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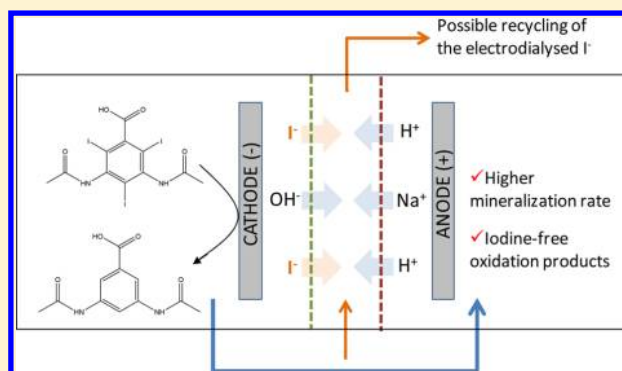
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S Supporting Information

ABSTRACT: Due to their resistance to biological wastewater treatment, iodinated X-ray contrast media (ICM) have been detected in municipal wastewater effluents at relatively high concentrations (i.e., up to $100 \mu\text{g L}^{-1}$), with hospitals serving as their main source. To provide a new approach for reducing the concentrations of ICMs in wastewater, electrochemical reduction at three-dimensional graphite felt and graphite felt doped with palladium nanoparticles was examined as a means for deiodination of the common ICM diatrizoate. The presence of palladium nanoparticles significantly enhanced the removal of diatrizoate and enabled its complete deiodination to 3,5-diacetamidobenzoic acid. When the system was employed in the treatment of hospital wastewater, diatrizoate was reduced, but the extent of electrochemical reduction decreased as a result of competing reactions with solutes in the matrix. Following electrochemical reduction of diatrizoate to 3,5-diacetamidobenzoic acid, electrochemical oxidation with boron-doped diamond (BDD) anodes was employed. 3,5-Diacetamidobenzoic acid disappeared from solution at a rate that was similar to that of diatrizoate, but it was more readily mineralized than the parent compound. When electrochemical reduction and oxidation were coupled in a three-compartment reactor operated in a continuous mode, complete deiodination of diatrizoate was achieved at an applied cathode potential of -1.7 V vs SHE, with the released iodide ions electrodialyzed in a central compartment with 80% efficiency. The resulting BDD anode potential (i.e., $+3.4\text{--}3.5 \text{ V}$ vs SHE) enabled efficient oxidation of the products of the reductive step. The presence of other anions (e.g., chloride) was likely responsible for a decrease in I^- separation efficiency when hospital wastewater was treated. Reductive deiodination combined with oxidative degradation provides benefits over oxidative treatment methods because it does not produce stable iodinated intermediates. Nevertheless, the process must be further optimized for the conditions encountered in hospital wastewater to improve the separation efficiency of halide ions prior to the electrooxidation step.



INTRODUCTION

Iodinated contrast media (ICM) are widely used in hospitals for imaging of soft tissues. They are typically applied in high doses (e.g., each examination requires more than 100 g of ICM), and they are excreted unaltered within 24 h in the patient's urine.¹ Because of their extensive use and persistence in the environment, ICM are frequently encountered in municipal wastewater at concentrations up to $100 \mu\text{g L}^{-1}$.^{2,3} This is potentially problematic because most biological and chemical wastewater treatment processes are unable to remove ICM. As a result, elevated concentrations of ICM and iodinated transformation products have been reported in effluent-impacted rivers^{2,4} and in drinking water.^{5,6}

With respect to removal during municipal wastewater treatment, diatrizoate is the most persistent of the ICMs. Microbial transformation of diatrizoate results in the cleavage of the two acetyl groups, leaving a suite of stable 2,4,6-triiodinated aromatic compounds.^{7,8} The formation of these transformation products is a concern because the metabolites of diatrizoate

with free amino groups might exhibit mutagenic effects.^{9,10} In addition, although diatrizoate is considered to be biochemically inert and pose a small environmental risk, some research has suggested that it may have nephrotoxic effects in animals and humans.^{11,12} Furthermore, a recent study¹³ reported that ICM can also be a source of iodine in the formation of iodinated disinfection byproducts during chlorination and chloramination of drinking water.

In response to concerns about ICMs in wastewater, researchers have proposed oxidative and reductive treatment strategies.^{14–17} Identifying cost-effective strategies for treatment has been a challenge because diatrizoate and many other ICM were difficult to oxidize.^{14,15,18} In contrast, reductive processes have shown promise because most ICMs are easily deiodi-

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nated.^{17,19,20} Diatrizoate was among the most persistent ICMs with respect to reduction,²¹ and thus, it may be a good surrogate for assessing the efficacy of reductive treatment.

Among the reductive treatment processes, electrochemical methods show considerable practice. Usually, high reduction rates are achieved with electrodes that contain noble metals either as the working electrodes or supported on less expensive ceramic, titanium, or carbon-based materials.^{22,23} Palladium is considered as the most ideal catalyst due to its strong ability to intercalate hydrogen in its lattice.²⁴ Pd-modified electrodes are known to accelerate electrocatalytic hydrogenation reactions through the production of H₂ and adsorbed atomic H on the cathode surface and, thus, may be the best option for reduction of ICMs.^{17,25}

Despite its ability to remove ICMs, reductive treatment alone may not be sufficient to completely eliminate their environmental risk, because the toxicity of the dehalogenated products is yet to be determined. Electrochemical reduction followed by electrochemical oxidation treatment may provide a means of avoiding this problem and achieving mineralization of the reduced products.^{26,27}

In this study, sequential treatment of diatrizoate by electrochemical reduction followed by oxidation was investigated, with the objective of combining the two processes in one electrolytic cell to enable a more complete conversion of ICMs in a cost-effective manner. To assess this approach, reaction rates and products were determined in an electrochemical cell with reduction of diatrizoate at a cathode consisting of graphite felt or Pd-nanoparticle-loaded graphite felt under different operating conditions. To investigate the potential for oxidation of deiodinated products, electrochemical oxidation experiments were performed with a boron-doped diamond (BDD) anode with both diatrizoate and its deiodinated analogue, 3,5-diacetamidobenzoic acid. Finally, reductive and oxidative electrochemical treatment processes were combined in an electrochemical cell and applied to the treatment of hospital wastewater. To avoid the reoxidation of the iodide released by the C–I bond cleavages in diatrizoate, a three-compartment electrolytic cell was used to separate iodide in the central compartment by electrodialysis.

MATERIALS AND METHODS

Chemicals. All chemicals were of analytical grade and commercially available, and are described in Text S1 of the Supporting Information (SI).

Preparation of Palladium Nanoparticle-Doped Graphite Felt Electrodes. Graphite felt electrodes (Morgan Industrial Carbons, Australia) were made by cutting the commercially available felt into pieces of 190 × 45 × 2.5 mm. The projected surface area of the electrode was of 171 cm². Electrodes were cleaned by immersion in reverse osmosis (RO) water/isopropyl alcohol 1:1 solutions three times before being thoroughly rinsed in RO water. After cleaning, the electrodes were encased in a stainless steel holder (8 mm mesh size) to ensure good electrical connection. Polyelectrolyte multilayers were electrostatically self-assembled on clean graphite felt electrodes following the method of Vago et al.²⁵ The procedure employed for electrode preparation and characterization is described in the Text S2 and S3 of the SI.

Experimental Setup. All experiments were conducted using a flow-through electrochemical reactor in batch or continuous mode. Separate electrochemical reduction and oxidation experiments were conducted in the divided cell in

the batch operating mode, with a cation exchange membrane (Ultrax CMI-7000, Membranes International, Ringwood, NJ, U.S.A.) placed between the cathodic and anodic chambers (SI Figure S1). The net volume of the cathodic and the anodic compartments were 340 and 200 mL, respectively. A boron-doped diamond (BDD), CD Technologies (La Chaux-de-Fonds, Switzerland), was used as an anode, with p-doped, polycrystalline, 2–3 μm thick, 700–800 ppm boron doping on monocrystalline silicon (dimensions 4.8 × 8.5 cm). Electrolysis experiments were conducted potentiostatically using a VSP potentiostat/galvanostat (BioLogic, Claix, France). All currents/potentials were measured using a 3 M Ag/AgCl reference electrode (+0.210 V vs standard hydrogen electrode) purchased from BASi (West Lafayette, IN, U.S.A.). The reference electrode was placed in the proximity of the working electrode, and current was recorded every 60 s.

Electrochemical reduction and oxidation experiments were performed using a 22 mM KH₂PO₄/K₂HPO₄ buffer (pH 7.0, conductivity 3.7 mS cm⁻¹), and hospital wastewater was collected from a hospital in southeast Queensland (pH 7.4, conductivity 3.7 mS cm⁻¹). Prior to the experiments, the hospital wastewater was filtered through a 0.7-μm glass microfiber filter (Whatman, U.K.). After performing the experiments with hospital wastewater, the reactor was thoroughly flushed with Milli-Q water. The initial concentration of diatrizoate used was either 5 or 50 μM. The experiments were performed at a cathodic (*Q_C*) and anodic (*Q_A*) flow rate of 110 mL min⁻¹.

In electrochemical reduction experiments, the reactors were run potentiostatically at cathode potentials (*E_{CAT}*) ranging from -1.1 to -1.7 V vs SHE. The cells were deoxygenated by purging nitrogen in the cathodic recirculation stream. To maintain a neutral pH and to avoid the introduction of foreign anions through direct addition of acid, 5–10 mM HNO₃ was used as an anolyte to enhance the migration of protons toward the cathodic compartment through the cation exchange membrane. To investigate the competition of oxygen with diatrizoate, a set of experiments was performed at *E_{CAT}* = -1.5 V vs SHE without N₂ sparging and at an initial O₂ concentration of 0.225 mM. To test the effect of conductivity on reduction rates, NaCl was added to the background electrolyte at a concentration of 10 mM. The effect of the increased pH on the electrochemical reduction was studied by employing 15 mM KOH/K₂HPO₄ buffer at pH 11.0 (conductivity 3.5 mS cm⁻¹) as a background electrolyte. Finally, to investigate the effect of mixing on electrochemical reduction, several experiments were performed at an increased recirculation flow rate of 200 mL min⁻¹.

Electrochemical oxidation was performed potentiostatically at an anode potential (*E_{AN}*) of +3.5 V vs SHE. In some experiments at acidic pH, no pH adjustment was performed because the initial pH 7.0 of the buffer solution rapidly decreased to pH 2.3 upon starting the reaction. For experiments at pH 7.0, a probe was placed in the holding vessel, and a peristaltic pump, controlled by the pH sensor (CPM 223, Endress + Hauser), dosed 10 mM KOH into the anodic compartment as needed. To investigate the effect of enhanced mixing, some electrochemical oxidation experiments were performed at an anodic recirculation flow rate of 200 mL min⁻¹.

When electrochemical reduction and oxidation were coupled in one cell, experiments were performed in a three-compartment cell operated in the continuous mode (SI Figure S2). A

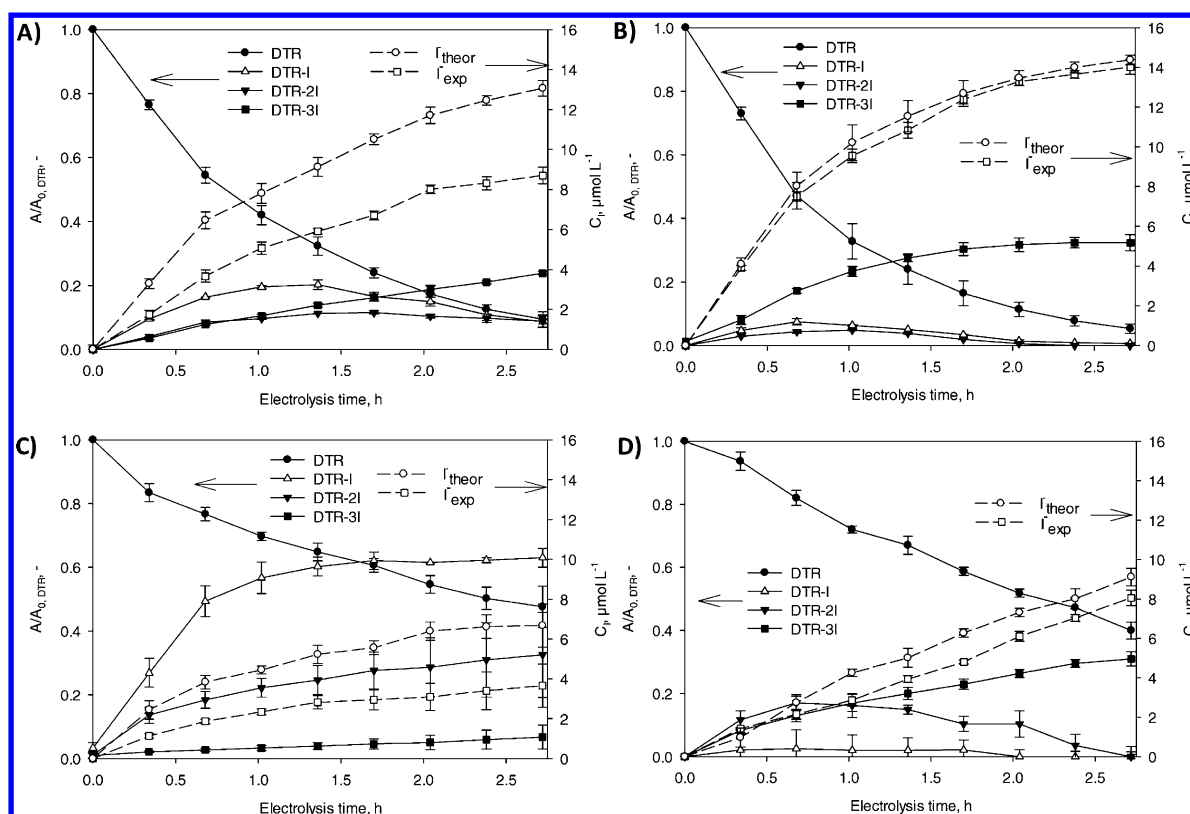


Figure 1. Qualitative profiles of diatrizoate (DTR) and its reduction products DTR-I (3,5-diacetamidodiiodobenzoic acid), DTR-2I (3,5-diacetamidoiodobenzoic acid), and DTR-3I (3,5-diacetamidobenzoic acid), were estimated using the method described in the text. Theoretical (I_{theor}^-) and experimental (I_{exp}^-) release of iodide ions in electrochemical reduction at -1.7 V vs SHE is depicted on the right axis: (A) bare graphite felt, 22 mM $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$, pH 7.0; (B) Pd nanoparticle-loaded graphite felt, 22 mM $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$, pH 7.0; (C) bare graphite felt, hospital wastewater, pH 7.4; and (D) Pd nanoparticle-loaded graphite felt, hospital wastewater, pH 7.4.

monovalent anion permselective membrane (ASV, Selemion, Chiba, Japan) was used to separate the cathodic from the central compartment, and a cation exchange membrane (Ultrex CMI-7000, Membranes International, Ringwood, NJ, U.S.A.) was used to separate the central compartment from the anodic chamber. The resulting interelectrode gap of the three-compartment cell was 2.1 cm. The net volumes of cathodic, anodic, and central compartments were 340, 200, and 120 mL, respectively. To measure the potentials of the electrodes, two 3 M Ag/AgCl reference electrodes were used, each placed in the proximity of the anode and cathode.

The reactor was operated potentiostatically by applying $E_{\text{CAT}} = -1.7$ V vs SHE. The resulting E_{AN} was followed by the open circuit voltage technique, against a 3 M Ag/AgCl reference electrode placed in the vicinity of the BDD (i.e., no current/potential was applied to the anode; only the resulting E_{AN} is recorded). The cathodic compartment was fed with a 5 μM solution of diatrizoate in 22 mM $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ buffer at pH 7.0. The experiments were also conducted in hospital wastewater (pH 7.4).

Following the reductive treatment, the fluid was fed into the anodic compartment. The central compartment was fed with 10 mM $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ buffer at pH 7.0. The flow rate through the cathodic, anodic, and central compartments was 4 mL min^{-1} , resulting in hydraulic residence times of ~ 85 , 50, and 30 min, respectively. To enhance the mixing, recirculation was applied in the anodic and cathodic compartments at a flow rate of 200 mL min^{-1} . No attempt was made to maintain the pH in the cathodic and anodic compartments. Following sequential

treatment, the pH of the buffered solution and the hospital wastewater were 5.9 and 5.8, respectively.

Chemical Analysis. Diatrizoate and its reduction products were analyzed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) using positive electrospray ((+)ESI) mode on a Shimadzu Prominence ultra fast LC (UFLC) system (Shimadzu, Kyoto, Japan) coupled with a 4000 QTRAP MS equipped with a turbo ion spray source (Applied Biosystems-Sciex, Foster City, CA, U.S.A.). Details of the analytical method description are summarized in the SI. Chloride and sulfate ions were quantified by ion chromatography, and iodide release was quantified by ion chromatography with ultraviolet detector (Dionex ICS-2000, Dionex, Sunnyvale, CA, U.S.A.). The limits of detection of chloride and iodide ion analysis were 500 and 5 $\mu\text{g L}^{-1}$, respectively. Dissolved organic carbon (DOC) was measured as nonpurgeable organic carbon (NPOC) (APHA, 1998; method 5310B), and total and inorganic carbon were determined using an Analytik Jena multi N/C 2100S total organic carbon analyzer. Dissolved oxygen was measured with a CyberScan PCD 650 m (Eutech, Singapore). Values are expressed as the mean of two experiments, with their standard deviations.

RESULTS AND DISCUSSION

Characterization of Pd Nanoparticles-Loaded Graphite Felt Electrodes. The electrodeposition method resulted in a graphite felt electrode doped with Pd nanoparticles. SI Figure S4 shows scanning electron micrograph (SEM) images of the Pd nanoparticles electrode. SI Figure S4 (top) shows a low

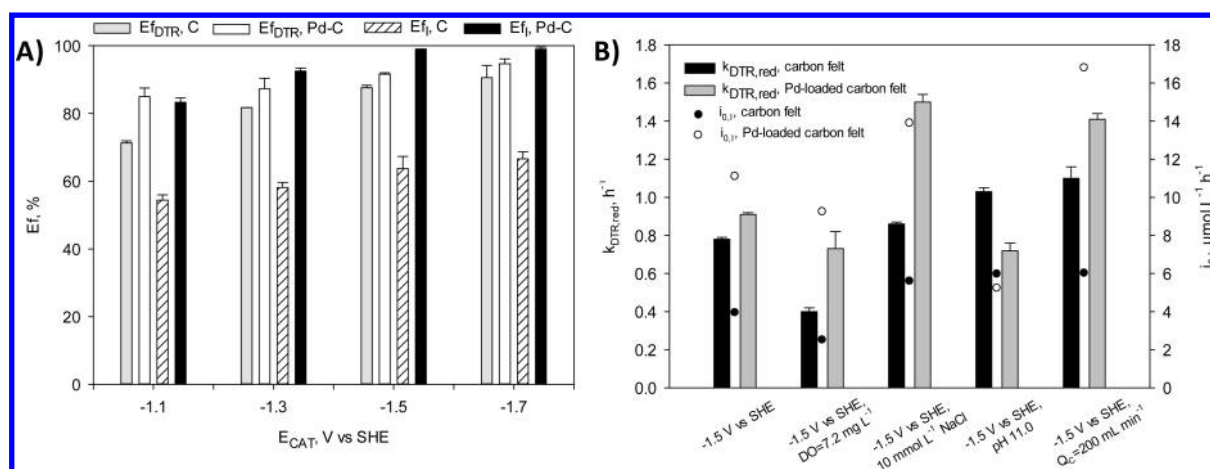


Figure 2. (A) Effect of cathode potential (E_{CAT}) on the diatrizoate removal efficiency (Ef_{DTR}) and deiodination efficiency (Ef_I) and (B) effect of operational parameters (i.e., dissolved oxygen (DO) concentration, conductivity, pH, and cathode flow rate (Q_C)) on the first-order rate constants of diatrizoate disappearance and initial rates of iodide release at bare (C) and Pd nanoparticle-loaded graphite felt (Pd-C) cathode at $E_{CAT} = -1.5$ V vs SHE.

magnification image of the graphite felt fibers, indicating only minor evidence of micrometer-sized particles. The high magnification image (SI Figure S4 bottom) shows nanometer-sized particles on the surface of the graphite felt. Image analysis (SPIP 5.0.7, Image Metrology) shows that the average radius of the nanoparticles was 20 nm with a standard deviation of 11 nm (SI Figure S5). The presence of Pd nanoparticles (NPs) was confirmed by energy dispersive X-ray spectroscopy (EDS) analysis (SI Figure S6). The cyclic voltammograms in H_2SO_4 (SI Figure S7) show the characteristic shapes of Pd-activated electrodes, in both the Pd-oxide and H_2 evolution potential windows.²⁵ Furthermore, they confirm that the Pd nanoparticles are in electrical contact with the graphite felt electrode.

Electrochemical Reduction at Bare and Pd Nanoparticle-Loaded Graphite Felt. To investigate the loss of diatrizoate due to its adsorption onto the graphite and Pd nanoparticle-loaded graphite felt, experiments were first performed in an open circuit at a relatively high initial diatrizoate concentration (i.e., 50 μM). No decrease in diatrizoate and DOC concentration was observed during recirculation of catholyte without applied electrochemical potential (SI Figure S8). In addition, iodide remained below the detection limit, confirming that the cathodes had no catalytic activity toward diatrizoate reduction in the absence of applied potential. Next, a series of electrochemical reduction experiments was performed at an initial diatrizoate concentration of 50 μM and E_{CAT} of -1.5 V vs SHE to assess a possible adsorption of reduction products onto the electrode surface. Carbon mass recovery of 100% indicated that there was no adsorption of the reduction products of diatrizoate to any of the employed cathodes.

Electrochemical reduction experiments were performed in 5 μM diatrizoate solutions in phosphate buffer (pH 7.0), at $E_{CAT} = -1.1, -1.3, -1.5$, and -1.7 V vs SHE. When a potential of -1.7 V vs SHE was applied, the diatrizoate concentration decreased, and reduction products, DTR-I (3,5-diacetamidodiiodobenzoic acid), DTR-2I (3,5-diacetamidoiodibenzoic acid), and DTR-3I (3,5-diacetamidobenzoic acid) were produced (Figure 1). Although there were two possible structures of products DTR-I and DTR-2I, the latter one was detected as a single peak. Because of the lack of analytical

standards for DTR-I and DTR-2I, formation of the reduction products was represented by assuming that the products exhibited the same instrument response as the parent compound. Calculations of the electrolysis time and theoretical release of iodide ions (I_{theor}^-) used to assess performance are explained in the SI, Text S5. Because the applied potentials were well below the water stability region, the reduction of water to hydrogen resulted in a decrease in the overall electrolytic efficiency. In addition, the efficiency also decreased due to mass transfer limits on the rate of reduction of the target contaminant. Thus, very low Coulombic efficiencies (ϵ) of diatrizoate reduction were obtained in all experiments, and efficiencies decreased with lowering the cathode potential (SI Table S2). For example, decreasing the E_{CAT} from -1.1 to -1.9 V vs SHE lowered the obtained ϵ from $0.026 \pm 0.001\%$ to $0.014 \pm 0.001\%$ at the Pd-treated cathode.

Effect of Cathode Potential. The disappearance of diatrizoate exhibited first-order kinetics under all conditions tested. First-order rate constants ($k_{DTR,red}$, h^{-1}) ranged from $0.43 \pm 0.02 h^{-1}$ to $0.88 \pm 0.15 h^{-1}$, with the Pd-treated graphite felt cathode exhibiting faster diatrizoate removal than the bare felt electrode (i.e., $k_{DTR,red}$ increased from $0.61 \pm 0.01 h^{-1}$ to $1.07 \pm 0.02 h^{-1}$ when E_{CAT} was decreased from -1.1 V to -1.7 V vs SHE). Considering the near linear dependence of the $k_{DTR,red}$ on the applied potential (SI Figure S11), diatrizoate reduction was likely limited by a combination of mass transport and electron transfer kinetics.²² Figure 2A illustrates the calculated diatrizoate removal efficiency (Ef_{DTR}) and deiodination efficiency (Ef_I) observed for the two cathode materials at different applied potentials after 2.7 h of electrolysis. Although diatrizoate removal was similar at the two cathodes, the extent of deiodination was significantly higher for the Pd nanoparticle-coated cathode. For example, quantitative release of 3 equiv of iodide was observed only at the electrode doped with Pd nanoparticles, and deiodination efficiencies $>80\%$ were obtained at -1.1 V vs SHE. At lower E_{CAT} (i.e., -1.3 to -1.7 V vs SHE), the final concentration of 3,5-diacetamidobenzoic acid (i.e., DTR-3I) reached 95% of the initial diatrizoate concentration at the Pd-activated cathode, thus closing the mass balance. These results are in agreement with the previous studies in which fast hydrodehalogenation of diatrizoate was reported on Pd catalysts.^{16,28} For the bare graphite felt

electrodes, the deiodination efficiency at the lowest applied potential (i.e., $E_{\text{CAT}} = -1.7$ V vs SHE) was only $66.6 \pm 2.1\%$ (SI Table S2). The same reduction products were detected at the graphite and Pd-treated electrodes, corresponding to the same sequential cleavage of C–I bonds at the aromatic ring by both treatments. The exact position of the iodine cleavage at the aromatic ring could not be determined. Other than the deiodinated products DTR-I, DTR-2I, and DTR-3I, no other intermediates were detected during LC–MS analysis.

Effect of Dissolved Oxygen. Dissolved oxygen was readily reduced at the cathode surface and, thus, may have competed with diatrizoate for the active sites. To investigate the effect of O_2 on the reduction efficiency, experiments were performed at $E_{\text{CAT}} = -1.5$ V vs SHE without nitrogen sparging of the solution. In the presence of oxygen, the cathodic current increased by around 5 mA, indicating that the reduction of oxygen was taking place. The diatrizoate removal rate decreased in the presence of oxygen from $0.78 \pm 0.01 \text{ h}^{-1}$ to $0.40 \pm 0.02 \text{ h}^{-1}$ for the bare graphite felt and from 0.91 ± 0.01 to $0.73 \pm 0.09 \text{ h}^{-1}$ for the Pd-activated cathode (Figure 2B). Nevertheless, much of the diatrizoate was still completely deiodinated at the Pd-treated electrode in the presence of oxygen.

Effect of Ionic Strength. The effect of ionic strength on the reduction rates was investigated by adding the 10 mM NaCl to the background electrolyte at $E_{\text{CAT}} = -1.5$ V vs SHE. Increasing the conductivity resulted in a faster reduction of diatrizoate at both the bare and the Pd-treated graphite felt (Figure 2B). More complete deiodination was observed at the bare graphite felt at higher conductivity (i.e., E_{f} was increased from $63.7 \pm 3.6\%$ to $75.9 \pm 2.5\%$). For the Pd-activated cathode, NaCl addition increased $k_{\text{DTR,red}}$ from $0.91 \pm 0.01 \text{ h}^{-1}$ to $1.50 \pm 0.04 \text{ h}^{-1}$. Increasing ionic strength decreases electrostatic forces between the ions and the electrode.²⁹ Under these conditions, an increased conductivity decreased the repulsion between the negatively charged diatrizoate and the negatively charged cathode, leading to increased contact of diatrizoate with the cathode surface. In addition, increased conductivity facilitates the movement of ions in the solution, meaning that diatrizoate anions could diffuse more easily into the structure of the graphite felt and reach a greater number of active sites, resulting in faster reduction rates.

Effect of pH. To determine the effect of pH, reduction experiments were performed at pH 11.0 and at $E_{\text{CAT}} = -1.5$ V vs SHE. The $\text{p}K_{\text{a}}$ of diatrizoate is 3.4.³⁰ Thus, the compound should be in the form of a carboxylate anion at both pH 7.0 and 11.0. The higher pH value accelerated the rate of reduction of diatrizoate at the bare graphite felt from $0.78 \pm 0.01 \text{ h}^{-1}$ to $1.03 \pm 0.02 \text{ h}^{-1}$ and increased the deiodination efficiency from $63.7 \pm 3.6\%$ to $71.7 \pm 0.6\%$. This effect of pH could have been due to decreased hydrogen production due to a decrease in standard potential for hydrogen evolution (i.e., from -414 mV at pH 7 to -650.8 mV vs SHE at pH 11, as calculated by the Nernst equation) because H_2 blocks catalytic sites on cathodes and lowers the effective surface area available for reduction. A decreased rate of hydrogen formation at pH 11.0 was also evident from the lower current density (i.e., 45 mA compared with 55 mA recorded at neutral pH). The effect of ionic strength on the rate of reduction can be excluded in the high-pH experiments because the conductivities of the two buffer solutions (i.e., at pH 7.0 and 11.0) were nearly the same (i.e., $3.5\text{--}3.7 \text{ mS cm}^{-1}$). The higher pH led to a slower reduction of diatrizoate on the Pd-activated electrode, with a decrease of the $k_{\text{DTR,red}}$ from $0.91 \pm 0.01 \text{ h}^{-1}$ to $0.72 \pm 0.04 \text{ h}^{-1}$ (Figure 2B).

The reduced $k_{\text{DTR,red}}$ may have been due to reduced in situ formation of H_2 at higher pH and, thus, reduced formation of adsorbed atomic H that reacted with the diatrizoate molecule. In agreement with this assertion, previous researchers have reported deactivation of Pd catalysts at high pH values caused by the formation of a passive oxide layer due to OH^- ions.^{31,32}

Effect of Mixing. Finally, the effect of mixing on reduction kinetics was investigated by increasing the flow rate to 200 mL min^{-1} . As indicated in Figure 2B, $k_{\text{DTR,red}}$ increased for both the graphite felt (i.e., from $0.78 \pm 0.01 \text{ h}^{-1}$ to $1.10 \pm 0.06 \text{ h}^{-1}$) and the Pd-treated electrode (i.e., from $0.91 \pm 0.01 \text{ h}^{-1}$ to $1.41 \pm 0.03 \text{ h}^{-1}$), likely as a result of decreased mass transfer limitations and enhanced contact of diatrizoate molecules with the active sites at the cathode surface.

Electrochemical Reduction of Diatrizoate in Hospital Wastewater. The characteristics of hospital wastewater are summarized in SI Table S3. Electrochemical reduction of diatrizoate was slower in hospital wastewater than in the buffered electrolyte solution for both the bare and the Pd nanoparticle-loaded graphite felt at $E_{\text{CAT}} = -1.7$ V vs SHE (Figure 1C and D). Although both cathodes were capable of removing only around 50–60% of diatrizoate after 3 h, more complete deiodination (i.e., $88.5 \pm 0.6\%$) was achieved for the Pd nanoparticle-loaded felt, versus $54.8 \pm 7.8\%$ observed for the bare graphite felt, yet the $k_{\text{DTR,red}}$ and initial iodide release rates ($i_{0,\text{I}}$) of $0.32 \pm 0.03 \text{ h}^{-1}$ and $4.20 \mu\text{mol L}^{-1} \text{ h}^{-1}$ observed at the Pd-activated cathode were significantly lower than the ones obtained for the buffer solution under the same operational conditions, that is, $1.07 \pm 0.02 \text{ h}^{-1}$ and $11.5 \mu\text{mol L}^{-1} \text{ h}^{-1}$, respectively.

Under all experimental conditions, the Pd-treated electrode outperformed the bare graphite felt electrode. The better performance of Pd nanoparticle–graphite felt may be related to an enhanced production rate of both adsorbed atomic H and H_2 .

Electrochemical Oxidation of Diatrizoate and DTR-3I on a Boron-Doped Diamond (BDD) Anode. Electrochemical oxidation experiments using a BDD anode were performed potentiostatically at $E_{\text{AN}} = +3.5$ V vs SHE, with 5 and $50 \mu\text{M}$ solutions of diatrizoate and its deiodinated analogue, 3,5-diacetamidobenzoate (i.e., DTR-3I). Similar rates of reaction were observed for electrochemical oxidation of both compounds, for example, $0.121 \pm 0.009 \text{ h}^{-1}$ and $0.142 \pm 0.005 \text{ h}^{-1}$ at acidic pH values, respectively (Table 1). This result was somewhat surprising, considering that researchers

Table 1. First-Order Rate Constants for Diatrizoate (DTR) ($k_{\text{DTR,ox}}$, h^{-1}) and DTR-3I ($k_{\text{DTR-3I,ox}}$, h^{-1}) Removal in Electrochemical Oxidation at a Boron-Doped Diamond (BDD) Anode at an Anode Potential (E_{AN}) = +3.5 V vs SHE^a

	$Q_{\text{A}} = 110 \text{ mL min}^{-1}$	$Q_{\text{A}} = 200 \text{ mL min}^{-1}$
pH 2.0		
$k_{\text{DTR,ox}} \text{ h}^{-1,b}$	0.121 ± 0.009	0.242 ± 0.007
$k_{\text{DTR-3I,ox}} \text{ h}^{-1,b}$	0.142 ± 0.005	0.273 ± 0.006
pH 7.0		
$k_{\text{DTR,ox}} \text{ h}^{-1,b}$	0.237 ± 0.011	0.338 ± 0.013
$k_{\text{DTR-3I,ox}} \text{ h}^{-1,b}$	0.270 ± 0.010	0.409 ± 0.011

^aValues are expressed as means of two experiments, with their standard deviations. The initial concentrations of diatrizoate ($C_{0,\text{DTR}}$) and DTR-3I ($C_{0,\text{DTR-3I}}$) were $5 \mu\text{M}$; anodic flow rate (Q_{A}) = 110 mL min^{-1} and $Q_{\text{A}} = 200 \text{ mL min}^{-1}$. ^b r^2 was always ≥ 0.985 .

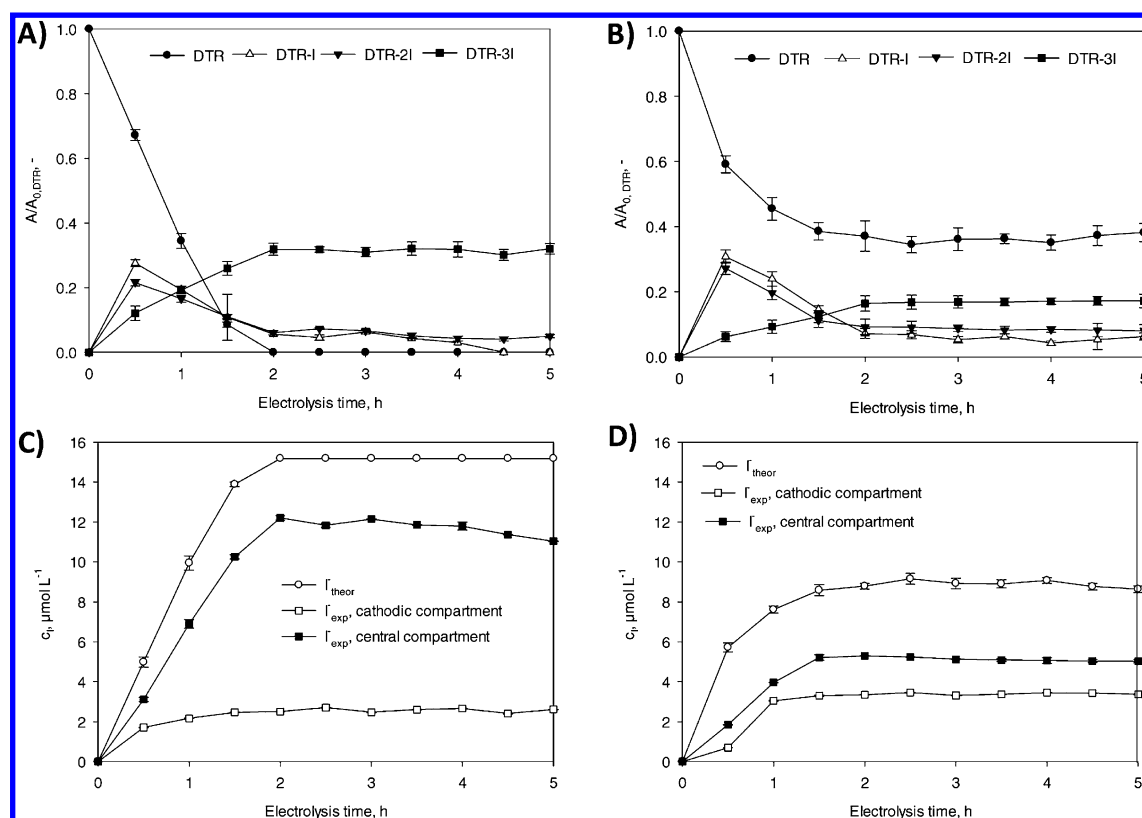


Figure 3. Continuous mode electrochemical reduction at Pd nanoparticle-loaded graphite felt at $E_{\text{CAT}} = -1.7$ V vs SHE: profiles of diatrizoate concentration and reduction products DTR-I, DTR-2I, and DTR-3I: (A) 22 mM $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$, initial pH 7.0, and (B) hospital wastewater, initial pH 7.4. Theoretical (I_{theor}) and experimental (I_{exp}) release of iodide ions measured in the central and cathodic compartment: (C) 22 mM $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$, initial pH 7.0, and (D) hospital wastewater, initial pH 7.4.

previously observed faster oxidative transformation of the deiodinated form of diatrizoate by advanced oxidation processes.^{15,21} For example, Jeong et al.²¹ reported bimolecular rate constants for the reaction of diatrizoate and its deiodinated analogue with aqueous HO^\bullet to be $9.6 \cdot 10^8$ and $6.0 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The low reactivity of diatrizoate with HO^\bullet was attributed to the presence of iodine substituents on the aromatic ring. Another study¹⁵ indicated faster transformation of the deiodinated form of diatrizoate by TiO_2 photocatalytic oxidation. However, in all experiments performed in the presence of phosphate buffer, both diatrizoate and DTR-3I were oxidized at very similar rates. At high E_{AN} applied, HO^\bullet radicals are produced in significant quantities, but they are generally considered to be loosely adsorbed on the BDD anode surface.³³ Thus, similar electrooxidation rates observed for diatrizoate and DTR-3I may be a consequence of different electrosorption of diatrizoate, DTR-3I, or their oxidation intermediates onto the anode surface.

To assess the nature of the oxidation products, experiments were performed at higher initial concentrations of diatrizoate and DTR-3I (i.e., $50 \mu\text{M}$), and samples were analyzed for DOC. The data indicated a higher degree of mineralization for the deiodinated product, DTR-3I (SI Figure S13). For example, after 1.6 h of electrolysis time, $35.1 \pm 1.1\%$ loss of DOC was observed. In electrochemical oxidation of diatrizoate, only $27.1 \pm 0.9\%$ of the initial DOC was lost. Increasing the pH yielded higher rate constants for both compounds, that is, $k_{\text{DTR,ox}} = 0.237 \pm 0.011 \text{ h}^{-1}$ and $k_{\text{DTR-3I}} = 0.270 \pm 0.010 \text{ h}^{-1}$. The higher pH value also led to more DOC mineralization (i.e., $44.2 \pm 2.2\%$ and $56.2 \pm 1.9\%$ for diatrizoate and DTR-3I,

respectively), suggesting the production of more easily oxidized products than in the case of acidic pH. Enhanced electrochemical oxidation at a higher pH value is likely a consequence of an enhanced generation of surface HO^\bullet under alkaline conditions, because of one-electron oxidation of OH^- ions.³⁴ Finally, increasing the flow rate from 110 mL min^{-1} to 200 mL min^{-1} accelerated the rate of loss of both compounds, likely as a result of reduced mass transfer limitations, and yielded $k_{\text{DTR,ox}}$ and $k_{\text{DTR-3I,ox}}$ of $0.242 \pm 0.007 \text{ h}^{-1}$ and $0.273 \pm 0.006 \text{ h}^{-1}$, respectively.

Electrochemical Oxidation of Diatrizoate and 3,5-Diacetamidobenzoic Acid in Hospital Wastewater. In electrochemical oxidation of hospital wastewater amended with $5 \mu\text{M}$ diatrizoate and DTR-3I, DTR-3I disappeared at a rate that was much faster than that of diatrizoate ($20.5 \pm 0.02 \text{ h}^{-1}$ versus $1.30 \pm 0.02 \text{ h}^{-1}$, respectively) (SI Figure S14A). In both experiments, $\sim 37\%$ of the initial DOC was removed after 1.6 h of electrolysis. Considering that the concentration of chloride ions in the hospital wastewater was relatively high (i.e., 21.7 mM), formation of reactive forms of Cl (e.g., Cl_2 , HOCl) likely contributed to oxidation of the compounds and their transformation products. Although oxidation could occur at the amide side chains, faster disappearance of the deiodinated compound might be attributed to oxidation by chlorine species on the activated aromatic ring of DTR-3I, compared with the fully substituted ring of diatrizoate. The insertion of a chlorine substituent is likely to increase the compound's persistence and toxicity.³⁵

In electrochemical oxidation of saline wastewater, it may be necessary to apply post-treatment (e.g., activated carbon) to

reduce the toxicity of the effluent. Alternatively, the formation of chlorinated products may be minimized by implementing an adequate pretreatment strategy to decrease the chloride concentration in the matrix prior to the oxidative treatment, although this energy-intensive process may be suitable only for small-scale applications.

Combined Electrochemical Reduction and Oxidation.

In the three-compartment electrolytic cell operated in continuous mode, diatrizoate and its reduction products accumulated in the cathodic cell, whereas iodide ions were detected in the cathodic and central compartment (Figure 3). When the system was operated with the phosphate buffer, the performance of the cathodic half-cell reached steady state after ~ 2 h of electrolysis. On the basis of the measured concentration of 3,5-diacetamidobenzoic acid (i.e., $4.7 \mu\text{M}$) (SI Figure S15), it could be concluded that diatrizoate was completely reduced to its deiodinated analogue. The concentration of iodide measured in the central and cathodic compartments was 12.1 and $2.4 \mu\text{M}$, respectively, indicating that around 80% of the total mass of I^- ions passed through the anion exchange membrane. Considering the mass of I^- remaining in the cathodic compartment, approximately 95% of I^- was recovered (Figure 3C). This missing I^- could have been transported to the anodic compartment by leakage through the cation exchange membrane. However, the amount of I^- reaching the anodic compartment is expected to be too low to cause a significant generation of hypoiodous acid in the anode compartment. Low cathode potential (i.e., $E_{\text{CAT}} = -1.7$ V vs SHE) and long hydraulic residence time applied (i.e., 85 min) led to an accumulation of OH^- ions in the cathodic compartment. The buffering capacity of the phosphate buffer was rapidly consumed, and the cathodic pH increased to 11.5 after 1 h of electrolysis. The resulting BDD anode potential (i.e., $E_{\text{AN}} = +3.4$ V vs SHE) led to an accumulation of H^+ ions and pH decrease to 3.5 in the first hour of electrolysis. The anodic pH was further increased to 5.9 in the next hour as a result of the higher pH of the incoming cathodic effluent.

For the hospital wastewater, around 60% of diatrizoate was removed by continuous treatment after ~ 2 h of electrolysis. Although DTR-3I was the main product detected in the reduced effluent, partially deiodinated products DTR-I and DTR-2I were also present. The concentration of DTR-3I in the cathodic compartment at steady state was $2.7 \mu\text{M}$ (SI Figure S15), which corresponds to a deiodination efficiency of 90%. Comparing the steady state concentration of iodide in the central compartment (i.e., $5.3 \mu\text{M}$) with the mass of iodide released during formation of DTR-3I (i.e., $8.9 \mu\text{M}$), it can be concluded that 59% of the released iodide was electrodialed to the central compartment. The efficiency of electrodialed I^- was likely lower than that observed in the buffered solution as a result of the presence of other anions in the hospital wastewater, such as Cl^- and NO_3^- .

The presence of 21.7 mM chloride in the hospital wastewater could be problematic to the electrochemical oxidation because of the formation of chlorinated byproducts.³⁵ Therefore, the performance of the anion exchange membrane with respect to Cl^- separation was evaluated (SI Figure S16). The system reached stable conditions in the first hour of electrolysis, with 57% of initial chloride ions transferred to the central compartment, and around 8.4 mM of Cl^- in the effluent of the cathodic compartment. Similar to the experiment with a buffer solution, the cathodic pH increased to 11.4 after 1 h of hospital wastewater electrolysis. Thus, electrodialed Cl^- and

I^- ions was likely suppressed by the passage of OH^- ions in both experiments.

In the anodic half-cell, diatrizoate and partially iodinated reduction products completely disappeared after 3 h of electrolysis. The completely deiodinated product was present in the effluent of the anodic compartment at a maximum concentration of $1.2 \mu\text{M}$. After ~ 4 h of electrolysis, the concentration decreased to $0.8 \mu\text{M}$ (SI Figure S17B). On the basis of the results of electrochemical oxidation experiments performed at neutral and acidic pH, incomplete removal of DTR-3I was likely a consequence of the low pH in the anodic compartment and insufficient hydraulic retention time (i.e., 50 min). The pH in the anodic compartment decreased to 3.2 after 1 h of electrolysis, and increased to pH 5.8 in the next hour. Although DTR-3I could not be completely oxidized, the effluent of the anodic compartment did not contain diatrizoate or its iodine-containing reduction products DTR-I and DTR-2I. No information is available on the biodegradability of 3,5-diacetamidobenzoic acid, but it is likely that the dehalogenated compounds will pose fewer problems than the parent compound.^{36,37}

In the case of hospital wastewater, none of the compounds was detectable in the oxidized effluent. However, this is likely a consequence of their oxidation by the reactive chlorine species produced by Cl^- that entered the anodic chamber. The extent of mineralization of the compound could not be determined for the experiment in a buffer solution because of the low initial diatrizoate concentration (i.e., $5 \mu\text{M}$). In other words, diatrizoate only accounted for less than 1% of the initial DOC. For hospital wastewater, DOC decreased from 83.1 ± 1.4 to $43.2 \pm 2.5 \text{ mg L}^{-1}$ in the first 1.5 h of electrolysis (SI Figure S18).

The cell potential remained relatively constant during the 5 h of electrolysis of both buffer and hospital wastewater, at 17.6 and 18.7 V, respectively (SI Figure S19). The cathodic currents averaged 203 and 220 mA for the buffer and the hospital wastewater, respectively, which corresponds to energy consumption of 14.9 and 17.1 kWh m^{-3} for the combined electrochemical reduction and oxidation treatment. This value corresponds to the energy consumption of a small reverse osmosis plant for seawater desalination (without an energy-recovery system).³⁸ However, it is important to note that in this study, the design of the electrolysis cell was not optimized and was limited to a plate-and-frame reactor because of the availability of a BDD anode with only planar geometry. The voltage drop across the cell could be easily lowered by decreasing an intermembrane and interelectrode distance. For example, tubular reactors with closely positioned annular anodes and cathodes, as well as use of ion exchange membranes of lower electrical resistance, could significantly decrease the mass transfer limitations and enable an improved contact of liquid with the electrode surface.

The investigated electrochemical process may be a suitable option for the removal of X-ray contrast media and possibly other halogenated pollutants in a decentralized treatment of hospital wastewater if the volumes to be treated are modest. The treatment may be operated using a stack of cells with sequentially arranged anodes and cathodes, similar to reverse osmosis membrane modules. This modular design would enable easy maintenance of the cells as well as add treatment capacity over time. Furthermore, the economics of the process can be improved by recycling of the iodide electrodialed in the central compartment.

■ ASSOCIATED CONTENT

■ Supporting Information

Preparation and characterization of Pd nanoparticle -loaded graphite felt electrodes, analysis of diatrizoate and its reduction products, schemes of the electrolytic reactors, and detailed results of electrochemical reduction and oxidation experiments (e.g., profiles of diatrizoate and its reduction products, concentration of iodide reduction rate constants). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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