



## Degradation of diuron via an electrochemical advanced oxidation process in a microscale-based reactor



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### HIGHLIGHTS

- Degradation of diuron by electrochemical AOP in a microreactor is reported.
- The degradation requires one order of magnitude lower of energy consumption.
- The rate constant is 1–2 orders of magnitude higher than conventional AOPs.
- Degradation pathway is reported and quantitatively analyzed.

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### ABSTRACT

The degradation of diuron, a toxic herbicide that is widely used in many countries, in an aqueous solution was performed in a microscale-based reactor using an electrochemical advanced oxidation process (EAOP). A graphite sheet and a stainless steel plate were used as an anode and a cathode, respectively. The effects of pH, conductivity of the solution, applied current, and height of the microchannel on the degradation of diuron were investigated. Approximately 90% degradation of diuron could be achieved within 100 s of residence time in the reactor that was applied with a direct current of 1 mA. The experimental results clearly suggests that the degradation occurs mainly by the interaction between diuron and the hydroxyl radical generated via dissociation of water at the anode, although direct reduction of diuron by supplied electrons was also observed. The degradation generates many reaction intermediates. However, a simple reaction model employing first-order kinetics could represent the degradation well. Most of the steps in the degradation pathway proceed at approximately the same rate. This rate is much higher than the degradation rate achieved by other conventional advanced oxidation processes.

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## 1. Introduction

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] is an herbicide that is widely used for weed elimination, both before and after the harvest. It is classified as a carcinogenic and genotoxic compound. Although diuron has low solubility in water, it is a bio-recalcitrant compound with great chemical stability. Hence, it can slowly dissolve in water and can penetrate through the soil, causing contamination of both underground and surface water. Due to its persistence (half-life over 370 days) in nature [1], diuron contamination is a very serious environmental problem in many countries [2–4]. The European Union Waste Framework Directive considers diuron as a priority chemical [5].

Many techniques have been proposed for the treatment of diuron-contaminated water, such as bio-degradation [6], adsorption [7], advanced oxidation processes (AOPs) including photocatalytic reaction [8,9], and Fenton's reaction [10]. Recently, electrochemical advanced oxidation processes (EAOPs) have also been developed for the treatment of many types of organic pollutants in water [11–13]. EAOP techniques rely on the generation of hydroxyl radicals (OH<sup>•</sup>) at the anode via dissociation of water, (according to Eq. (1) [14]), when sufficient potential is applied to the electrodes. Although boron-doped diamond is often used as an electrode for EAOPs [14,15], graphite has also been used in EAOPs to produce hydroxyl radicals under low supplied potential [16]. Under low current density, the graphite electrodes can be operated for several hours without significant corrosion [17]:



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The hydroxyl radicals then react with organic compounds, causing mineralization in a similar manner as in the case of other advanced oxidation processes. The efficiency of degradation of an organic compound by the EAOPs on a conventional scale is usually limited by two main issues, i.e., mass transfer of the compound to the surface of the anode and the requirement of supporting electrolyte to achieve a reasonable cell voltage if the solution does not have adequate conductivity [18,19]. Hence, in this work, the EAOP was applied in a microreactor, which offers many advantages over a conventional reactor, such as (i) an increase in the surface-to-volume ratio, (ii) small mass and heat transfer resistances, (iii) simple control over residence time, and (iv) enhanced control of the reaction conditions [20]. The small distance between the electrodes within the microreactor also drastically reduces the Ohmic resistance, which allows the EAOP to be operated without the supporting electrolyte [18,19]. Therefore, the degradation of organic pollutants such as chloroacetic acid [21], tetrachloroethane [22] by the EAOPs has been investigated in microfluidic apparatuses.

The aim of this research is to use a microscale-based reactor to investigate diuron degradation via the EAOP, both in terms of reaction kinetics and degradation mechanism. Additionally, mathematical models were developed to accommodate the kinetic study so that the behavior of diuron degradation can be better understood.

## 2. Experimental

### 2.1. Degradation of diuron in a microscale-based reactor

The microreactor used in this work was a microchannel 10 mm wide and 21 mm in length. The microchannel was formed using a Teflon sheet with a pre-cut opening placed between two conductive electrodes. The thickness (height) of the microchannel was in the range of 250–750  $\mu\text{m}$  and was determined by the thickness of the Teflon sheet. Unless mentioned otherwise, the channel thickness was fixed at 250  $\mu\text{m}$ . The anode was a graphite sheet, whereas the cathode was a stainless steel plate. Fig. 1 shows assembly details of the reactor. In the experiment, 10 ppm aqueous solution of standard diuron (99.5%; Sigma Aldrich) was supplied into the microchannel at a controlled flow rate in the range of 1.9–7.6 ml/h via a syringe pump. The flow rate range of 1.9–7.6 ml/h corresponds to an average velocity range of 0.21–

0.84 mm/s and a mean residence time in the range of 100–25 s. The pH and conductivity of the solution were adjusted using hydrochloric acid or sodium hydroxide and sodium chloride, respectively. The solution was continuously fed into the reactor for 1 h before starting the experiment to ensure adsorption equilibrium of diuron with the walls of the microreactor, particularly with the graphite electrode. The electrochemical reaction was initiated by supplying direct current (DC) across the gap between the electrodes (i.e., microchannel). After reaching a steady state, the solution leaving the reactor was collected and analyzed.

### 2.2. Analyses of samples

The concentration of diuron was analyzed using a reverse-phase high-performance liquid chromatography (HPLC, Shimadzu, Class 10VP) equipped with a C18 column (Luna 5 $\mu$  C18(2), Phenomenex) and a multiple-wavelength UV diode array detector. The mobile phase contained 70% (v/v) acetonitrile and 30% (v/v) deionized water. The analysis was performed using a total flow rate of 1.5 ml/min and a column temperature of 30  $^{\circ}\text{C}$ . Total organic carbon (TOC) was determined using a TOC analyzer (Shimadzu, TOC-VCPH). The concentration of hydrogen peroxide formed during the reaction was measured using a UV-visible spectrophotometer (Shimadzu, UV-1700) via a colorimetric method [23]. Structures of degradation intermediates were analyzed using liquid chromatography (Dionex ultimate) equipped with a tandem mass spectrometer (LC-MS/MS, Bruker Daltonics). This was operated using 60% (v/v) acetonitrile and 40% (v/v) deionized water as a mobile phase with total flow rate of 0.2 ml/min.

### 2.3. Development of a mathematical model

A mathematical model was developed to describe diuron degradation and the formation of reaction intermediates within the microreactor. The model was used as an analytical tool for kinetic parameter estimation. In the 'rigorous model', kinetic equations were combined with transport phenomena equations to simulate velocity profiles and concentration profiles of all of the compounds within the reactor. The Navier–Stokes equation (Eq. (2)), the continuity equation (Eq. (3)), and the convection–diffusion equation (Eq. (4)) were implemented throughout the reactor via *Laminar Flow model* and *Transport of Diluted Species model* in COMSOL v.4.2 numerical simulation package, while the kinetic equation was supplied as an external module via COMSOL-Matlab LiveLink v.4.2. Several reaction kinetics schemes were tested under the assumption that the reaction occurs homogeneously in the liquid phase. For each calculating iteration, the set of diuron concentrations at all positions within the reactor that satisfy all transport equations were sent to the external module to find the rate constant using the simplex search method via *fminsearch* function. The schematic diagram for the calculation in the external module is shown in Fig. 2. Only one value of the rate constant was obtained for each reaction after the calculation in this module. The reaction rates at all positions were then recalculated and sent back to COMSOL where the calculations on transport phenomena were repeated. The calculation continued until all calculated values converged and the steady-state concentration at the outlet of the reactor matched the experimental data. The model was developed under the assumption that the height of the channel is very small compared to the width and the length, such that the formulation could be performed in two dimensions. The calculation grids were generated automatically by COMSOL under the setting that the mesh size was in the range of 3.1–10.8  $\mu\text{m}$ . It was tested by a preliminary calculation that the mesh size smaller than this gave the same results. It should be noted that the rate constants obtained from the data at different residence time were insignificantly dif-

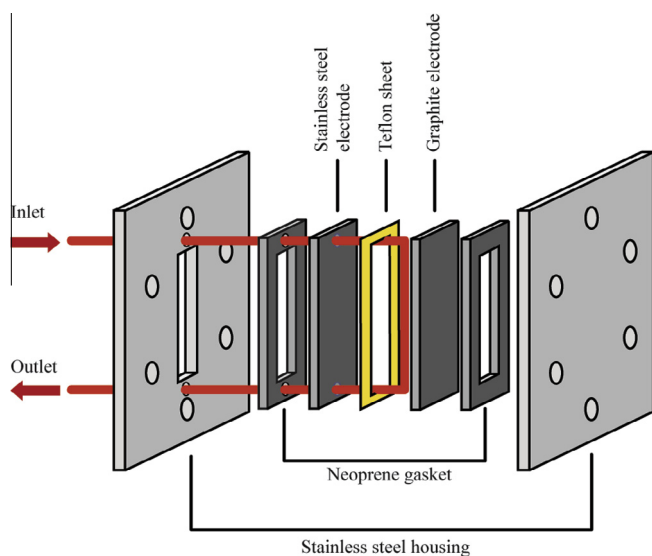


Fig. 1. Schematic diagram of microreactor assembly.

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