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Photo-assisted electrochemical treatment of municipal wastewater reverse osmosis concentrate

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HIGHLIGHTS

- Organics in RO concentrate were treated by a hybrid advanced oxidation process.
- Hybrid photolytic and electrochemical process showed synergistic DOC degradation.
- Electrochemical breaks down fluorescence and photolysis destroys core structure.
- Hybrid treatment consumes less energy than photolysis alone.

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ABSTRACT

The combination of a photochemical (UV) and electrochemical (EL) process led to enhanced degradation of dissolved organic matter in reverse osmosis (RO) concentrate produced from municipal wastewater. Treatment by UV and EL alone resulted in 25% and 35% removal of dissolved organic carbon (DOC) after 5 h, respectively. However, the hybrid process (UVEL) degraded more than 80% of DOC after the same treatment time. Fluorescence excitation–emission matrix spectroscopy and size exclusion chromatography suggest simultaneous and cooperative degradation of backbone aliphatic bonds by UV and aromatic ring cleavage by EL within the UVEL process. Overall, UVEL treatment led to efficient and non-selective degradation of dissolved organics over a wide range of molecular weights. Further, energy consumption and halogenated by-product formation (typically a limiting factor for the application of oxidation technology) were reduced in the UVEL process relative to the UV and EL processes, respectively.

1. Introduction

Municipal wastewater effluent treated by RO produces highly purified product water with many valuable uses (e.g., landscape irrigation, industrial process water, and aquifer recharge). However, the RO process also produces a highly concentrated version of the wastewater effluent, which may contain elevated concentrations of contaminants such as dissolved and suspended solids comprising BOD, COD, pathogens, and trace organics (e.g., pharmaceuticals and personal care products, endocrine disrupting compounds, and disinfection byproducts) not fully removed by the preceding biological treatment process [1–3]. The potential human and environmental health hazards associated with discharging wastewater RO concentrate containing elevated levels of pathogens, BOD/COD, and trace organics are not fully understood [4–10]. Therefore, it seems prudent to explore treatment technologies that can ensure effluent discharge standards are met, particularly when dilution (i.e., mixing the RO concentrate with large volumes of unconcentrated wastewater treatment plant effluent) is not possible. In particular, further disinfection and organic removal may be necessary.

Both photochemical and electrochemical processes can be used for disinfection and organic removal. Direct UV irradiation of wastewater gives rise to photo-activated chemical reactions that translate absorbed photonic energy into direct chemical bond breakage or the production of free radicals [11,12]. Utilization of photolysis for advanced oxidation is typically achieved by the addition of catalysts or UV reactive compounds (i.e., H_2O_2 and TiO_2) to provide a source of the requisite hydroxyl radicals [12]. Electrochemical oxidation targets mineralization of organic compounds by electron abstraction at the anode surface or by the

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production of highly reactive oxidants, such as $^{\cdot}OH$, produced *in situ* electrochemically [13]. *In situ* production of chemical reactants eliminates the need to purchase, transport, and store chemicals produced off-site, which can save money and energy as well as reduce carbon emissions and potential security vulnerabilities [14].

Electrochemical oxidation may be an attractive option for treating wastewater RO concentrate because it becomes more efficient and effective with increased conductivity and chloride concentration. High conductivity reduces the voltage needed to achieve a target current density, which results in considerable energy savings. However, electrochemical processes traditionally suffer from high investment costs, especially for advanced anode materials, such as boron-doped diamond. For this reason, improving electrochemical oxidation efficiency is paramount in order to reduce the required active electrode area and, thus, the initial capital cost for a given electrochemical treatment system [15–17]. Advanced anode materials have garnered considerable attention recently due to their ability to improve oxidation efficiency by enhancing the rate of direct oxidation at or near the electrode surface. Generally, advanced anodes are characterized as "nonactive" materials with high oxygen evolution overpotentials, such as antimony-doped tin oxide, lead dioxide, and boron-doped diamond, and favor the complete oxidation of organics to CO_2 due to their weak surface interactions with hydroxyl radicals [18]. Boron-doped diamond also shares the ability of some active materials, such as Ti/RuO_2, to promote indirect bulk oxidation by the production of intermediate oxidants, of which chlorine is commonly targeted [19,20]. Specifically, chloride ions become oxidized at the anode; thus, introducing an entire family of potential secondary oxidants and disinfectants. Indirect organic oxidation may occur via reaction with chlorine radicals ($^{\cdot}Cl$) adsorbed on the anode surface or by reactive chlorine species such as Cl_2, HOCl, or OCl^- in the bulk solution [13]. However, the formation of halogenated by-products is an obvious concern when treating waters containing both halide ions and dissolved organic matter.

Significant research has been undertaken to determine the effectiveness of hybrid photo-assisted electrochemical oxidation processes with particular emphasis on the UV excitation of photoanodes (e.g., thin-film TiO_2, DSA®) [21–25]. However, due to its minimal anodic photoactivity, we have not been able to find previous research studying the use of boron-doped diamond (a highly promising material with superior electrochemical properties) electrodes in hybrid photo-assisted electrochemical oxidation processes [26]. Herein, we tested a hybrid photo-assisted electrochemical process (UVEL) with the electrochemical and photochemical reactors placed in series within a batch recirculation system. This unique reactor configuration can, therefore, take advantage of the electrochemical benefits of boron-doped diamond electrodes (wide potential window, low background current, high chemical stability, high resistance to deactivation [27–30]) without the need to invest energy and resources to enhance its photoactivity. The aim of this research is to study the practical limitations (extent of mineralization, energy consumption, by-product formation) of a photo-assisted electrochemical reactor, which integrates highly efficient boron-doped diamond electrodes to treat a target water of growing public and environmental concern.

2. Methodology

Biologically treated wastewater effluent was provided by Western Treatment Plant (Victoria, Australia), which used a sequential activated sludge-lagoon treatment (AS-lagoon) process. RO concentrate was prepared from the effluent using a laboratory scale plate-and-frame unit (Sepa CF, GE-Osmonics, Minnetonka, MN) and a commercial interfacial composite RO membrane (AG; GE-Osmonics, Minnetonka, MN) operated at a constant pressure and temperature of 17 bar and 20 °C and an average permeate flux of 46.8 LMH. The effluent was concentrated to a recovery of 65%. Major water quality parameters are given in Table 1.

Electrochemical oxidation (EL) experiments were performed in a flow-through, undivided, spacer-filled electrochemical cell. A DiaChem® (Electrocell, Amherst, NY) boron-doped diamond anode was used with a geometric active area of 10 cm^2. Electrochemical oxidation was performed at a constant current density of 20 mA/cm^2 with a flow rate of 0.033 m^3/h and Reynolds number of 360. Photolysis (UV) experiments were conducted using an annular reactor with a centrally mounted lamp. A low-pressure mercury-vapor lamp emitting at 254 nm with an intensity of 8500 $\mu W/cm^2$ was used as the UV-C irradiation source (G36T15NU; Australian Ultra Violet Services, Victoria, Australia). The average irradiated area was 464 cm^2 with a path length of 1.94 cm; other UV reactor conditions were reported elsewhere [11]. A Titan 1500 chiller (Aqua-Medic, Bissendorf, Germany) was used to maintain a constant solution temperature of 20 °C during all the experiments. The UVEL reactor subjected the wastewater RO concentrate (WWROC) to both electrochemical oxidation and UV photolysis in series, recirculation mode (Fig. 1). Specific power consumption was estimated from the power consumed over the operating time and normalized by the total volume processed.

Dissolved organic carbon (DOC) was determined by measuring the total organic carbon (TOC) content (Sievers 5310 C, GE, Boulder, Colorado, USA) of 0.45 μm filtered samples. The TOC analyzer was equipped with an auto-sampler and inorganic carbon was internally purged automatically (Sievers 900 ICR; GE, Boulder, Colorado, USA) prior to DOC analysis. The absorbance was measured using a Unicam UV–vis spectrophotometer with a quartz cell of 1 cm pathlength. The excitation–emission matrix (EEM) spectra of the samples were obtained with a fluorescence spectrometer (LS55, Perkin Elmer, Waltham, Massachusetts, USA). The size exclusion chromatography (SEC) analyses were carried out at the Water Research Centre of the University of New South Wales, Australia. The SEC system (LC-OCD Model 8, DOC-Labor Dr. Hüber, Germany) consisted of a SEC column (Toyopearl TSK HW-50S, diameter 2 cm, length 25 cm) to separate organic molecules by size (i.e., 100–200,000 Da). Trihalomethane concentrations were determined by the Australian Water Quality Centre in Adelaide, Australia using previously described methods [31].

3. Results

3.1. DOC removal and energy consumption

After 5 h of treatment of the WWROC, the electrochemical and photochemical processes resulted in approximately 25% and 35%

Table 1
Water quality of secondary wastewater RO concentrate.

Parameter	Unit	Value
Conductivity	mS/cm	3.8
pH	–	8.8
DOC	mg/L	22
A_{254}	/cm	0.42
Na^+	mg/L	600
Ca^{2+}	mg/L	47
Mg^{2+}	mg/L	53
Cl^-	mg/L	954
Br^-	mg/L	3.9
SO_4^{2-}	mg/L	207
TN, as N	mg N/L	32
TP, as P	mg P/L	8
Alkalinity, as $CaCO_3$	mg $CaCO_3$/L	242
Color (Pt–Co)	mg Pt–Co/L	55
Turbidity	NTU	0.5