



Effect of iron ion on doxycycline photocatalytic and Fenton-based autocatalytic decomposition



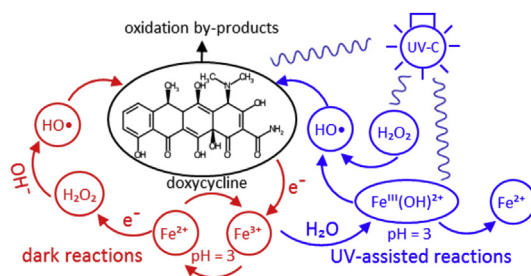
Juri Bolobajev, Marina Trapido, Anna Goi*

Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia

HIGHLIGHTS

- Doxycycline forms complexes with ferric iron at pH 3.0.
- Iron redox cycling supports the doxycycline autocatalytic decomposition by H_2O_2 .
- Doxycycline oxidation by $H_2O_2/Fe(III)$ proceeds via hydroxyl radicals.
- Ultraviolet/ H_2O_2 showed the highest doxycycline degradation rate and mineralization.
- The efficacy was: $UV/H_2O_2 \approx UV/H_2O_2/Fe(III) > H_2O_2/Fe(II) > H_2O_2/Fe(III) \approx UV/Fe(III) > UV$.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 December 2015
 Received in revised form
 26 February 2016
 Accepted 10 March 2016
 Available online 25 March 2016

Handling Editor: Jun Huang

Keywords:

Doxycycline
 Autocatalytic decomposition
 Ferric iron–doxycycline complex
 Ferric iron reduction
 Hydroxyl radical

ABSTRACT

Doxycycline plays a key role in Fe(III)-to-Fe(II) redox cycling and therefore in controlling the overall reaction rate of the Fenton-based process ($H_2O_2/Fe(III)$). This highlights the autocatalytic profile of doxycycline degradation. Ferric iron reduction in the presence of doxycycline relied on doxycycline-to-Fe(III) complex formation with an ensuing reductive release of Fe(II). The lower ratio of $\bullet OH$ -to-contaminant in an initial $H_2O_2/Fe(III)$ oxidation step than in that of classical Fenton ($H_2O_2/Fe(II)$) decreased the doxycycline degradation rate. The quantum yield of doxycycline in direct UV-C photolysis was $3.1 \times 10^{-3} M E^{-1}$. In spite of doxycycline-Fe(III) complexes could produce the adverse effect on the doxycycline degradation in the UV/Fe(III) system some acceleration of the rate was observed upon irradiation of the Fe(III)–hydroxy complex. Acidic reaction media (pH 3.0) and the molar ratio of DC/Fe(III) = 2/1 favored the complex formation. Doxycycline close degradation rates and complete mineralization achieved for 120 min (Table 1) with both UV/ H_2O_2 and UV/ $H_2O_2/Fe(III)$ indicated the unsubstantial role of the reduction of Fe(III) to Fe(II) in UV/ $H_2O_2/Fe(III)$ system efficacy. Thus, factors such as doxycycline's ability to form complexes with ferric iron and the ability of complexes to participate in a reductive pathway should be considered at a technological level in process optimization, with chemistry based on iron ion catalysis to enhance the doxycycline oxidative pathway.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Doxycycline (DC) is a semisynthetic antibiotic of the tetracycline class that is active against Gram-positive and Gram-negative bacteria (Todar, 2002). DC exists in one of the classes of antibiotics that are most consumed (Van Boeckel et al., 2014). The intensive use of

* Corresponding author.

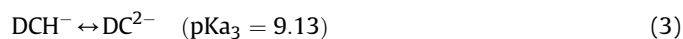
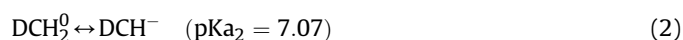
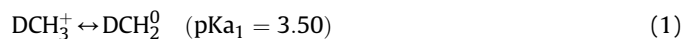
E-mail address: Anna.Goi@ttu.ee (A. Goi).

the tetracycline class antibiotics resulted in the release of these compounds to the environment. Surface and natural waters concentrations of antibiotics of the tetracycline class are in the range of 0.07–4.2 and 0.11–0.42 $\mu\text{g L}^{-1}$, respectively (Borghi and Palma, 2014). In sewage treatment plants, concentrations of 0.067–2.48 $\mu\text{g L}^{-1}$ in influent and 0.064–0.915 $\mu\text{g L}^{-1}$ in effluent have been reported (Batt et al., 2007; Lindberg et al., 2005). The wastewater from livestock farming that uses tetracycline to support intensive breeding had the concentration of chlortetracycline of as high as 2960 $\mu\text{g L}^{-1}$ and after the treatment of 524 $\mu\text{g L}^{-1}$ (NIER, 2007). In spite of the tetracyclines low concentrations the developing and/or maintaining bacteria resistance to the tetracycline in the environment and negative impact on microbial community structure and function caused by their antimicrobial properties were observed (Mojica and Aga, 2011).

Thus, because of DC high bioresistivity, it passes through conventional sewage treatment systems (Le Minh et al., 2010) and requires the application of effective treatment methods for degradation. Advanced oxidation processes that are based on the formation of highly reactive oxidation species, mainly hydroxyl radicals ($\cdot\text{OH}$), are effective for tetracycline class antibiotic degradation (Bautitz and Nogueira, 2007; Canonica et al., 2008; Gomez-Pacheco et al., 2011; Rivas et al., 2011; Yuan et al., 2011). These technologies also implicate Fenton-based catalytic and photocatalytic (hydrogen peroxide (H_2O_2)/ferrous ion (Fe(II)), ultraviolet (UV)/ H_2O_2 /ferric ion Fe(III)) processes that use iron ion as an environmentally friendly catalyst for oxidation enhancement.

Iron is one of the most abundant elements in natural water and is involved in many natural redox reactions that include H_2O_2 and organic compounds. Tetracycline organic ligands form stable complexes with metal ions, such as Fe(III) (Ghandour et al., 1992; Vartanian et al., 1998; Gu and Karthikeyan, 2005; Sunaric et al., 2009). Although Fe(II) does not form complexes with tetracycline (Sultan et al., 1988), the tetracycline- Fe(III) complex formation constant (first proton association constant, pK_1) of 13.4 ± 0.063 (Ghandour et al., 1992) is close to that of other well-known chelating agents such as nitrilotriacetic acid ($\text{pK}_1 = 15.9$; Martell, 1975) and citric acid ($\text{pK}_1 = 11.4$; Martell, 1975).

DC consists of four fused rings with $-\text{OH}$ and $-\text{CH}_3$ substitutions on positions 5 and 6, respectively (Fig. 1(A)). The compound has three distinct acid groups (tricarboxylamide (C1:C2:C3), phenolic diketone group (C10:C11:C12), and dimethylamaine (C4)) (Fig. 1(A)). The acid dissociation constants (pK_a) (Şanlı et al., 2009) causing DC to exist as cationic (DCH_3^+), zwitterionic (DCH_2^0) or anionic (DCH^- and DC^{2-}) species under acidic, moderately acidic to neutral, and alkaline conditions (Eqs. (1)–(3)), respectively.



Thus, the metal binding site in the tetracyclines is strongly pH dependent (Vartanian et al., 1998; Mitscher et al., 1972; Albert and Rees, 1956). At acidic pH, binding occurs at the O_3 (Fig. 1(A)) atom on ring A of the tetracycline class compounds. At neutral pH, the tetracyclines are deprotonated at the hydroxyl group at the C12 position, and binding involves an O10 and O12 oxygen donor via chelation. Under alkaline conditions, binding involves the dimethylamino nitrogen and the O12a hydroxyl oxygen donor on the A ring, and the tetracycline molecule is doubly deprotonated. Complexes of the tetracyclines with transition metals (Fe(III) , Cu(II) , Ni(II) , Zn(II)) incorporate two solvent molecules (Vartanian et al.,

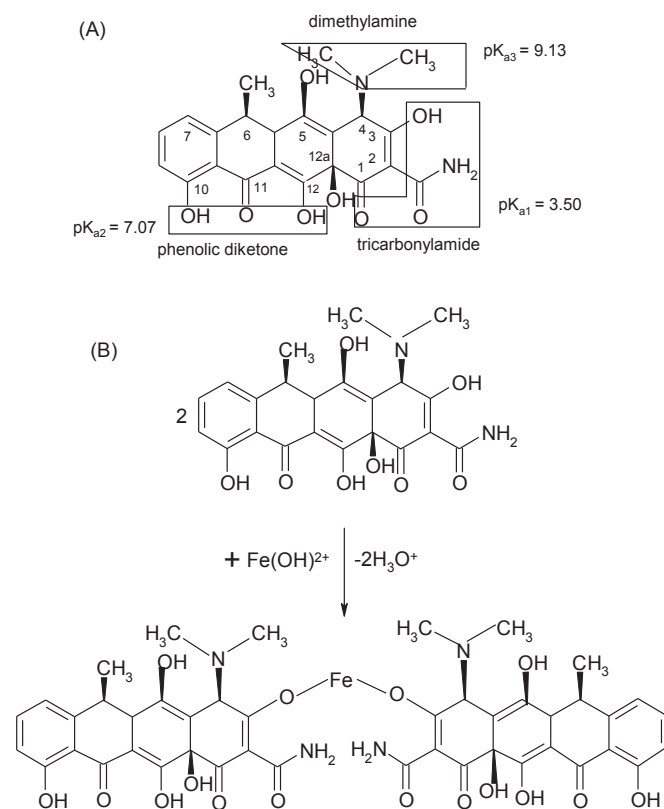


Fig. 1. (A) Chemical structure and pK_a of DC (Gu and Karthikeyan, 2005; Şanlı et al., 2009). (B) Proposed mechanism of Fe(III) binding with DC in acidic pH.

1998; Sultan et al., 1988). These complexes reduce Fe(III) (Wang et al., 2015) that may enhance Fenton-based oxidation significantly. They may also cause (Sunaric et al., 2009) a negative interference and decrease the H_2O_2 oxidation reaction rate of the tetracyclines. The effect was strongly dependent on metal ion concentration and pH.

Although few studies assess the effect of the Fenton (Sunaric et al., 2009) and photo-Fenton (Bautitz and Nogueira, 2007) processes on the tetracycline class compound degradation, the influence of the tetracyclines and the iron ion interaction on the efficacy and process chemistry has not been evaluated. In addition, the degradation of DC by photocatalytic and Fenton-based processes to our knowledge is not studied or studied in a less extent than the degradation of the others tetracyclines.

In this study, the formation of the DC- Fe(III) complexes, the ability of DC to participate in the Fe(III) reductive pathway, the formation of hydroxyl radicals ($\cdot\text{OH}$), hydrogen peroxide consumption and the extent of DC mineralization were investigated. The studies on kinetics of doxycycline autocatalytic degradation and a comparison of the Fenton-based process efficiency with that of the classical Fenton and the photocatalytic processes (UV/ Fe(III) , UV/ H_2O_2 and UV/ H_2O_2 / Fe(III)) were performed.

The ability of DC to reduce Fe(III) may contribute substantially to the oxidation chemistry of the process enhanced by iron ion catalysis and help explain the DC decomposition mechanism in environmental pollution abatement.

2. Experimental

2.1. Reagents

All chemicals used were of analytical grade. Doxycycline hyclate

Download English Version:

<https://daneshyari.com/en/article/4407672>

Download Persian Version:

<https://daneshyari.com/article/4407672>

[Daneshyari.com](https://daneshyari.com)