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Photo-assisted degradation of 2,4,5-trichlorophenol by Electro-Fe(II)/Oxone® process using a sacrificial iron anode: Performance optimization and reaction mechanism

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HIGHLIGHTS

- ▶ Degradation of 2,4,5-TCP by Electro-Fe(II)/Oxone® with UV (EFOU) was explored.
- ▶ It was found that EFOU could be optimized by applying different current modes.
- ▶ The strategy of oxidant addition in optimizing probe degradation was investigated.
- ▶ Decay pathway of 2,4,5-TCP by EFOU were proposed based on LC–ESI/MS analysis.

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ABSTRACT

The degradation of chlorinated organic compound (2,4,5-trichlorophenol, 2,4,5-TCP) in Electro-Fe(II)/Oxone® system simultaneously exposed to UV (254 nm) irradiation (i.e., EFOU) was investigated in this study. In this oxidation process, once an electric current is applied between the anode (an iron sheet) and the cathode (a graphite bar), a predetermined amount of Oxone® is added to the reactor and UV light is simultaneously irradiated. It was found that an acidic condition is favorable to the process and over 92% removal of 0.2 mM 2,4,5-TCP in the pH range of 2.5–4.35 was rapidly obtained by the proposed EFOU process. Nevertheless, around 80% of 2,4,5-TCP was decayed at pH of 7.70 in 20 min suggesting that the proposed EFOU process is efficient even at neutral pH. Experimental results show that applied current of 1 mA results in the best performance, while the process is slightly inhibited at higher currents due to excessive generation of ferrous ions. The investigation on the mode of current-application shows that the EFOU process can be further optimized by controlling a proper electrolytic duration to reach a balance of Fe(II) generation and energy consumption. Additionally, it is found that tandem addition of Oxone® could minimize the scavenging effect between the radicals (from the first dose) and fresh Oxone® (from the second dose) and improve the overall performance of EFOU. Furthermore, aromatic intermediates such as 2,5-dichlorohydroquinone, 4,6-dichlororesorcinol, 2,4-chlorophenol, and many others are identified by using LC–ESI/MS analysis, based on which a possible decay pathway of 2,4,5-TCP by EFOU process is therefore proposed.

1. Introduction

2,4,5-Trichlorophenol (2,4,5-TCP) is an important representative of chlorinated organic compounds and has been widely used as disinfectants, fungicides, wood preservers and plant growth regulators over the past few decades. 2,4,5-TCP has also been used in the production of a variety of biocides. It is used as the precursor for the synthesis of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and of the bactericide, hexachlorophene [1]. Especially, it is formed as the primary intermediate upon the decay of 2,4,5-T by the advanced oxidation processes (AOPs) [2,3] or microbial activities [4]. 2,4,5-TCP is considered to have significant toxicological effects and potential carcinogenicity. 2,4,5-TCP has been included in the “persistent, bioaccumulative, and toxic chemical list” by the US EPA, imposing a serious threat to human health and natural ecosystems. It is resistant to biodegradation in aerobic and anaerobic systems [5], thereby tending to bioaccumulate in the environment. Moreover, 2,4,5-TCP is considered to be more resistant to biodegradation than other trichlorophenols [6]. As a result, it is listed as one of the priority pollutants by US EPA [7]. Although its use as a biocide has been banned in many countries, the application of

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2,4,5-TCP as a fungicide in wood and leather impregnation can be still found. The broad application of 2,4,5-TCP during the past few decades has led to its widespread distribution in the natural environment. Low levels of 2,4,5-TCP were found in drinking water in several places in the world [8] and it has been also detected in the leachates from municipal landfills [9]. The wide presence of 2,4,5-TCP in the aquatic environment poses a pollution concern because of its high toxicity and stability. Removal of this pollutant from aquatic environments is therefore a major concern in water industry.

The removal of 2,4,5-TCP was investigated by using various treatment methods, including adsorption [8], biodegradation [6,10], and the combination of biological and photocatalytic treatment [11,12]. However, the need for the disposal of spent sorbent is a limitation of the adsorption method. The microbiological treatment shows restraint in removing 2,4,5-TCP [5], the treatment is only possible at low concentration due to bio-inhibition [12] and it usually requires a longer treatment time. AOPs have been proven to be promising technologies that can efficiently mineralize organic compounds into CO_2, H_2O, and simple acids under mild experimental conditions. Barbeni et al. [13] reported that complete mineralization of 2,4,5-TCP into CO_2 and HCl was achieved with half-lives of 30–90 min by simulated sunlight irradiation in oxygenated aqueous suspensions of TiO_2. However, TiO_2 photocatalysis is a heterogeneous process, generally suffering from slower mineralization yields and inefficient separation/recycling for the TiO_2 catalyst. Moreover, these AOPs usually need to be combined with other treatment techniques in order to reduce the cost and the treatment time. Recently, a new approach by using electro-Fenton was proposed. The electro-Fenton generally involves the in situ electro-generation of hydrogen peroxide and ferrous ions electrochemically, either separately or concurrently [14]. Therefore, three kinds of electro-Fenton processes have been explored: (a) the on-site electrochemical generation of H_2O_2 coupled with the addition of a small quantity of ferrous ions as catalyst, (b) the simultaneous electro-generation of H_2O_2 and Fe(II), and (c) the electro-generated ferrous ions from a sacrificial iron anode with an externally dosed hydrogen peroxide. This electrochemically electro-Fenton process is considered to be more environmental friendly and more potent than chemical AOPs due to the faster production of hydroxyl radicals under the control of applied current [15].

Previously, as an analogue to electro-Fenton process, Electro-Fe(II)/Oxone® (EFO) process by coupling electrochemical process with ferrous mediated activation of Oxone® demonstrated a promising performance for the treatment of 2,4,5-T in aqueous solution [16]. In this study, an attempt has been made to further enhance the above process by introducing the UV light, in which the 2,4,5-TCP aqueous solution treated under Electro-Fe(II)/Oxone® is simultaneously exposed to UV irradiation (i.e., EFOU). This combined photoassisted electrochemical treatment was examined through the degradation of 2,4,5-TCP under various operating conditions.

2. Experimental section

2.1. Chemicals and reagents

All chemicals are of analytic reagent grade and all solvents are of HPLC grade and used as received without further purification. 2,4,5-TCP (95.0%) obtained from Wako Pure Chemical Industries, Ltd. was used as the probe in this study. 2,4-dichlorophenol (neat) and 4,6-dichlororesorinol were obtained from Suelco and Tokyo Chemical Industries, respectively. Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, DuPont product, 95%), $FeSO_4 \cdot 7H_2O$ (99.0%), 2,5-dichlorohydroquinone (98%), and sodium sulfate (Na_2SO_4, 99.0%) were purchased from Sigma Aldrich Inc. (USA). Distilled-deionized water with a resistivity of 18.2 $M\Omega\,cm^{-1}$ generated from a Bamstead NANOpure water treatment system (Thermo Fisher Scientific Inc., USA) was used to prepare all the solutions. Acetonitrile (from Tedia company, Inc.) was degassed before being used in high performance liquid chromatography (HPLC). Sulfuric acid and/or sodium hydroxide were used to adjust the initial pH of the solutions. Excess methanol was employed to quench the reaction.

2.2. Reactor operating conditions

All the experiments were homogeneous and performed in an air-conditioned laboratory at 23 ± 2 °C. All the tests were duplicated and average values were used in presenting the results. The reactions were carried out in a 50 mL undivided single-compartment quartz beaker placed in the center of a computer-controlled CCP-4V photochemical reactor (from Luzchem Research Inc.), where a cooling fan was equipped to maintain constant temperature. Two phosphor-coated low-pressure mercury lamps emitting monochromatic light at 253.7 nm with light intensity of 1.5×10^{-6} Einstein $L^{-1}\,s^{-1}$ for each lamp were symmetrically arranged within the photoreactor as the irradiation source. The UV lamps were warmed up for at least 10 min prior to reaction to ensure a stable output. Oxone® solutions were freshly prepared before each experiment to minimize variations in concentration caused by self-decomposition of the oxidant. An Agilent E3641A DC potentionstat–galvanostat power supply was employed to provide the constant current by using commercial iron (Fe) sheet with a total surface area of 10 cm^2 as the sacrificial anode and a graphite bar as the cathode. The sketch of electrolytic cell with UV irradiation is depicted in Fig. 1. The probe (0.20 mM 2,4,5-TCP) and electrolyte (0.05 M Na_2SO_4) were used without pH adjustment, unless otherwise stated. The reaction is initiated by adding an appropriate amount of Oxone® into the reactor and simultaneously switching on the UV lamps once a specified constant electrical current is applied between the anode and cathode. The initial volume of the reaction solution was fixed at 50 mL. The solution was continuously agitated by a magnetic stirrer to ensure homogeneity throughout the reaction. Exact amount of an aliquot (0.5 mL) was withdrawn from the solution at predetermined time intervals and mixed with the same amount of methanol to quench the reaction, and the samples were then filtered with 0.45 μm PTFE filters (Whatman) before the LC analysis.

2.3. Analysis

The 2,4,5-TCP remaining in the solution was monitored by a HPLC which consists of a Waters 515 HPLC pump, a Waters 717

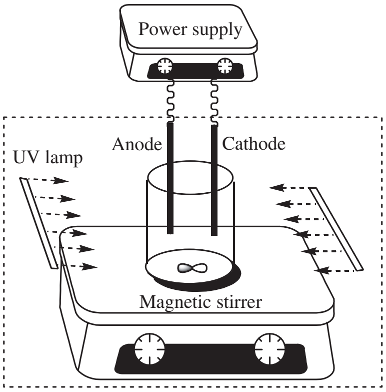

Fig. 1. Sketch of electrolytic cell with UV irradiation.