



Degradation of phenol by synergistic chlorine-enhanced photo-assisted electrochemical oxidation



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HIGHLIGHTS

- Phenol was treated by a hybrid photo-assisted electrochemical oxidation process.
- Hybrid photolytic and electrochemical process showed synergistic DOC removal.
- Hybrid treatment is competitive with conventional advanced oxidation processes.
- Hybrid treatment had the lowest energy demand tested, reduced DBP formation, and no residual toxicity.

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ABSTRACT

Hybridization of a UV-C photoreactor with an electrochemical cell led to the discovery of a distinctive synergistic mechanism for the degradation and mineralization of phenol when free chlorine-producing anodes were utilized in the presence of chloride. After 6 h, photochemical (UV) treatment resulted in 29% phenol mineralization and electrochemical (EL) treatment resulted in 35% and 52% mineralization using boron-doped diamond (BDD) and ruthenium oxide on titanium (DSA-Cl₂) anodes, respectively. However, the photo-assisted electrochemical (UVEL) process removed 88% and 96% of total organic carbon (TOC) after 6 h with BDD and DSA-Cl₂ anodes, respectively. The hybrid UVEL process generated highly reactive hydroxyl and chlorine radicals by the photolysis of *in situ* electrogenerated free chlorine. As a result, the UVEL treatment produced fewer chlorinated by-products compared to EL alone. UVEL with DSA-Cl₂ had the highest TOC removal after 6 h (96%), one of the highest mineralization rates (0.38 h⁻¹), and the lowest energy demand per order TOC removed ($E_{EO} = 104 \text{ kW h m}^{-3} \text{ order}^{-1}$) without any residual toxicity after dechlorination. Generally, conventional advanced oxidation processes (UV/O₃ and UV/H₂O₂) were most effective at mineralization up to 50%, but UVEL appeared more cost effective for mineralization beyond 75%.

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1. Introduction

Trace organic pollutants are of growing concern because of their ability to survive physical, chemical and biological treatment processes and due to their toxicity at very low concentrations [1]. Improved treatment options for the destruction of such persistent organic pollutants are required to meet current and future regulations designed to protect human health and the environment [2–4]. In recent years, advanced oxidation processes (AOPs) are proving a viable option to decontaminate waters polluted with persistent, trace organic contaminants. AOPs are used to remove

disinfection by-products (DBPs) and their precursors from drinking water as well as refractory organics from industrial and municipal wastewaters. AOPs can effectively convert all dissolved organic carbon into carbon dioxide and mineral acids with rate constants three to four orders of magnitude greater than conventional oxidation processes [5–7]; however, the high energy demand and capital cost of most AOPs motivate research to develop more energy efficient and cost effective methods [8–11].

Electrochemical oxidation for advanced water treatment has received a great deal of attention recently for treating organic polluted saline waters because the high salinity reduces energy demand and the high chloride concentration improves degradation due to enhanced indirect oxidation by electrogenerated chlorine [12–25]. Indirect organic oxidation may occur via reaction with chlorine radicals ([•]Cl) adsorbed on the anode surface or by reactive

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chlorine species such as Cl_2 , HOCl , or OCl^- in the bulk [26,27]. The formation of halogenated by-products is an obvious concern when treating waters with active chlorine. However, it has been reported that UV irradiation between 200 and 400 nm can photolyze free chlorine into hydroxyl and chlorine radicals, which could further enhance the oxidative potential and reduce by-product formation [28–30].

Herein, we tested a hybrid photo-assisted electrochemical process utilizing state-of-the-art anodes designed to convert chloride to free chlorine and associated free radicals (see [Supplemental Information, Table S1](#)). Previous photo-electrochemical research emphasized complex reactor designs for the purpose of photo-excitation of photo-catalytic anodes [31–35]. This research was limited by the complexity of the hybrid reactor as well as the photo-catalytic activity of the anodes. Since it has minimal anodic photo-activity, we have not been able to find any published research on the use of boron-doped diamond electrodes in hybrid photo-electrochemical oxidation processes [36]. The design proposed in this research has the potential to be easily integrated into the existing infrastructure where individual flow-through photo-chemical and electrochemical reactors are considered standard. In addition, this unique reactor configuration can take advantage of the electrochemical benefits of boron-doped diamond electrodes (wide potential window, low background current, high chemical stability, high resistance to deactivation [37–40]) without the need to invest energy and resources to enhance its photoactivity, which typically add dramatically to the capital cost and restrict future process scale-up. This study aims to analyze the chlorine-enhanced UVEL process with respect to oxidation efficiency and energy consumption as compared to conventional UV-peroxide and UV-ozone AOPs.

2. Materials and methods

Electrochemical oxidation experiments (EL) were performed in a flow-through, undivided, and spacer-filled electrochemical cell (Micro Flow Cell[®]; Electrocell, Amherst, NY). The anodes studied were DiaChem[®] boron-doped diamond (BDD), platinum (Pt), ruthenium oxide on titanium (DSA- Cl_2), and iridium oxide on titanium (DSA- O_2). All electrodes were supplied by Electrocell (Amherst, NY) and were rectangular with a geometric active area of 10 cm^2 each. A laboratory direct current power supply (Sorensen; Ametek, San Diego, CA) provided a current density of 20 mA/cm^2 for all experiments except for the studies that varied current density from 5 to 20 mA/cm^2 . Photochemical experiments (UV) were conducted using an annular photoreactor with a centrally mounted lamp (S5Q-PA; R-Can, Ontario, Canada). A low-pressure mercury-vapor lamp emitting 254 nm light was used as the UV-C irradiation source with an intensity of $4300 \mu\text{W/cm}^2$ determined by H_2O_2 actinometry. The average irradiated area was 836 cm^2 . The hybrid UVEL system subjected the treated solution to both electrochemical oxidation and UV photolysis in series, batch recirculation mode (Fig. 1). A Haake A10 chiller (Thermo Fisher Scientific Inc., Waltham, MA) was used to maintain a constant solution temperature of $22 \text{ }^\circ\text{C}$ during all the experiments.

The conventional and advanced oxidation processes studied were ozone (O_3), UV with ozone (UV/ O_3), and UV with hydrogen peroxide (UV/ H_2O_2). Ozonation experiments were carried out by continuously feeding the jacketed beaker shown in Fig. 1 with an ozone/air gas stream by means of a porous ceramic diffuser (model CD-1KB; Ozone Solutions, Hull, IA). The high output ozone generator (HG-1500; Ozone Solutions, Hull, IA) was fed with 1.0 L/min dry air to produce an output dose of 0.75 g/h ozone. Photo-oxidation experiments were conducted by running the photochemical reactor with an initial concentration of 50 mg/L

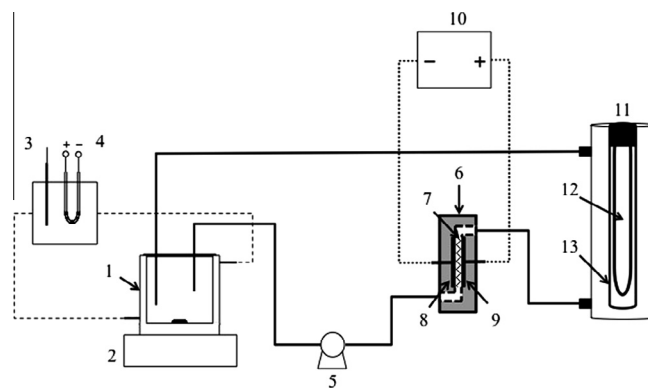


Fig. 1. Schematic diagram of the hybrid photo-assisted electrochemical reactor. (1) Jacketed beaker; (2) magnetic stirrer; (3) thermometer; (4) temperature control device; (5) pump; (6) commercial undivided electrochemical cell; (7) mesh turbulence promoter; (8) cathode; (9) anode; (10) DC power supply; (11) commercial annular photoreactor; (12) UV-C lamp; and (13) quartz sleeve.

H_2O_2 dosed from reagent grade 30% aqueous H_2O_2 stock (Sigma–Aldrich) [41].

Solutions were comprised of reagent grade salts dissolved in ultra-pure Milli-Q water (Millipore). Chloride, alkalinity, and TOC were present at concentrations comparable to real municipal wastewater effluent (Table 1). Phenol (Sigma–Aldrich) was used as the target organic at an initial concentration of 26 mg/L (20 mg/L as TOC) for all experiments. Phenol is considered to be an intermediate in the oxidation pathway of high molecular weight aromatic hydrocarbons and is frequently used as a model compound for advanced wastewater studies [42–44].

Analyses included measuring the total organic carbon (TOC) content with a Shimadzu TOC-V analyzer (Shimadzu Corp., Kyoto, Japan) and UV-vis absorbance at wavelengths between 200 and 1000 nm using a Perkin Elmer Lambda 20 UV-vis spectrometer with 1 cm optical path length (Perkin Elmer, Waltham, MA). Free chlorine was measured by a spectrophotometer at 528 nm (Hach Pocket Colorimeter II, Loveland, CO) using a specific reagent (DPD Free Chlorine Reagent Hach 21055-69) and standard samples for calibration with a detection limit of 0.05 mg/L. Eaton Analytical Laboratories (Monrovia, CA) was commissioned to measure the concentration of haloacetic acids (HAAs) by Standard Method 6251B, trihalomethanes (THMs) by EPA Method 551.1, and perchlorate by EPA Method 314.0. Samples were collected after 6 h of treatment of the model wastewater effluent by EL and UVEL with BDD and DSA- Cl_2 anodes.

The toxic effects of the feed and treated water samples toward *Vibrio fischeri* (Flinn Scientific Inc., Batavia, IL) were determined in this study. It is well established that free chlorine is toxic to bioluminescent bacteria. Therefore, samples were dechlorinated by the addition of 100 mg/L sodium thiosulfate prior to all toxicity measurements to isolate the effect of persistent oxidation by-products other than residual free chlorine. *V. fischeri* was cultured in Photo-bacterium Broth [45,46]. Bacterial cultures were maintained for at

Table 1
Model wastewater recipe.

| Parameter | Unit | Value |
|--------------------------------|-----------------------------|-------|
| Conductivity | mS/cm | 3.4 |
| pH | – | 8.3 |
| TOC | mg/L | 20 |
| A_{254} | /cm | 0.145 |
| Na^+ | mg/L | 645 |
| Cl^- | mg/L | 890 |
| Alkalinity, as CaCO_3 | mg CaCO_3/L | 150 |

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