

Performance evaluation of three atmospheric plasma reactors for the treatment of aged/stabilized landfill leachate containing PFAS

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ABSTRACT: This study investigates the efficiency of three different types of plasma systems including multipin corona discharge (MCD), submerged dielectric barrier discharge (SDBD), and multipin self-pulsing discharge plasma (MSPD) with bubbling, employing air as the feed gas, for treating aged landfill leachate samples. The focus lies on the removal of contaminants, including refractory organics, ammonia, and per- and polyfluoroalkyl substances (PFAS). Within 30 minutes, all discharges reduced TOC levels to a minimum of 35% of initial concentrations. NH₄⁺-N removal ranged from 34% to 42%, with MCD attaining the highest removal efficiency at 42%. Remarkably, MSPD outperformed other configurations, achieving impressive removal percentages, including 99% within 30 minutes. This study underscores the potential of plasma-based technologies, with MSPD showing promising capabilities in degrading persistent PFAS contaminants in landfill leachate.

Keywords: Landfill leachate, Plasma treatment, corona discharge, advanced oxidation process, PFAS, PFOS, electrical discharges

1. INTRODUCTION

In the face of global progresses in waste valorization and recycling, landfill disposal still accounts for nearly 70% of solid waste management (Sabour, Alam, & Hatami, 2020). The consequence of this practice is the generation of landfill leachate (LFL), laden with diverse contaminants including refractory organics, ammonia, heavy metals, and, notably, per- and polyfluoroalkyl substances (PFAS) (Qi et al., 2018; Wang, Reguyal, & Zhuang, 2021). LFL poses serious threats to both the environment and human health if not managed effectively (Ramakrishnan et al., 2015; Wang et al., 2021).

Conventional treatment methods often struggle with the removal of recalcitrant PFAS due to their robust C-F bonds (Lenka et al., 2021; Wanninayake., 2021). Existing methods like biological treatment, adsorption, and membrane separation have limitations, including the generation of secondary pollutants (Appleman, Dickenson, Bellona, & Higgins, 2013; Appleman et al., 2014; Franke, McCleaf, Lindegren, & Ahrens, 2019; Kah, Oliver, & Kookana, 2021; Soriano, Gorri, Biegler, & Urtiaga, 2019).

While PFAS contamination in LFL is increasingly reported (Feng, Song, & Mo, 2021; Propp et al., 2021), data on efficient plasma treatment for their removal is notably scarce and limited to few studies (Singh, Brown, Mededovic Thagard, & Holsen, 2021). This study, therefore, aims to fill this knowledge gap by evaluating plasma-based LFL treatment, shedding light on the potential of this technology for managing recalcitrant contaminants in landfill leachate.

This study delves into the efficacy of plasma-based technologies for LFL treatment, focusing on PFAS removal. Three plasma discharge configurations, multipin corona discharge (MCD), submerged dielectric barrier discharge (SDBD) and multipin self-pulsing discharge plasma (MSPD), were examined, utilizing air as the plasma feed gas. The study assessed organics, ammonia, and PFAS removal from aged landfill leachate samples.

2. Methods

2.1. Plasma Reactors

Three distinct reactors with varying geometries and plasma discharges were employed to treat 50 mL raw leachate samples for 15 and 30-minute batch experiments, each utilizing the same input power (6 W) and air flow rate (250 mL/min) for direct comparison. These conditions were set to ensure uniform plasma generation.

2.1.1. **Multipin Self-Pulsing Discharge (MSPD) Reactor:** Featuring a 128 mm high Pyrex cylindrical container with a 43 mm internal diameter that incorporated a multipin high-voltage electrode (HV), with 32 evenly spaced stainless steel pointed edge pins, positioned 4 mm above the leachate surface. A grounded electrode (42 mm in diameter stainless-steel wire ring) was situated 10 mm below the leachate surface. Air was introduced through a ceramic diffuser covering the reactor's base, facilitating leachate mixing and maximizing plasma-liquid contact (Fig. 1a).

2.1.2. **Multipin Corona Discharge (MCD) Reactor:** This 105x85x80 mm Plexiglas container had ports for gas inflow, outflow, and HV electrode insertion. The HV electrode, a rectangular stainless steel plate with 82 pointed edge pins, generated a corona discharge localized near the pins' sharp edges. Leachate was grounded through a 1 mm thick stainless steel electrode, and continuous mixing was achieved via a magnetic stirrer (Fig. 1b).

2.1.3. **Submerged Dielectric Barrier Discharge (SDBD) Reactor:** Comprising a 280 mm long Pyrex tube with a 7 mm external diameter and a 5 mm internal diameter, the SDBD reactor utilized a stainless-steel wire HV electrode (1 mm diameter) concentrically positioned within the Pyrex tube. The leachate served as a grounded electrode, with a cylindrical porous diffuser (10 mm in length) fixed at the tube's end. Air, introduced from the top, passed through a 5 cm long plasma generation region and introduced reactive species into the leachate. Notably, the SDBD configuration efficiently transferred reactive species into the solution, independent of solution conductivity (Fig. 1c).

These reactors provided distinct plasma discharge mechanisms for treating landfill leachate samples, each with its advantages and applications.

2.2. Plasma Generation and Control:

For plasma ignition in the MCD and MSPD reactors, a Spellman PTV30*350 high voltage power supply (30 kV, 12 mA) in negative polarity was utilized and safeguarded by a 2.5 M Ω resistor (Altuntas et al., 2021). Plasma was generated by charging a high voltage capacitor (2.1 nF) connected in parallel to both reactors. Voltage was measured using a high voltage probe (Tektronix P6015A) connected to a Tektronix TDS5032B oscilloscope (350 MHz, 5 GS/s), while current was determined by measuring the voltage drop across a non-inductive resistor between the ground electrode and the grounding point.

In the MCD reactor, electrical breakdown was prevented by limiting the current through the high voltage power supply, while in the MSPD reactor, breakdown occurred continuously as bright plasma channels (streamers and leaders) with high electron density connecting to the leachate surface. A constant input power of 6 W was maintained in the MSPD reactor by regulating the

capacitor charging current from the power supply within the frequency range of 60-100 Hz. Detailed voltage and current waveforms, as well as energy and power calculations, are available elsewhere (Altuntas et al., 2021).

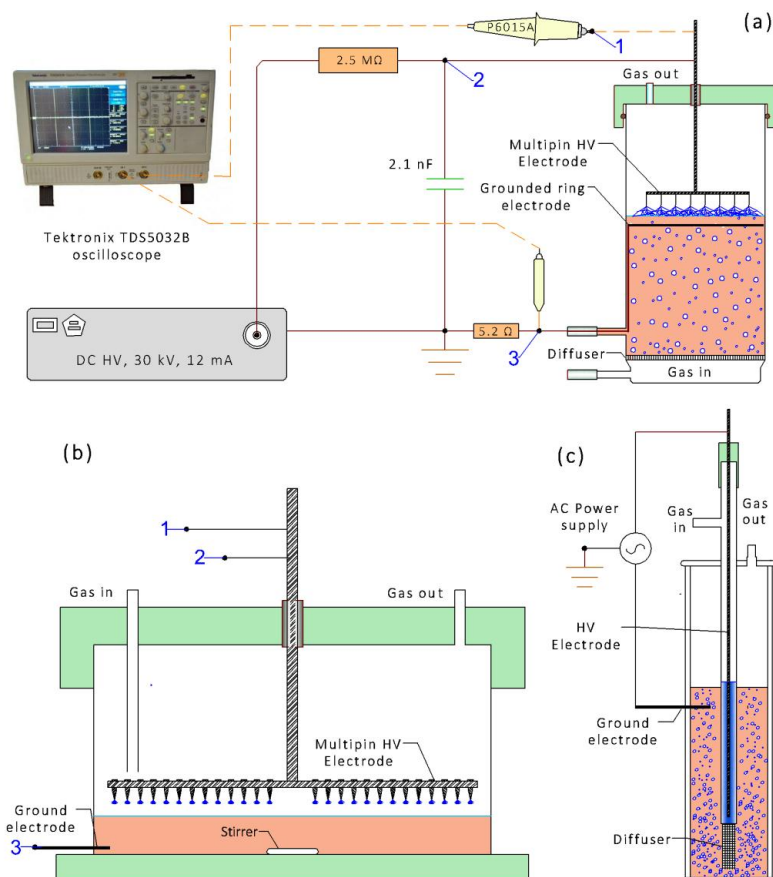


Figure 1. Schematic representation of the experimental setups (a) MSPD reactor, (b) MCD reactor and (c) SDBD reactor. 1, 2 and 3 represents the connection points for the MSPD and MCD reactor in the electrical schematic using the HV DC power supply

2.3. Analysis:

The characterization of leachate was performed by measuring pH (IRSA-CNR 29/2003 vol. 1 n. 2060), conductivity (IRSA-CNR 29/2003 vol. 1 n. 2030), total suspended solids (TSS) and volatile suspended solids (VSS) (APHA, AWWA, 2012), total organic carbon (TOC) (IRSA-CNR 29/2003 vol. 1 n. 5040), biological oxygen demand (BOD₅) (IRSA-CNR 29/2003 vol. 1 n. 5120 B2), Total Kjeldahl Nitrogen (TKN) (IRSA-CNR 29/2003 vol. 1 n. 5030, ammonia-nitrogen (NH₄⁺-N) (IRSA-CNR 29/2003 vol. 1 n. 4030 C), nitric-nitrogen (NO₂⁻-N) (IRSA-CNR 29/2003 vol. 1 n. 4040 A1) and nitrate-nitrogen (NO₃⁻-N) (IRSA-CNR 29/2003 vol. 1 n. 4050). The conductivity and pH were measured by Metrohm conductometer and Crison pH-meter GLP 22. TOC and TKN analysis were carried out using TOC-V CSN Shimadzu Italia S.R.L. and VELP scientifica UDK 129 Distillation Unit, respectively. PFAS were analyzed using an HPLC system coupled with a mass spectrometer detector.

3. Results and discussion

3.1. Organics and nitrogen removal

The performance of three plasma discharge systems in terms of organic matter and ammonia

removal, along with the production of NO_2^- -N, NO_3^- -N, and BOD_5 , is illustrated in Figure 3 for 15 and 30 minutes of plasma treatment. The results showed a rather moderate TOC removal for all three discharges to at least 35% of their initial concentration within 30 minutes. Notably, there was no significant difference in TOC values between 15 and 30 minutes of plasma treatment for the MCD and SPD reactors. In contrast, the SDBD reactor exhibited an increase in TOC removal from 32% to 40% with extended treatment time. This minor enhancement in performance of the SDBD reactor can be attributed to its design, which allows for more efficient diffusion of reactive species compared to the other two discharges. This design feature enables the breakdown and degradation of organic compounds, including chromogenic substances responsible for colorization in the leachate, resulting in visibly clearer samples after just 15 minutes of plasma treatment, with near-transparency achieved after 30 minutes. Additionally, BOD_5 values increased slightly post-plasma treatment, indicating the conversion of complex organic molecules into more readily biodegradable forms and the potential for direct mineralization of oxidized organic matter to CO_2 due to plasma application. Previous studies focusing on the removal of recalcitrant organics from LFL using plasma jet and pulsed discharge plasma also could not achieve high organics removal in terms of COD values even for extended treatment times (Theepharaksapan & Matra, 2018; Zhang, Liu, Yang, Cao, & Qian, 2017) and observed a COD removal of less than 35% after 60 min of plasma application.

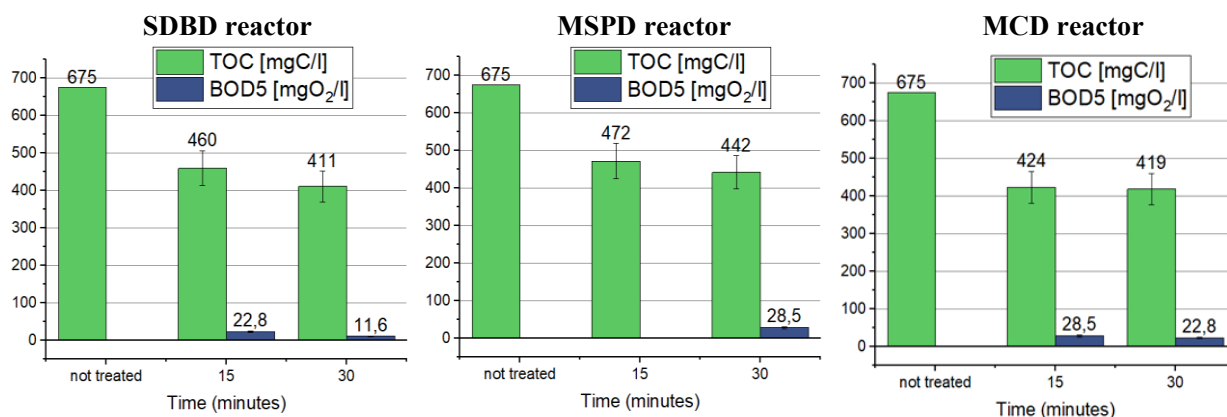


Figure 2. Profile of organics (in terms of TOC and BOD_5 values) for SDBD, MSPD and MCD reactors after 15 and 30 min of plasma application at 6 W

All the reactors have shown a rather moderate NH_4^+ -N removal ranging from 34% to 42% for 15 and 30 min of plasma application (Fig. 3). The highest NH_4^+ -N removal efficiency of 42% was observed for the MCD reactor and, similarly, with SDBD and SPD reactors maximum NH_4^+ -N removal was 36.9% and 38.5%, respectively, in 30 min. The difference between 15 minutes and the 30 minutes treatment was almost in every case relatively small and the NH_4^+ -N removal rate seems to decrease after the first 15 min of treatment. Despite the absence of NO_2^- -N, NO_3^- -N in LFL sample, all plasma reactors exhibited a slight increase in these nitrogen species after treatment, commonly associated with atmospheric nitrogen oxidation in plasma generated in ambient air. However, it remains uncertain whether these nitrogen species originated solely from NH_4^+ -N in the LFL or from nitrogen in the plasma gas. The SDBD reactor recorded the lowest concentrations, while the MCD reactor displayed the highest NO_3^- -N (17.9 mg/L), and the MSPD reactor had the highest NO_2^- -N (32.8 mg/L) after 30 minutes of treatment,

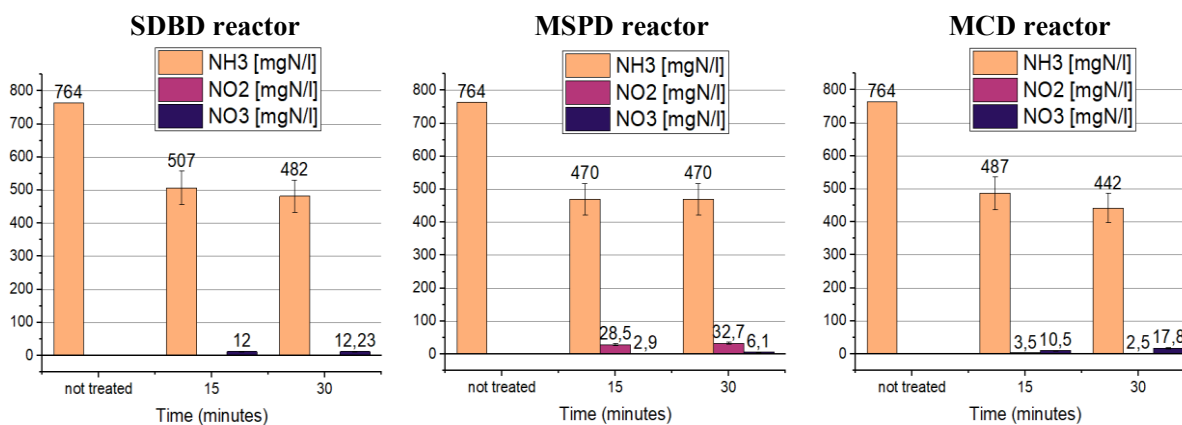


Figure 3. Profile of nitrogen species ($\text{NH}_3^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$) for SDBD, MSPD and MCD reactors after 15 and 30 min of plasma application at 6 W

3.2. PFAS removal performance

In Fig. 4 the performance of the three reactors was evaluated considering and comparing the removal of: PFOS - perfluorooctan sulfonate, PFHpS - perfluoroheptan sulfonate, PFHxS - perfluorohexan sulfonate and PFPS - perfluoropentan sulfonate. As evidenced by the results, MSPD is significantly more effective than the other reactors in PFASs degradation. After 30 minutes of treatment with MSPD configuration 93% of PFOS was degraded, PFHpS was completely degraded, PFHxS was degraded by 99.8% and PFPS by the 95.2%. These removal percentages are very impressive if compared with those obtained with SDBD reactor (34.5% of PFOS, 33.4% of PFHpS, 39.6% of PFHxS and 0.6% of PFPS) and MCD reactor (56.7% of PFOS, 18.9% of PFHpS, 3.8% of PFHxS and no removal of PFPS)

MSPD configuration is able to generate and spread the plasma on the surface of the solution, where PFAS are concentrated thanks to their surface-active properties. Moreover, the argon bubbled from the bottom in the configuration used in this study allows to bring more PFAS molecules to the liquid surface in contact with plasma, exploiting the surfactant properties of long chain PFAS to improve their degradation

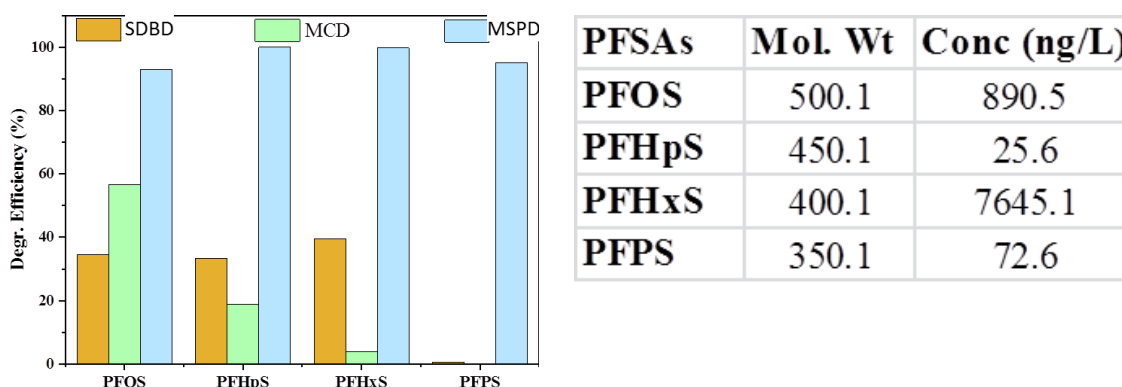


Figure 4. Degradation efficiencies (%) of PFASs after 30 minutes of treatment with SDBD, MCD and MSPD reactors along with their concentrations listed in the table on the right.

4. CONCLUSIONS

All the reactors showed a moderate organics (i.e. in terms of TOC) and ammonia removal performance. Due to surface active properties of PFAS molecules the configuration of MSPD

reactor allowed it to achieve remarkable PFAS removal even in the presence of high relative concentration of organic constituents in the leachate sample.

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