



Photodegradation of ciprofloxacin adsorbed in the intracrystalline space of montmorillonite



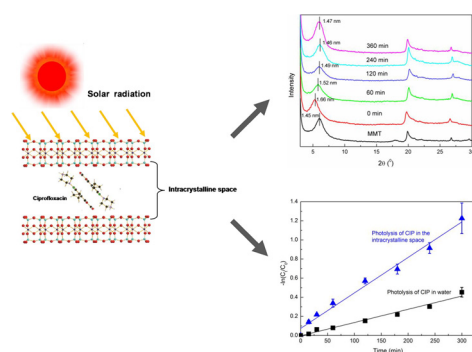
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GRAPHICAL ABSTRACT



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ABSTRACT

Although photolysis of antibiotics in aqueous solution was widely studied for a better understanding of their photolytic behavior in aqueous phase, the knowledge about photodegradation of antibiotics adsorbed on solid surfaces is still very limited. In this study, photodegradation of ciprofloxacin (CIP), a fluoroquinolone antibiotic, adsorbed in the intracrystalline space of montmorillonite (MMT) was examined using a xenon light source (300 W, $\lambda > 320$ nm). The gradual decrease of basal spacing of MMT from 1.66 to 1.46 nm with irradiation confirmed CIP decomposition in the intracrystalline space under simulated solar irradiation. Nearly 70 percent of adsorbed CIP was degraded after 5 h irradiation, and the reaction followed the first-order kinetics with a rate constant roughly 3 times than that in aqueous solution, indicating more efficient photodegradation of CIP after being adsorbed in the intracrystalline space of MMT. Spectroscopic analysis revealed that direct photolysis was the main photolytic mechanism. The hydroxyl radical induced by irradiated MMT might play an important role. The major photoproducts were identified with liquid chromatography-tandem mass spectrometry, and the main degradation pathways were proposed. The results demonstrated that the photoproduct distribution and degradation pathways of CIP adsorbed in the intracrystalline space differed from those in aqueous solution.

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1. Introduction

The widespread use of antibiotics in both human medicine and animal husbandry has resulted in their frequent detection in surface water, ground water, soils and sediments [1–5]. The presence of antibiotics in the environment may lead to the development of bacterial resistances and provoke toxic effects on aquatic organisms [67]. Therefore, as emerging pollutants, antibiotics in the environment have received great attention. When antibiotics enter the environment, they undergo various degradation pathways to reduce their environmental concentrations, including biotic (bioaccumulation, biodegradation) and abiotic (sorption, hydrolysis, photolysis, oxidation) processes. Generally, the type and degree of attenuation processes that occur could determine the subsequent environmental fate of antibiotics. For some photo-labile antibiotic compounds such as fluoroquinolones (FQs) and tetracyclines (TCs), photodegradation is expected to play an important role in their fate in some sunlit surface waters.

In recent years, the photolysis of antibiotics in aqueous environment has been intensively studied using different light sources including UV lamp, xenon lamp, and sunlight [8–11]. As revealed by these studies, antibiotics in aqueous solution generally undergo direct and indirect photolysis. Direct photolysis occurs via absorption of light by the chemical itself and leads to cleavage of chemical bond. The kinetics of direct photolysis in dilute solution can be fitted with pseudo-first-order model. Light conditions and pH of solution are found to be the main factors affecting direct photodegradation. Many antibiotics such as sulfa-drugs [12], tetracyclines [13], macrolides [14], cephalosporins [15,16] and fluoroquinolone antibiotics [16,17] have been reported to undergo direct photolysis. Indirect photolysis involves absorption of light by photochemically active substances in water, producing reactive species that react with target analytes. Recent research has demonstrated that dissolved organic matters (DOMs), $\text{NO}_3^-/\text{NO}_2^-$, and $\text{HCO}_3^-/\text{CO}_3^{2-}$ in natural water could act as significant photosensitizers of indirect photolysis [18–21]. These substances produce transient species under solar radiation, such as triplet-state DOMs, hydroxyl radicals, singlet oxygen and other radical species, which can react with antibiotics and result in their degradation. Besides direct and indirect photolysis, self-sensitized photolysis was suggested as one of the possible explanations for the increased rate constant at increased initial concentrations of TC [13]. In the photolysis studies of FQs, the reactive oxygen species (ROS) scavenging experiments revealed that the FQs underwent self-sensitized photo-oxidation via hydroxyl radical ($\cdot\text{OH}$) and singlet oxygen ($^1\text{O}_2$) [22,23].

Overall, previous studies on the photolysis of antibiotics in aqueous solution have led to a better understanding of the photochemical behavior of antibiotics in aqueous solution. For ciprofloxacin (CIP), an FQ frequently detected in surface waters, a better knowledge about its photochemical behavior in aqueous solution has been achieved [24–29]. CIP could be degraded quickly in different water matrices under ultraviolet and simulated solar irradiation, and the reaction followed pseudo first order kinetics [26–28]. The photolysis of CIP depended on solution pH, and the alkaline condition favored CIP degradation [25,28]. Also, it was found that variations in solution pH could result in the formation of different byproducts via different pathways [26]. The pH-dependent photochemical behavior could be attributed to the pH-dependent speciation of CIP. The photodegradation of CIP occurred mainly via substitution of fluorine, defluorination, hydroxylation of the quinolone core and the cleavage of piperazine ring [24,26–29]. Salma et al. [28] determined eighteen transformation products at different pH (3,5,7, and 9) using deuterated CIP, and further concluded that the first step in the photolysis of CIP was mainly defluorination, followed by degradation at the piperazine ring. Haddad et al. [29] identified the transformation products using LTQ-orbitrap XL mass spectrometer, and pointed out that all byproducts retained the core quinolone structure. Furthermore, their findings from non-purgeable organic carbon measurements clearly demonstrated that

mineralization did not take place in the photolysis of CIP.

In contrast, the knowledge about the photodegradation of antibiotics adsorbed on solid surfaces is still very limited. Indeed, when antibiotics reach the aquatic environment, significant fractions of them are adsorbed to solid matrices such as organic matter, clay mineral, sediment, and suspended particles [3–7]. Thus, it is worth noting that photochemical reactions at the surface of solid matrices may represent important degradation pathways in some sunlit surface waters. When organic compounds are adsorbed on solid surfaces, their photodegradation is often highly dependent on the chemical and physical properties of the adsorbent [30–33]. The rate of degradation may be promoted via energy transfer reactions or efficient light scattering, or it may be inhibited by excited-state quenching or light shielding [32,34,35]. Moreover, many adsorbents, including some clay minerals, could donate electron during photolysis [36]. Therefore, the photochemical behavior of antibiotic compounds in adsorbed state might differ from that in aqueous solution.

Clay minerals are important constituents of soils, suspended particles and sediments, and are generally considered as one class of the most chemically active components. Many have large specific area (SSA) and high cation exchange capacity (CEC), such as montmorillonite (MMT). In aqueous environment, some antibiotic compounds, particularly cationic ones, tend to be adsorbed by clay minerals. Our previous work indicated that MMT, a 2:1 type clay mineral, exhibited great adsorption capability for CIP and TC, and the adsorption resulted in their intercalation into the intracrystalline space [37,38]. However, to date no work has been done to probe the photochemical behavior of antibiotics adsorbed in the intracrystalline space of clay minerals. In this work, we choose CIP, a widely used FQ, as the target compound, and investigate the photolysis of CIP adsorbed into the intracrystalline space of MMT. The main objective of this work is to understand the photochemical behavior of CIP adsorbed in the intracrystalline space. We attempt to (1) determine whether or not CIP adsorbed in the intracrystalline space could be degraded by simulated solar light; (2) elucidate the photodegradation kinetics and mechanisms of CIP in the intracrystalline space; (3) identify the byproducts of CIP and speculate the possible photolytic pathways; (4) compare the photochemical behavior of CIP adsorbed in the intracrystalline space with that in aqueous solution. This study will help understand the photochemical behavior of FQs adsorbed on solid matrices.

2. Materials and methods

2.1. Materials

The MMT (SD0107 A) with a purity > 98% was obtained from Sand Technology Co., Ltd (Zhejiang, China). The CEC and SSA provided by the manufacture were 1.12 mmol/g and 35 m²/g, respectively. The major chemical compositions (provided by the manufacture) were summarized in Table 1. It was used without further purification. Ciprofloxacin hydrochloride (> 98%) and hexadecyltrimethylammonium bromide (HDTMA) (> 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used as received. Acetonitrile, methanol, phosphoric acid, and triethylamine were HPLC grade, and obtained from J&K Chemical Co., Ltd (Beijing, China). All aqueous solutions were prepared with Milli-Q ultrapure water.

Table 1
Major chemical compositions of montmorillonite (SD0107 A).

Component										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	P ₂ O ₅	TiO ₂	ZrO ₂	BaO
%	60.44	16.1	4.53	4.88	4.17	0.21	0.02	0.32	0.01	0.01

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