorption process from aqueous solutions by the hydroxyapatite as adsorbent. The hydroxyapatite was chosen as an adsorbent due to its adsorption properties, lack of toxicity and low price. Besides, the adsorption behaviour of OTC on hydroxyapatite has not yet been studied in the literature till now. Kinetic adsorption experiments were carried out to establish the effect of time on the adsorption process and to determine the adsorption rate for OTC removal.

## 2. Materials and methods

### 2.1. Materials

Oxytetracycline hydrochloride ($C_{22}H_{24}N_2O_9 \cdot HCl$, MW = 496.89, CAS Number 2058-46-0, 95% purity) was purchased from Sigma-Aldrich (Germany). Other chemicals, including $Ca(OH)_2$, $H_3PO_4$ (85 wt %), NaOH, HCl and $CH_3—CH_2—OH$ were purchased from Chemical Company (Romania). All reagents were of analytical grade.

### 2.2. Preparation and characterization of nanohydroxyapatite adsorbents

The hydroxyapatite samples were prepared by using $Ca(OH)_2$ and $H_3PO_4$ as raw materials, as presented elsewhere (Ciobanu et al., 2015a; Ciobanu et al., 2015b; Ciobanu et al., 2016). 250 mL aqueous solution of $Ca(OH)_2$ (0.1 M) were added drop-wise to an appropriate amount of $H_3PO_4$ (0.1 M) aqueous solution to achieve predetermined Ca/P atomic ratio of 1.67, under magnetic stirring for 1 h at 60 ± 1 °C. The pH was continuously monitored and adjusted to 11 ± 0.5 by adding NaOH (1 M) aqueous solution. The suspension was aged for 3 h at 60 ± 1 °C and then filtered and washed with ethanol and triply distilled water. The obtained powder was calcined at 800 °C in an electrically heated furnace in order to increase its crystallinity. The uncalcined and calcined hydroxyapatite samples were labeled *HA-uc* and *HA-c*, respectively.

Powder X-ray diffraction (XRD) patterns of the samples were recorded with a X'PERT PRO MRD diffractometer (PANalytical, Netherlands) by using monochromatic CuKα radiation (λ = 0.15418 nm). From XRD data the phase composition and average crystallite size of the hydroxyapatite powders were obtained. The morphology and elemental composition on the surface of the hydroxyapatite samples were evaluated by using scanning electron microscopy (SEM) together with energy dispersive X-ray spectroscopy (EDX) with QUANTA 200 3D microscope (FEI, Netherlands). The BET specific surface areas were obtained from the $N_2$ adsorption isotherms recorded by a Quantachrome Nova 2200e Win2 apparatus (Quantachrome, Germany). The pH at the point of zero charge ($pH_{pzc}$) of the hydroxyapatite samples was determined by the pH drift method (Khan and Sarwar, 2007). All pH measurements were run with a Multi-Parameter Consort C831 (Consort, Belgium). The FTIR spectra of the samples were recorded on a DIGILAB SCIMITAR-SERIES spectrophotometer with an attenuated total reflectance (ATR) accessory. Measurements were carried out in the attenuated total reflectance mode using a ZnSe prism, between 400 and 4000 $cm^{-1}$, with resolution setting 4 $cm^{-1}$.

### 2.3. Batch adsorption experiments

The adsorption measurements were carried out by batch equilibrium experiments in 50 mL glass flasks. Various OTC solutions with different initial concentrations were prepared by diluting the OTC (1000 mg/L) stock solution. About 20 mL of OTC solutions of specified concentrations were mixed with fixed amounts of adsorbent. Prior to the adsorbent addition, the mixture pH was adjusted to required value either by 1 N NaOH or HCl solutions. The flasks were sealed and incubated under stirring at 150 rpm for a given time to attain the equilibrium. Then, the mixtures were filtered with 0.45 μm cellulose acetate syringe filters prior to the concentration measurement.

For equilibrium measurements, the effects of the solution pH (2—10), adsorbent dosage (0.1–5 g/L), initial OTC concentration (10–300 mg/L) and contact time were examined in one-step batch mode. The influence of various parameters was investigated by varying one parameter at a time and keeping constant the other parameters. The OTC concentration was quantified by means of UV–visible spectroscopy using a UV–Vis Jasco V-550 spectrophotometer (Jasco, Japan) at 355 nm (wavelength of maximum adsorption value of OTC).

The adsorption capacity $q_t$ (mg/g) at time $t$ and the removal rate or percentage removal $R$ (%) of OTC were determined by the following equations:

$$q_t = \frac{C_0 - C_t}{m} \cdot V \quad (1)$$