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Efficacy and mechanistic insights into endocrine disruptor degradation using atmospheric air plasma

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HIGHLIGHTS

- Atmospheric air plasma effectively degrades endocrine disruptors in a model dairy effluent.
- The plasma was created at the gas–liquid interface and is an abundant source of reactive oxygen and nitrogen species.
- The degradation of endocrine disruptors followed first order kinetics.
- A degradation mechanism for the three endocrine disruptors is proposed.

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ABSTRACT

Endocrine disruptors are a class of contaminants found in water and process effluents at low concentrations. They are of concern due to their high estrogenic potency. Their presence in the environment has led to the search for effective techniques for their removal in wastewater. For this purpose, an atmospheric air plasma reactor was employed for the study of the degradation of three endocrine disruptor chemicals (EDC) namely; bisphenol A (BPA), estrone (E1) and 17β-estradiol (E2) within a model dairy effluent. Identification of the plasma induced active species both in the gas and liquid phases were performed. Also studied was the influence of an inhibitor, namely tertiary butanol, on the degradation of the EDCs. The results demonstrate that air plasma could successfully degrade the tested EDCs, achieving efficacies of 93% ($k = 0.189\ min^{-1}$) for BPA, 83% ($k = 0.132\ min^{-1}$) for E1 and 86% ($k = 0.149\ min^{-1}$) for E2, with the process following first order kinetics. The removal efficacy was reduced in the presence of a radical scavenger confirming the key role of oxygen radicals such as ·OH in the degradation process. The intermediate and final products generated in the degradation process were identified using UHPLC-MS and LC-MS. Based on the intermediates identified a proposed degradation pathway is presented.

1. Introduction

Endocrine disrupting compounds (EDCs) are organic chemicals which are either excreted endogenously from humans and animals or are derived from uses in clinical practices [1]. An EDC is defined as an exogenous agent that alters the function(s) of the endocrine system, leading to adverse health effects in organisms [2]. Endocrine disruptors vary widely in their structure and have numerous uses in everyday items including; electrical appliances, clothing, furniture and cosmetics. They can also include pesticides (e.g., DDE, dicofol), plastics (bisphenol A, phthalates), food preservatives (UV-filters), hormonal agents and phytoestrogens. The presence of EDCs has been widely detected in surface waters, process effluents and sewage sludge treatment plants (STP). Hartmann et al. [3] has reported that the main source of animal-derived estrogens (60–70%) in the human diet is milk and dairy products. Estrogen content is mostly distributed in the fat phase because of its solubility. Food processing operations do not typically affect the hormone patterns. Animal fecal and urinary excretions may also result in the occurrence of estrogens in dairy effluents [4]. Recently, free and conjugated forms of estrogens including 17β-estradiol and estrone have been detected in milk and milk products [3]. Inappropriate disposal, leaching and poor removal by conventional wastewater treatment processes (WWTP) are identified areas of

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concern. Various studies have reported on the occurrence of these emerging contaminants, including those from dairy and meat process effluents [5,6].

When effluents containing chemicals are used for agricultural crops they can be transported to surface or ground waters. Colbron et al. [7] reported that EDCs are associated with reproductive and sexual abnormalities in animals and wildlife. The effects of EDCs include; fish feminization, changes in reproduction and behavior, decrease in number of spermatozoids, increase in breast cancer rates and an increase of certain anomalies in the human reproductive system [8–10]. With particular concern to human health, it is paramount that these chemicals are effectively treated before entering drinking water supplies, however for such hydrophobic contaminants, conventional treatment may be ineffective. Biological processes have been used for their treatment however, such chemicals have been found to be resistant and/or toxic to microbes and consequently they cannot be readily treated by biological processes [11,10]. Consequently, such treatment processes may not reach the required regulatory limits for these contaminants. It is reported that the regulatory limits for all EDCs is <0.0001 mg/L [12]. Chlorination of EDCs and its chlorinated products have been reported to elicit estrogenic activity [13]. Moreover, chlorination leads to the production of disinfection by-products (DBPs) that may be residually present in the treated effluent and pose a potential risk to consumers. Several authors had reported on the removal of these chemicals by advanced oxidation process (AOPs) such as ozonation [14], UV/H2O2 [15] and TiO2 photocatalysis [16]. However, in the case of the later, an additional step for the removal of the reagents used and incomplete mineralization might increase the operational costs. As a result, there is a need to find a sustainable, effective and economical process for degrading and removing EDCs from effluents.

Recently, dielectric barrier discharge non-thermal plasma (DBD-NTP) oxidation has emerged as a promising technology for eliminating organic micropollutants with high removal rates and environmental compatibility [17]. Plasma is a partially or wholly ionized state which consists of positively and negatively charged ions, free electrons, free radicals and intermediate highly reactive species, atoms, molecules and UV photons [18,19]. Plasma can be generated either in the gas or liquid phase simultaneously [20]. The electron impact dissociation of oxygen and water molecules leads to generation of numerous active species such as $O^{\cdot}$, $^{\cdot}OH$, $N^{\cdot}$, $HO_2^{\cdot}$, N_2^{*}, N^{*}, OH^{-}, O_2^{-}, O^{-}, O_2^{+}, N_2^{+}, N^{+}, O^{+}, and O_3, H_2O_2 following subsequent chemical reactions [21,22]. These species react with chemicals causing oxidation. Moreover, pollutant degradation could be initiated by UV light or shock waves. Recently, several authors have reported on the potential of DBD plasma technology for the removal of toxic chemicals from wastewaters such as pollutant dyes [23], pesticides [24,25], mycotoxins [26], volatile organic compounds [27,28] and antibiotics [29]. Recently Gao et al. [30], reported on the degradation of estrogenic endocrine disruptors by DBD plasma technology. A DBD plasma source combined with a Pt–TiO_2 photocatalyst was developed by Chen et al. [31] which demonstrated effective degradation of 17β-estradiol. The application of DBD plasma to the treatment of bisphenol A and tributyltin was studied by Hijosa-Valsero et al. [32], demonstrating that plasma can be an alternative AOP for the removal of persistent and toxic pollutants from water and wastewater. Abdelmalek and co-authors [33] used a gliding arc discharge plasma reactor to study the degradation of the endocrine disruptor bisphenol A with ferrous ions. They found that both hydroxyl radicals and hydrogen peroxide are responsible for the degradation effect and the addition of ferrous ions (II) allowed for greater mineralization via the production of additional hydroxyl radicals, according to the Fenton reaction.

The selection of an oxidation process may depend upon many factors such as the degree of degradation, the by-products formed in the process, the total cost, safety and reliability of the process [34]. Most studies to date on pollutant degradation using plasma have been carried out in the absence of competing organic matter. In this study, a novel high voltage and low-frequency DBD prototype reactor was employed which utilized atmospheric air as the inducer gas for the degradation of EDCs in a model dairy effluent. Furthermore, identification of degraded products and possible mechanisms of EDC degradation in the presence of dairy effluent is also studied.

2. Materials and methods

2.1. Materials

Analytical grade standards of Bisphenol A (BPA), Estrone (E1) and 17β-Estradiol (E2) of purity (>96%), HPLC grade methanol, acetonitrile, ethyl acetate, ammonium hydroxide solution (32%) puriss p.a. (NH4OH), acetic acid (AcOH), formic acid (HCOOH), sodium acetate (NaOAc), ammonium formate, tert-butyl alcohol(TBA) and LC-MS grade water were obtained from Sigma-Aldrich (Ireland).

2.2. Sample preparation

A model dairy effluent was prepared by dissolving 4 g of skim milk powder, 0.4 g of milk fat and 0.01% of NaOH per liter of distilled water [35]. The model effluent was used to overcome inherent variability in commercial effluent composition. Large particulate matter was removed by filtering the model effluent through a Whatman (UK) filter paper and a 0.45 μm membrane (Millipore). Each endocrine disruptor (BPA, E1 and E2) was dissolved in acetonitrile to obtain a standard stock solution with the concentration 100 mg/L. The prepared stock solution was diluted and spiked with the filtered model effluent to obtain a concentration of 2 mg/L.

2.3. Experimental procedure

2.3.1. Atmospheric air plasma treatment

The experimental set-up employed for this work is shown in Fig. 1. The experimental apparatus consisted of two aluminium plate electrodes of circular geometry (outer diameter = 158 mm) which were covered with dielectric materials of 2 mm thickness for ground electrode and 10 mm thick acrylic sheet for the high voltage electrode. For each experiment, 20 mL of dairy effluent spiked with EDC's (at an initial concentration of 2 mg/L) was added to petri dish and placed within a polypropylene (PP) container of dimensions 310 mm × 230 mm × 22 mm which acts as a closed reactor and as an additional dielectric barrier. This container was further sealed inside a high barrier Cryovac BB3050 film in order to prevent loss of reactive species generated during plasma treatment. The voltage was delivered through a step-up transformer (Phenix Technologies, Inc., USA) whose primary winding received an input at 230 V, 50 Hz and delivered a high voltage output in the range 0–120 kV_{RMS}. Plasma treatment was performed at varying voltage (60–80 kV) and treatment durations (0–15 min). Treatment of samples was carried out in duplicate at ambient temperature (16–18 °C). After processing, containers were stored at room temperature of 16–18 °C for 24 h to ensure that the generated and contained reactive species reacted with the samples. Ozone concentrations were measured using short-term ozone detection tubes obtained from Gastec (Product No. 18M, Gastec, Japan). These tubes contain a reagent which changes color after coming into contact with the specified gas and are calibrated for