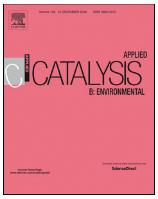
Applied Catalysis B: Environmental 235 (2018) 75–83

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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



Fe and Cu in humic acid extracts modify bacterial inactivation pathways during solar disinfection and photo-Fenton processes in water

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ARTICLE INFO

Keywords:
SODIS
Triplet states
Organic matter
Disinfection
Metal
Water treatment

ABSTRACT

The literature suggests a dual role for humic acids involving both agonistic and antagonistic processes in the photo-chemical cycle in water. In this work, the use of Fe- and Cu-containing humic acid (HA) extracted from coal waste was evaluated for the enhancement of solar-based disinfection processes, namely solar light (*hv*), *hv*/H_2O_2, and *hv*/H_2O_2/Fe^{2+} (photo-Fenton) processes. The differences in the enhancement of each process are reported herein. The degree of bacterial inactivation during solar disinfection under solar and visible light in the presence of the HAs was negatively correlated with the presence of metals, and was attributed to $^3DOM^*$ and $^1O_2$-mediated events. However, the presence of metals greatly enhanced disinfection when H_2O_2 was added by inducing a photo-Fenton process, and significantly reduced the inactivation times ($>$ 50%) due to homogeneous Fe- (Fenton) and Cu-based (Fenton-like)-assisted inactivation pathways. The addition of small quantities of Fe to HA-containing samples further enhanced the inactivation due to the ample generation of highly photo-active Fe-HA complexes. The result was a further ~60% reduction in exposure time to achieve a 7-log bacterial reduction, as well as the degradation of the HA itself as a sacrificial electron donor, via an Fe-mediated ligand to metal charge transfer process. This work reveals new pathways in disinfection assisted by metal-containing HAs, and demonstrates their efficiency in reducing microbial loads with simultaneous elimination of the additive.

1. Introduction

Solar disinfection of drinking water (SODIS) is a well-established process for water sterilization in developing countries [1]. Despite the relative success of this process, its limitations, namely its requirement for low turbidity, low treatment volumes (up to 2 L), temperature dependence, and the risk of microbial regrowth during storage after treatment [2], have prompted an array of works on its enhancement. One of the most promising improvements is the photo-Fenton process. This method not only builds upon the base process (the use of solar light) [3], but also takes advantage the ubiquitous presence of iron and the photo-generation of hydrogen peroxide to produce the highly oxidative hydroxyl radical [4], which can readily and effectively inactivate the majority of microorganisms. The addition of Fe and H_2O_2 enhances the overall efficiency of the system, but the elucidation of the exact inactivation pathways is far from a simple process; when near-neutral (natural) water is involved, the presence of inorganic substances, such as carbonate and sulfate, and organic substances, such as natural organic matter (NOM) [5] induce further pathways, for which information is scarce.

Abbreviations: CDOM, chromophoric DOM; DOM, dissolved organic matter; EDS, energy dispersive X-ray spectroscopy; HA, humic acid; HA_{MC}, humic acid$_{\text{mineral content}}$; HS, humic substances; hv, acronym for “light”; ICP-MS, inductively coupled plasma mass spectrometry; LMCT, ligand-to-metal charge transfer; NOM, natural organic matter; ROS, reactive oxygen species; SEM, scanning electron microscopy; SODIS, solar disinfection

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https://doi.org/10.1016/j.apcatb.2018.04.062
Received 6 March 2018; Received in revised form 21 April 2018; Accepted 25 April 2018

Humic substances (HS) comprise the majority of dissolved organic matter (DOM) in aquatic systems. HS may also be considered the main precursor of excited triplet states (exogenous photosensitizers), which are able to degrade organic compounds and inactivate microorganisms such as bacteria and viruses [6–11]. Humic acids absorb light in the UVA and visible spectrum to form excited states that can attack biomolecules or react with oxygen to generate reactive oxygen species (ROS). More specifically, under UV–vis irradiation and in the presence of O_2, the substances can produce ROS such as singlet oxygen ($^1O_2$) and superoxides ($HO_2/O_2{}^-$) (Eqs. (1)–(4)) [12–14].

$$HA + h\nu \rightarrow {}^1HA^* \tag{1}$$

$$^1HA^* \rightarrow {}^3HA^* \tag{2}$$

$$^3HA^* + O_2 \rightarrow HA^* + {}^1O_2 \tag{3}$$

$$^3HA^* + O_2 \rightarrow HA^{\bullet +} + O_2^{\bullet -} \tag{4}$$

The literature describes the different roles of organic matter in photosensitization events, which depending on the type of functional groups present in the HS. For instance, ketonic [15,16] and quinonic groups [17,18] have been shown to be the most photo-chemically active. Various methods, including spectroscopic and fluorescence methods, have been used to characterize the organic matter and predict or correlate its photo-activity with specific characteristics [19–22]. Additionally, the quantity of HAs present also plays an important role in the net outcome; in addition to its action as a light screen [23,24], Porras et al. investigated the photo-transformation of drugs and pesticides using different humic substances in different quantities, and showed a correlation between the structural characteristics of the humic substances and their photo-transformation activity. An antagonistic effect was noted at high HA concentrations, indicative of light attenuation or self-inhibition [25,26].

The organic substances present in natural water can also affect solar-based treatment processes, including SODIS [27,28], photo-catalysis [29,30], and photo-Fenton [31,32] processes. For instance, Giannakis et al. described both the beneficial action of HAs in maintaining a homogeneous photo-Fenton reaction [33] and the implications when a heterogeneous mode was employed for the inactivation of viruses [34]. The organic matter could enhance or inhibit photo-assisted disinfection processes, regardless of the target microorganism [3]. In all the aforementioned studies, pure NOM isolates or model NOM compounds were used. Their ability to complex iron is the source of the enhanced activity (Eq. (5)) [35,36], but the literature lacks studies of naturally metal- and mineral-bearing humic substances and their effects on solar-related disinfection processes, in which they could initiate Fenton (Fe-based) and Fenton-like (Cu-based reactions) as follows (Eqs. (6)–(19)):

$$(Fe^{3+} - HA) + h\nu \rightarrow Fe^{2+} + HA_{ox}^{+} \tag{5}$$

Fenton

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \tag{6}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow (Fe^{3+}(HO_2))^{2+} + H^+ \tag{7}$$

$$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+ \tag{8}$$

$$(Fe^{3+}(OH)(HO_2))^{+} \rightarrow Fe^{2+} + HO_2^{\bullet} + OH^- \tag{9}$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^- \tag{10}$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow (Fe^{3+}(HO_2))^{2+} \tag{11}$$

$$Fe^{2+} + O_2^{\bullet -} + H^+ \rightarrow (Fe^{3+}(HO_2))^{2+} \tag{12}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \tag{13}$$

$$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2 \tag{14}$$

Fenton-like

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + HO^{\bullet} + HO^- \tag{15}$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + O_2^{\bullet -} + 2H^+ \tag{16}$$

$$Cu^+ + O_2 \rightarrow Cu^{2+} + O_2^{\bullet -} \tag{17}$$

$$Cu^+ + O_2^{\bullet -} \xrightarrow{2H^+} Cu^{2+} + H_2O_2 \tag{18}$$

$$Cu^{2+} + O_2^{\bullet -} \rightarrow Cu^+ + O_2 \tag{19}$$

The aim of this research was to study the role of HA, as a model of DOM, on bacterial disinfection in several solar-based processes. The presence of metals (i.e., Fe and Cu) and their photo-chemical implications were investigated. After characterization of the HA samples, their effects on SODIS ($h\nu$), $h\nu/H_2O_2$, and $h\nu/H_2O_2/Fe$ (photo-Fenton) processes were considered. Special attention has been given to the use of solar light alone, as it is the process on which the other two are based. The complex photo-Fenton process has been broken down into its constituent steps, and the use of HAs that inherently contain metals have been assessed. A detailed disinfection and spectroscopic study to investigate the variables involved, namely the quantity (initial concentration) and composition of the HS, was attempted using three HAs (HA_1, HA_5, and HA_{16}) containing different amounts of mineral matter (1, 5, and 16%, respectively). The results indicate the pitfalls and opportunities for enhancement of the photo-chemical disinfection of water when HAs are naturally present or intentionally added.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals were of reagent grade. Hydrogen peroxide 30% and iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) were provided by Merck. Titanium (IV) oxysulfate ($TiOSO_4$) for the spectrophotometric determination of H_2O_2 was provided by Fluka. All solutions were prepared with Milli-Q water (18.2 MΩ cm) immediately prior to irradiation. Reagent grade NaOH, HCl, and HF were provided by Sigma-Aldrich.

2.2. Preparation of humic acid (HA) fractions

The terrestrial humic acid sample referred to as HA_{MC} (humic acid mineral content) was obtained from an air-modified low-rank coal mine in the Amaga region in Colombia and extracted in the laboratory as reported previously [25]. The obtained HA_{MC} fraction was washed with deionized water and finally freeze-dried; this sample was labeled as HA_{16} (based on its mineral matter content percentage). A given quantity of HA_{16} was demineralized by stirring in a 0.1:0.3M solution of HCl:HF for 36 h at room temperature under a nitrogen atmosphere. This demineralized humic acid fraction was washed with deionized water and freeze-dried; the resulting sample was labeled as HA_5. Finally, a portion of the HA_5 was demineralized using the same procedure to yield the sample labeled as HA_1. Thermogravimetric analysis of the humic acids HA_{16}, HA_5 and HA_1 was carried out with a TA-Instruments Q500 using air at 900 °C, and the samples produced 16, 5, and 1% of mineral-containing ash, respectively.

The morphology and elemental composition of the ash samples were determined using scanning electron microscopy (SEM) with a JEOL JSM 6490 instrument with a LaB_6 filament and equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer at a 20 kV accelerating voltage. The powder samples were sputter coated with gold using a Sputter Coater SC502 prior to analysis. The backscattered electron (BSE) detection mode was used. Finally, elemental analysis was performed using a LECO Truspec analyzer. 2 mg of the solid sample was combusted, and compositional analysis of the total gas was carried out by selective thermal conductivity (TCD) cells and infrared (IR).