Colloids and Surfaces A: Physicochem. Eng. Aspects 417 (2013) 57–64

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Adsorption and circular dichroism of tetracycline on sodium and calcium-montmorillonites

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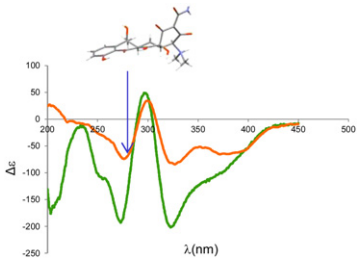
HIGHLIGHTS

- Molecular changes of TC adsorbed on Na^+ and Ca^{2+}-montmorillonite were studied.
- Cation exchange and Ca-complexes occur when TC are adsorbed on Ca^{2+}-montmorillonite.
- TC adsorption promotes the extended conformation of the molecule.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 August 2012
Received in revised form 22 October 2012
Accepted 30 October 2012
Available online 9 November 2012

Keywords:
Tetracycline
Circular dichroism
Adsorption
Montmorillonite

ABSTRACT

The interaction of tetracycline (TC) with a Na^+-montmorillonite and a Ca^{2+}-montmorillonite in aqueous media was investigated using a batch technique complemented with *X*-ray diffraction (XRD) and circular dichroism (CD). The adsorption of TC decreases by increasing the pH in both cases, although Ca^{2+}-montmorillonite is a more effective adsorbent than Na^+-montmorillonite in the pH range 6–8.5. In both cases, TC locates in the interlayer spacing, increasing the d_{001} basal spacing from nearly 13.7 Å to nearly 22.0 Å. CD data of TC solutions indicates that increasing the pH induces structural changes from the twisted conformation to the extended conformation of the TC molecule. The presence of Ca^{2+} in the solution enhances this effect in the pH range 6–10.5. Adsorption on Na^+-montmorillonite and Ca^{2+}-montmorillonite significantly induces the adoption of the extended conformation of TC. Chelation of TC with Ca^{2+} ions in the interlayer is also demonstrated. Therefore, Ca^{2+} ions in the interlayer behave as active sites for TC adsorption on montmorillonite, leading to the formation of montmorillonite-Ca^{2+}-TC complexes. The conformational changes that TC suffers upon adsorption may have important effects on the bioavailability and antimicrobial activity of the antibiotic.

1. Introduction

Tetracyclines are antibiotics that show bacteriostatic activity toward gram-negative and gram-positive microorganisms [1], reason why they are widely used in medicine and veterinary. The so-called tetracycline (TC) is one of these products. The chemical properties of TC have been extensively studied [2–4]. It has different acid groups in its chemical structure and can exist under different ionic species and conformations depending on the pH of the aqueous solution. The presence of such groups in the TC molecule generates potential sites of interaction with metal ions [4]. This interaction is important to understand and predict the bioavailability of TC, since in blood plasma this drug is transported as calcium complexes [3].

Clay minerals are widely used in pharmaceuticals, having a variety of applications ranging from carriers in sustained-release dosage forms to suspending agents, and giving rise to an increasing interest in the analysis of possible interactions of clay particles with

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http://dx.doi.org/10.1016/j.colsurfa.2012.10.060