



Degradation of flumequine in aqueous solution by persulfate activated with common methods and polyhydroquinone-coated magnetite/multi-walled carbon nanotubes catalysts



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ARTICLE INFO

Article history:

Received 9 May 2015

Received in revised form

27 July 2015

Accepted 4 August 2015

Available online 8 August 2015

Keywords:

Flumequine

Persulfate

Polyhydroquinone-coated magnetite/multi-walled carbon nanotubes

Catalytic degradation

Mechanisms

ABSTRACT

In recent years, flumequine (FLU) has been ubiquitously detected in surface waters and municipal wastewaters. In light of its potential negative impacts to aquatic species, growing concern has been arisen for the removal of this antibiotic from natural waters. In this study, the kinetics, degradation mechanisms and pathways of aqueous FLU by persulfate (PS) oxidation were systematically determined. Three common activation methods, including heat, Fe^{2+} and Cu^{2+} , and a novel heterogeneous catalyst, namely, polyhydroquinone-coated magnetite/multi-walled carbon nanotubes ($\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{PHQ}$), were investigated to activate PS for FLU removal. It was found that these three common activators enhanced FLU degradation obviously, while several influencing factors, such as solution pH, inorganic ions (especially HCO_3^- at 5 mmol/L) and dissolved organic matter extracts, exerted their different effects on FLU removal. The catalysts were characterized, and an efficient catalytic degradation performance, high stability and excellent reusability were observed. The measured total organic carbon levels suggested that FLU can be effectively mineralized by using the catalysts. Radical mechanism was studied by combination of the quenching tests and electron paramagnetic resonance analysis. It was assumed that sulfate radicals predominated in the activation of PS with $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{PHQ}$ for FLU removal, while hydroxyl radicals also contributed to the catalytic oxidation process. In addition, a total of fifteen reaction intermediates of FLU were identified, from which two possible pathways were proposed involving hydroxylation, decarbonylation and ring opening. Overall, this study represented a systematical evaluation regarding the transformation process of FLU by PS, and showed that the heterogeneous catalysts can efficiently activate PS for FLU removal from the water environment.

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1. Introduction

In the past few decades, the residues of antibiotics have been extensively detected in various aquatic environments worldwide due to the high consumption rates in both human and veterinary medicine (Kim and Carlson, 2007; Michael et al., 2013). Flumequine (FLU), a broad-spectrum antibiotic of the fluoroquinolone family, has been widely used especially against gram-negative bacteria (Čvančarová et al., 2013). Particularly, FLU is directly applied as feed

additive in aquaculture, often in too high amounts owing to its poor bioavailability in aquatic species (Burridge et al., 2010). In light of its continuous introduction into natural waters and low removal efficiency by sewage treatment plants (Batt et al., 2007; Gulkowska et al., 2008), FLU has been detected in water environments at concentrations ranging from 2.5 to 50 ng/L (Pozo et al., 2006; Tamtam et al., 2008). Previous studies have reported that FLU in aquatic ecosystems could cause some adverse toxic effects on aquatic organisms by inhibiting their growth and reproduction or exhibiting its genotoxic and carcinogenic properties (Zoukova et al., 2011; Ma et al., 2012). In addition, FLU could potentially trigger specific transcriptional alterations in microbial communities and contribute to the development of resistant bacteria (Sukul and Spittler, 2007; Martinez, 2009). Thus, the presence of

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Nomenclature

AOPs	advanced oxidation processes
BET	Brunauer–Emmett–Teller
BQ	benzoquinone
DBE	double bond equivalent
DMPO	5,5-dimethyl-pyrroline-N-oxide
DOM	dissolved organic matter
EDS	energy dispersive spectrometer
EPR	electron paramagnetic resonance
ESI	electro-spray interface
EtOH	ethanol
Fe ₃ O ₄ /MWCNTs/PHQ	polyhydroquinone-coated magnetite/ multi-walled carbon nanotubes
FLU	flumequine
FT-IR	Fourier-transform infrared
HA	humic acid
HQ	1,4-hydroquinone
ISCO	in situ chemical oxidation

LC-MS	liquid chromatography-mass spectrometry
MWCNTs	multi-walled carbon nanotubes
MWCNTs-COOH	carboxyl-functionalized multi-walled carbon nanotubes
OH•	hydroxyl radicals
PHQ	polyhydroquinone
PS	persulfate
SEM	scanning electron microscope
SO ₄ •-	sulfate radicals
SPE-LC-MS	solid phase extraction-liquid chromatography-mass spectrometry
SQ	semiquinone radicals
SR-AOPs	sulfate radicals-based advanced oxidation processes
TBA	<i>tert</i> -butyl-alcohol
TIC	total ion current
TOC	total organic carbon
XPS	X-ray photo-electron spectroscopy
XRD	X-ray powder diffraction

this antibiotic in aquatic environments has become a major concern.

Recently, many treatment approaches have been investigated for the environmental removal of antibiotic FLU in aqueous phase, including advanced oxidation processes (AOPs) (Klamerth et al., 2010; Miranda-García et al., 2011; Garcia-Segura et al., 2012; Rodrigues-Silva et al., 2013a, 2013b), direct photolysis (Sirtori et al., 2012) and biotransformation by different fungi (Williams et al., 2007; Čvančarová et al., 2013). Among them, AOPs have been commonly suggested as the cost-effective mechanisms for the removal of persistent micropollutants from aqueous systems (Prieto-Rodríguez et al., 2013; Luo et al., 2014). Notably, sulfate radicals-based AOPs (SR-AOPs) have recently attracted increasing interests in water treatment and in situ chemical oxidation (ISCO) (Fang et al., 2013a; He et al., 2014a). Previous studies have indicated that sulfate radicals (SO₄•-) are more selective than hydroxyl radicals (OH•) for the oxidation of organic pollutants and could achieve better mineralization (Anipsitakis et al., 2006; Nie et al., 2014). Due to its relatively high stability, solubility, low cost and high redox potential (2.01 V), persulfate (PS, S₂O₈²⁻) is commonly used as a source of SO₄•- in laboratory studies and field applications (Tsitonaki et al., 2010). Activation of PS can be accomplished by various methods, such as UV (Ahmed and Chiron, 2014; He et al., 2014b), heat (Nie et al., 2014), transition metals (Fe²⁺, Co²⁺, Cu²⁺) (Liu et al., 2012; Ji et al., 2014; Rao et al., 2014) or metal oxides (Fe₃O₄, CuO) (Yan et al., 2011; Fang et al., 2013a; Liang et al., 2013), and quinones (Fang et al., 2013c), to generate SO₄•- with a higher redox potential (2.60 V). Recently, PS oxidation has been commonly used for aqueous removal of a variety of pharmaceuticals, such as carbamazepine (Ahmed and Chiron, 2014; Rao et al., 2014), ciprofloxacin and sulfamethoxazole (Yan et al., 2011; Ji et al., 2014) and β-lactam antibiotics (He et al., 2014b). Unfortunately, to date, very little is known regarding the PS degradation process of FLU, the first generation of fluoroquinolones, while these evaluations are of vital importance for the purposes of environmental remediation and wastewater treatments.

The objective of the present study was to investigate the transformation processes and mechanisms of aqueous FLU by PS activated with different methods, including heat, Fe²⁺, Cu²⁺ and a kind of newly-synthesized catalyst. A wide range of operating parameters influencing the treatments, including solution pH, additions of inorganic anions, cations and dissolved organic matters,

were studied from the reaction kinetics' perspective. The polyhydroquinone-coated magnetite/multi-walled carbon nanotubes (Fe₃O₄/MWCNTs/PHQ) nanocomposites were prepared and characterized, and their catalytic performance in heterogeneous activation of PS for FLU removal in aqueous solution was evaluated. Two sets of quenching tests and electron paramagnetic resonance (EPR) experiments were conducted to analyze and elucidate the role of radical species generated in the catalytic system. In addition, the degradation intermediates of FLU were identified by liquid chromatography-mass spectrometry (LC-MS), from which the transformation pathways were proposed.

2. Materials and methods

2.1. Chemicals

The antibiotic FLU (CAS NO. 42835-25-6, purity 98%) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and used without further purification. Potassium persulfate (purity ≥ 99.5%) was obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Carboxyl-functionalized multi-walled carbon nanotubes (MWCNTs-COOH, purity > 95%; outside diameter 20–40 nm) were purchased from Shenzhen Nanoport Co., Ltd. (Shenzhen, China). Methanol and formic acid used in the HPLC and LC-MS measurements were of HPLC grade and supplied from Merck (Darmstadt, Germany). The spin-trapping agent 5,5-dimethyl-pyrroline-N-oxide (DMPO) was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). All the other reagents used in this study such as FeSO₄, FeCl₃, 1,4-hydroquinone (HQ), humic acid (HA), *tert*-butyl-alcohol (TBA) and ethanol (EtOH) were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water (>18.2 MΩ cm) was prepared with a Milli-Q Plus system (Millipore, Bedford, USA), and employed throughout the studies.

2.2. Preparation and characterization of Fe₃O₄/MWCNTs/PHQ

In view of some recently reported activation potentials of Fe₃O₄ (Yan et al., 2011; Fang et al., 2013a), MWCNTs (Lee et al., 2015), and quinone species (Fang et al., 2013c) for PS oxidation, the Fe₃O₄/MWCNTs/PHQ tricomposites were thus prepared in this work to investigate their possible interactions for a more efficient activation

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