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Humic acid and trihalomethane breakdown with potential by-product formations for atmospheric air plasma water treatment

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ABSTRACT

In this study an atmospheric air plasma reactor was studied for the degradation of HA and THMs in water. Plasma treatment showed significant breakdown efficacies for HA and THMs. At an applied voltage of 80 kV about 93% of HA and >70% of THMs were degraded after 15 min and 30 min treatment time respectively, with the degradation following a first order kinetic model. Plasma induced reactive species including nitrates and H_2O_2 were quantified in the treated water. The results of FTIR analysis revealed that the molecular structure of HA was altered by the plasma treatment, with a decrease in aromaticity observed.
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Introduction

Over the past century chlorine has been widely used as an oxidant in water and wastewater treatment. Chlorine's efficacy is demonstrated for microbial inactivation of a wide variety of pathogens along with oxidation of various chemical contaminants. However, the potential formation of disinfection by-products (DBPs), such as trihalomethane, is a concern [1]. DBPs, including trihalomethanes, can be formed as a consequence of the reaction of chlorine with natural organic matter (NOM) present in both surface and ground water [2]. NOM comprises of two fractions; humic substances (HS), which are composed of humic acids, fulvic acids, and non-humic substances (non-HS), which include carbohydrates, lipids, and amino acids [3]. Furthermore, humic acids constitute a major fraction of NOM, of which the soluble portion (aromatic compounds) of humic substances may react with chlorine to form trihalomethanes [4]. It has been reported that these THMs are carcinogens [5]. Epidemiologic studies in humans suggest a weak association with bladder, rectal and colon cancer [6,7] along with reproductive and developmental effects [8,9].

Due to these health concerns, many jurisdictions specify maximum allowable concentrations. The United States Environmental Protection Agency [10] specifies maximum levels for trihalomethanes (THMs) and haloacetic acids (HAAs) of 80 and 60 μg/L, respectively [11]. European Union regulations limit THMs to 100 μg/L. However, many national reports find frequent occurrence of THM exceedance [12]. It is important to limit THMs and THMs causing substances (humic acids) in water.

Several approaches such as nanofiltration, ultrafiltration, reverse osmosis coagulation [13], activated carbon adsorption [14], Fenton treatment [15], nano-TiO_2 photocatalysis [16], membrane filtration [17], biological treatment [18], and ozonation [19] have been employed to remove humic substances and THM's. Biological processes, including the use of bio-filters may lead to the accumulation of suspended solids and release of bacteria [20]. Separation technologies such as biofilms and membrane filtration may be limited due to fouling [21]. Ozone's efficacy for humic substance breakdown in water has been demonstrated, however the process may result in the formation of brominated by-products [22]. In addition, the use of such advanced oxidation processes (AOP) which are capable of oxidizing some of the NOM present in raw water sources require an additional step for mineralization increasing the operational cost. Therefore, there is a need to develop novel approaches to remove humic substances and THMs in energy efficient manner.

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Recently, atmospheric plasma technology has emerged as an advanced oxidation process for waste water treatments, potentially offering effective removal rates and environmental compatibility [23]. The use of atmospheric air as the inducer gas facilitates a potentially environmentally friendly and economically feasible approach. Atmospheric air plasma has been reported to be efficient in the breakdown of dyes [24], pesticides [25,26], aflatoxins [27] and for inactivation of pathogenic bacteria [28]. It is known that dielectric barrier discharge (DBD) plasma initiates several physical processes (UV light, shock waves) and chemical processes ($O^{\bullet}$, O_3, H_2O_2) [29], processes which may directly or indirectly act on humic substances. However, limited studies investigate the potential of atmospheric plasma for the breakdown of THMs [30] and HA [31,32]. It is also important to understand the potential for the formation of DBPs after plasma treatment of humic substances to demonstrate the technology's suitability for water treatment.

The objective of this work is to study the efficacy of atmospheric air plasma for the degradation of HA and THMs. In addition, the potential for DBP formation post plasma treatment is also studied.

Materials and methods

Materials

Humic acid (HA) and a trihalomethanes (THM) mix containing; chloroform ($CHCL_3$), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (BF) were all analytical grade and purchased from Sigma–Aldrich, Ireland. The THM mix was dissolved in methanol to obtain a standard stock solution with a concentration of 100 mg/L. The prepared stock solution was diluted to obtain a minimum concentration of 20 mg/L. Samples of 100 mg/L and 200 mg/L of HA solution were prepared in deionized water and filtered through 0.45 μm Millipore membranes.

Atmospheric air plasma treatment

A prototype high voltage atmospheric air plasma reactor, based on a dielectric barrier discharge (DBD) design was used in this study and described previously by Sarangapani et al. [26]. Briefly, plasma is generated between two circular aluminium plate electrodes (outer diameter = 158 mm) using two thick acrylic dielectric layers (Fig. 1). The applied voltage to the electrode was provided by a step-up transformer (Phenix Technologies, Inc., MD, USA) which has the input of 230 V, 50 Hz from the mains supply. Experiments for THM and HA were conducted separately. For each experiment 20 mL of THM and HA solution was added to petri dishes and subjected to different doses of direct plasma treatment. The atmospheric air conditions at the time of treatment was 40 ± 1% relative humidity (RH) and 16 ± 2 °C, as measured using a humidity-temperature probe connected to a data logger (Testo 176T2, Testo Ltd., UK). Plasma treatment was performed at variable discharge voltage levels (60–80 kV) and treatment durations (0–30 min). After processing, the sealed reactors containing the sample were stored at room temperature of 16–18 °C for 24 h to facilitate diffusion of the reactive species and reaction with the spiked compounds. No attempt was made to optimise the diffusion process, as the objective to this work was to study the effects of plasma treatment under controlled conditions. Electrical characterisation of the discharge was performed using an Agilent InfiniVision 2000 X-Series Oscilloscope (Agilent Technologies Inc., USA). The voltage across the electrode was recorded using a high voltage North Star PVM-6 probe together with a 10:1 voltage divider. The current waveform was measured using a current transformer probe (Bergoz CT-E1.0S).

Analysis

THMs analysis was carried out using GC–MS, (Varian 3800 GC, JVA Analytical Ltd., Ireland) with a 2200 Varian ion trap MS. SPME extractions for all plasma treated samples were performed using carboxen–polydimethylsiloxane (CAR–PDMS) fibres. The fibres were conditioned at 300 °C for 1 h before use, and blank desorption's were carried out periodically. Each sample (20 mL) was transferred into a vial (40 mL). The incubation and extraction temperature was 35 °C, and the samples were equilibrated for 10 min before extraction. The magnetic stirring speed was 1000 rpm. The fibre, attached to a syringe, was placed in the sample headspace for 15 min, drawn back into the needle, and transferred without delay (<5 s) into the GC injection port, where it was desorbed for 3 min at 280 °C. All analyses were performed in triplicate. The oven temperature program was 40 °C for 4 min, increased at 5 °C min^{-1} to 80 °C, then increased at 20 °C min^{-1} to 180 °C, with a split less injection mode employed. The analytical column was a Zebron ZB-5MS column and the carrier gas was helium, at 1 mL min^{-1}. The mass detector was operated in the electron impact (EI) mode at 70 eV and electron multiplier voltage

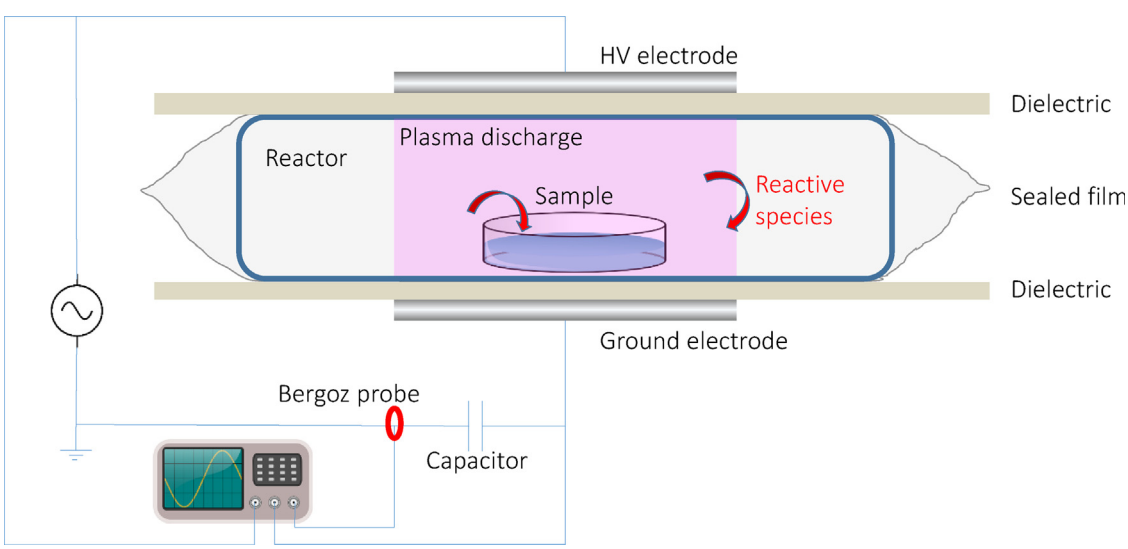

Fig. 1. Schematic of the experimental setup.

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