



Comparative study on the removal of humic acids from drinking water by anodic oxidation and electro-Fenton processes: Mineralization efficiency and modelling



Clément Trellu^a, Yoan Péchaud^a, Nihal Oturan^a, Emmanuel Mousset^a, David Huguenot^a, Eric D. van Hullebusch^a, Giovanni Esposito^b, Mehmet A. Oturan^{a,*}

^a Université Paris-Est, Laboratoire Géomatériaux et Environnement (EA 4508), UPEM, 77454 Marne-la-Vallée, France

^b University of Cassino and the Southern Lazio, Department of Civil and Mechanical Engineering, Via Di Biasio, 43, 03043 Cassino, Frosinone, Italy

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ABSTRACT

The management of natural organic matter in drinking water treatment plants is an important matter of concern. It can generate toxic disinfection by-products as well as decrease the efficiency of membrane filtration and oxidation processes. This is the first study that investigates the use of anodic oxidation (AO) and electro-Fenton (EF) for the removal of humic acids (HAs) from aqueous solutions. Both sorption and catalytic oxidation of HAs are assessed and discussed. These electrochemical advanced oxidation processes are based on the *in situ* production of hydroxyl radicals, a highly oxidizing agent. The EF process involves the use of carbon-based porous materials (carbon sponge) as cathode, leading to the fast adsorption of hydrophobic HAs. It has been observed that adsorbed HAs can react with hydroxyl radical produced in the bulk from Fenton's reaction. Then, the release in the solution of more hydrophilic by-products from the oxidation of HAs leads to a rebound effect of the organic matter concentration. Therefore, the AO process using non-carbonaceous cathode materials appears to be more suitable for HAs removal. Using boron-doped diamond anode and stainless steel cathode, the mineralization efficiency of a HAs solution ($\text{TOC}_0 = 16.2 \text{ mg L}^{-1}$) reached more than 99% after 7 h of AO treatment with a current intensity of 1000 mA. By considering both sorption and oxidation processes, this study proposed a new modelling approach to monitor TOC evolution during AO and EF processes.

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1. Introduction

Humic substances (HS) are major components of the natural organic matter (NOM) in soil and water. They are complex and heterogeneous mixtures of polydispersed materials formed by biochemical and chemical reactions during humification of plant and microbial remains [1]. The major extractable component of HS in peat and grassland soils is humic acids (HAs) (70–80%) [2]. They are complex aromatic macromolecules containing phenolic groups, quinone structures, aliphatic compounds, nitrogen and oxygen as

bridge units and carboxylic groups variously placed on aromatic rings [1,2].

HS are non-toxic compounds, but they have a significant influence on selection, design and operation of water treatment processes. The greatest concern is their precursor role in the formation of highly toxic disinfection by-products such as trihalomethanes [3–5]. NOM can be removed from drinking water by several treatment options. The most common and economically feasible process is considered to be coagulation and flocculation followed by decantation and sand filtration [6]. Concentrations of dissolved organic carbon can range from 0.1 mg L^{-1} in groundwater to 50 mg L^{-1} in bogs [7]. These concentrations depend on the nature of the watershed, but are also strongly influenced by seasonal variations and particulate organic carbon inputs such as runoff or algae bloom [7]. Therefore, the increased requirements in drinking water quality lead to invest additional methods for NOM removal. The following methods can constitute alternative processes: advanced oxidation processes (AOPs) [8,9], ozonation [10], sonolysis [11] or UV-based processes [12]. However, the preferential degradation

Abbreviations: AO, anodic oxidation; BDD, boron doped diamond; CS, carbon sponge; EAOPs, electrochemical advanced oxidation processes; EF, electro-Fenton; HAs, humic acids; HA_{ads} , humic acids adsorbed; HA_{hob} , low or non-degraded humic acids; $\text{HA}_{\text{hob,ads}}$, low or non-degraded humic acids adsorbed; HA_{tot} , total humic acids; IoA, index of agreement; ME, model efficiency; TOC_{sol} , TOC in the solution; TOC_{ads} , TOC adsorbed; RMSE, root mean square error; SS, stainless steel.

* Corresponding author.

E-mail address: mehmet.oturan@univ-paris-est.fr (M.A. Oturan).

of hydrophobic organic compounds has been observed in many studies. Moreover, incomplete oxidation can lead to increase the potential of formation of disinfection by-products [8].

Electrochemical advanced oxidation processes (EAOPs) are new attractive techniques for water treatment [13–20]. They are based on the *in situ* generation of hydroxyl radicals ($\bullet\text{OH}$), the second strongest oxidizing agent known [21]. Their high efficiency for the removal of a large range of persistent organic pollutants (POPs) with complete mineralization to CO_2 has already been shown [22–29]. However, NOM can reduce removal efficiency, due to complexation with POPs as well as $\bullet\text{OH}$ scavenging [30]. The management of NOM is also crucial for the treatment strategy combining EAOPs and membrane processes because it is the main responsible of membrane fouling [31,32].

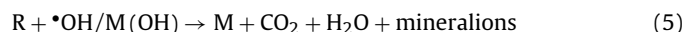
Hydroxyl radicals react with a wide spectrum of NOM of both hydrophobic and hydrophilic character. Rate constants for reactions with NOM have been measured at $1\text{--}5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [33]. One of the most popular EAOPs is anodic oxidation (AO) process in which organic compounds directly react with heterogeneous hydroxyl radicals $\text{M}(\bullet\text{OH})$ [34], formed by oxidation of water at the surface of anodes (M) with high oxygen overpotential [35,36] (Eq. (1)). Particularly, boron doped diamond (BDD) anode has very high catalytic activity and allows producing large amount of hydroxyl radicals.



The other popular EAOPs is the electro-Fenton (EF) process, in which $\bullet\text{OH}$ are produced homogeneously in the bulk of treated solution from the electrochemically generated Fenton's reagent (mixture of H_2O_2 and Fe^{2+}) [37–40] (Eq. (2)). H_2O_2 is *in situ* electrogenerated at the cathode following Eq. (3) from two-electrons reduction of dissolved O_2 [17,40]. A catalytic amount of ferrous iron salt is sufficient to turn up the process, due to the catalytic electro-regeneration of ferrous iron at the cathode (Eq. (4)) [41–43].



These formed homogeneous/heterogeneous $\bullet\text{OH}$ can then react with the organic matter (R) to oxidize it until ultimate oxidation state is reached, i.e., mineralization (Eq. (5)):



To the best of our knowledge, it is the first time that the following processes are studied for removal of HAs: AO using BDD anode, EF using Platinum (Pt) anode, and EF using BDD anode. Carbon sponge (CS) was used as cathode, since it produces high amount of H_2O_2 for the EF process [44]. Stainless steel (SS) and CS were also compared as cathode material for the AO process. Sorption of HAs onto CS cathode was highlighted and the impact of this phenomenon on the electrocatalytic oxidation of HAs was assessed. Therefore the goal of this study was (i) to show the ability of EAOPs for total removal of HAs from water (ii) to assess and compare the effectiveness of various EAOPs for removal of HAs from aqueous solutions (iii) to understand HAs removal mechanisms during EAOPs (iv) to propose a new modeling approach to monitor TOC removal by taking into account both sorption and oxidation processes.

2. Material and methods

2.1. Chemicals

HAs were purchased from Acros Organics. A purification step was performed as described below. Iron(II) sulphate heptahy-

drated and sulphuric acid were of reagent grade obtained from Acros Organics. Sodium sulphate was of reagent grade purchased from Sigma Aldrich. Solutions were prepared with ultrapure water from a Millipore Milli-Q system (Molsheim, France) with resistivity $> 18 \text{ M}\Omega \text{ cm}$.

2.2. Preparation of humic acid solutions

A purification step of commercial HAs was performed, similarly to the protocol of Arai et al. [45]. The stock solution was prepared by dissolving 1 g of commercial HAs in 2 L of Milli-Q water at pH 3. This solution was filtered through Whatman GF/F filter ($0.7 \mu\text{m}$ as pore diameter). Then, HAs were precipitated by decreasing pH at 1.2 and the solution was centrifuged at 3000 rpm during 20 min. Supernatant was then removed and precipitated HAs were dissolved in deionized water and stocked at pH 3.

2.3. Electrochemical treatments

All electrochemical treatments were carried out during 9 h in a 400 mL batch electrochemical cell containing 330 mL of HAs solution at initial TOC concentration of 16.2 mg L^{-1} (TOC_0). The anode material was Pt ($14 \text{ cm}^2 \times 0.1 \text{ cm}$) from Platecxis (Noisy-le-Sec, France) or a BDD thin-film onto a Nb substrate ($24 \text{ cm}^2 \times 0.2 \text{ cm}$) purchased from Condias GmbH (Itzehoe, Germany). The cathode material was CS ($24 \text{ cm}^2 \times 1.2 \text{ cm}$, 60 pores per inch) from Magneto BV Holland (The Netherlands) or SS ($24 \text{ cm}^2 \times 0.2 \text{ cm}$) from Goodfellow (France). Electrodes were set up with a gap of 3 cm between the anode and the cathode. The constant current intensity was provided by a power supply (HAMEG, Germany (model 7042-5)). Air was continuously bubbled inside the solution through a glass frit in order to keep enough dissolved oxygen in the solution for the hydrogen peroxide production at the cathode following Eq. (3). A magnetic stirrer ensured the homogenization of the solution in the electrochemical cell. Similarly to optimal experimental conditions determined by Özcan et al. [44], a suitable amount of electrolyte was dissolved in the solution (Na_2SO_4 at 0.05 M) and pH was adjusted at 3.0 with 1 M H_2SO_4 . For EF process, an optimal concentration of 0.1 mM Fe^{2+} (under the form of ferrous sulphate heptahydrated) was added [44]. According to the electrochemical cell configuration, processes were denoted as AO-SS (BDD anode, SS cathode), AO-CS (BDD anode, CS cathode), EF-Pt (Pt anode, CS cathode, 0.1 mM Fe^{2+}) and EF-BDD (BDD anode, CS cathode, 0.1 mM Fe^{2+}).

2.4. Analytical procedures

Due to the complexity of the HAs mixture, organic matter content concentration was determined by a global parameter, i.e. the total organic carbon (TOC) content of the solution (TOC_{sol}), in mg L^{-1} . Samples (3.5 mL) were collected at 8 or 9 different time points during the electrolysis. TOC was measured by using a Shimadzu TOC-V analyzer. Calibration was achieved with potassium hydrogen phthalate (99.5%, Merck).

For the analytic determination of organics adsorbed onto the CS cathode (TOC_{ads}), the treated solution was removed from the electrochemical cell. Then, 330 mL of NaOH at 0.1 M was used for desorption of HAs from the cathode, similarly to the extraction method of HAs from soil [46]. After 15 min of continuous stirring, a sample was analysed after inorganic carbon removal from the solution by decreasing the pH at 3 and purging the sample with O_2 gas. Values were given in mg L^{-1} , based on the amount of carbon adsorbed on the cathode compared to the volume of the solution treated. Therefore, the total TOC (TOC_{tot}) in the solution was deduced as $\text{TOC}_{\text{tot}} = \text{TOC}_{\text{sol}} + \text{TOC}_{\text{ads}}$.

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