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Assessing the Destruction and Gaseous Carry-over of PFAS during Hydrothermal Carbonization (HTC) of Sewage Sludge

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INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are chemically and thermally stable, widely used in various industries, and have been found in environments like soil and water. These substances, particularly PFOA and PFOS, are harmful to human and environmental health. Hydrothermal carbonization treatment (HTC) is an effective method for eliminating PFAS, involving high temperatures and pressures to break down these molecules into safer compounds such as carbon dioxide and water. The HTC process also transforms sludge into hydrochar, a carbon-rich material useful for energy or soil enhancement, producing gaseous, liquid, and solid outputs. A novel aspect of this study is the analysis of PFAS transfer to the gaseous phase. In this framework, a unique PFAS-free gas sampling set-up was developed for the condensation of the liquid products, the cleaning of the gaseous products and the collection of PFAS from the gaseous phase on the adsorptive surface of specialized cartridges. The role of HTC pressure and pH were also co-assessed.

METHODS

HTC reactor experiments: Sludge from an Up Flow - Anaerobic Sludge Blanket Reactor- UASB reactor (Fig.1) in Antissa village (Lesvos, Greece) with Total Solids (TS) of 7% was spiked with eight PFAS and treated in a Parr 4570A HTC reactor. Five experiments were conducted with variations in pressure and pH (Table 1) within the HTC reactor (Fig.2). To determine the PFAS removal in liquid and solid products, samples were pretreated with solid-phase extraction (SPE) as described by Arvaniti et al. (2012) and analysed using LC-MS/MS.

Active gas sampling in a HTC reactor: Gas samples were collected via an active sampling method, using ABN SPE cartridges connected to the gas outlet, and were stored at -20 °C until analysis. For PFAS extraction, mass-labeled standards were added to each cartridge before being eluted with methanol into a polypropylene tube. The samples were then concentrated under nitrogen and transferred to a vial for analysis (UPLC-QTOF).

5 experiments of HTC @ 250 at °C		
Experiment #	Description	Short name
Experiment 1	Blank/ sludge without PFAs, HTC @ 250 at °C	Blank
Experiment 2	Sludge spiked with PFAS, HTC @ 250 at °C	HT1
Experiment 3	Sludge spiked with PFAS, HTC @ 250 at °C + High pressure	HT2
Experiment 4	Sludge spiked with PFAS, HTC @ 250 at °C + pH correction with KOH	HT3
Experiment 5	Sludge spiked with PFAS, HTC @ 250 at °C + pH correction with KOH + High pressure	HT4

Table 1. Experimental conditions - HTC

Fig. 1. Image of the UASB reactor

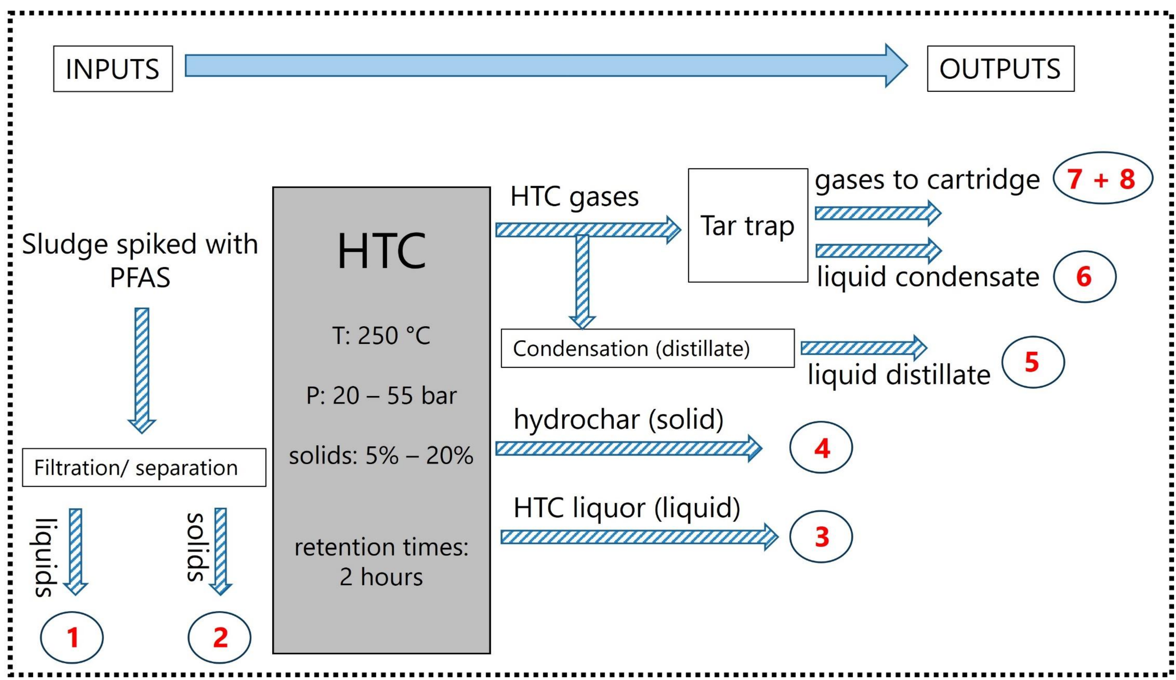

Fig. 2. Experimental scheme with sampling points

RESULTS AND DISCUSSION

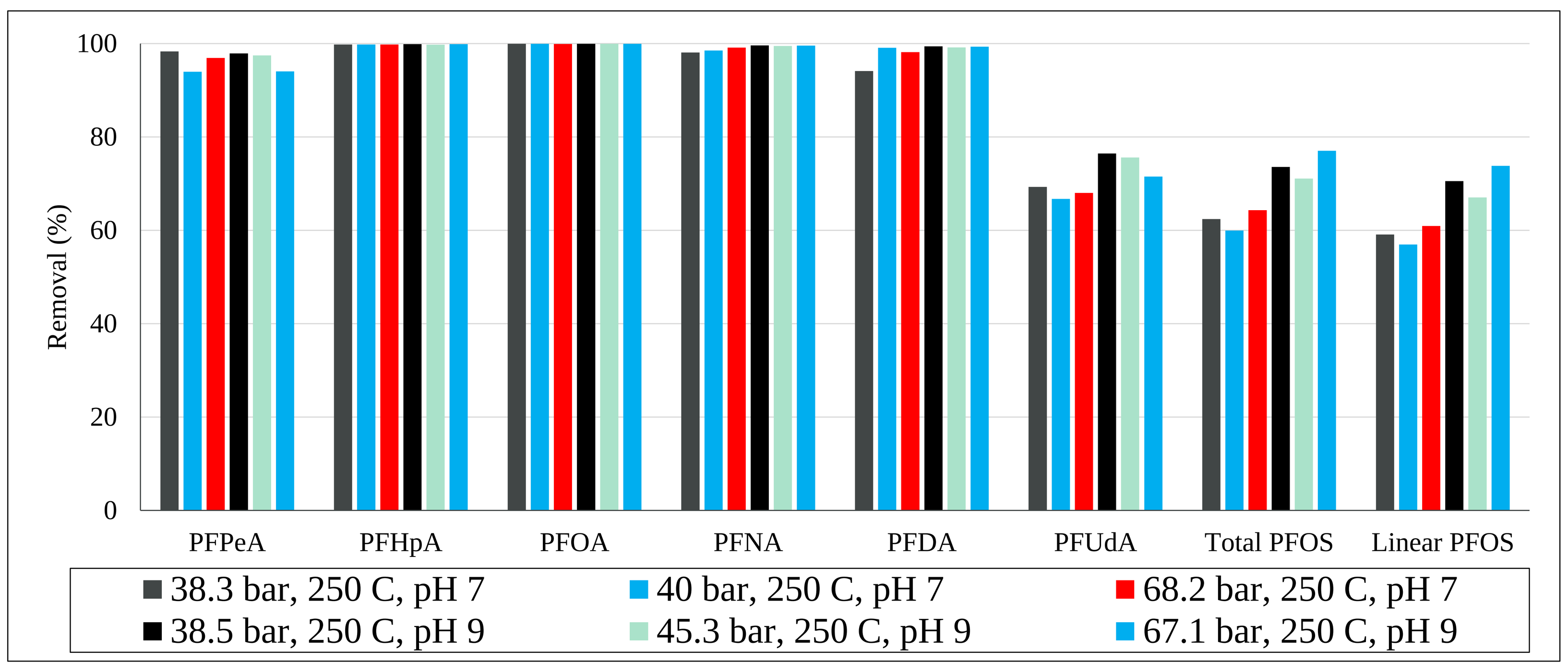

Fig. 2. PFAS concentration in liquid products of HTC

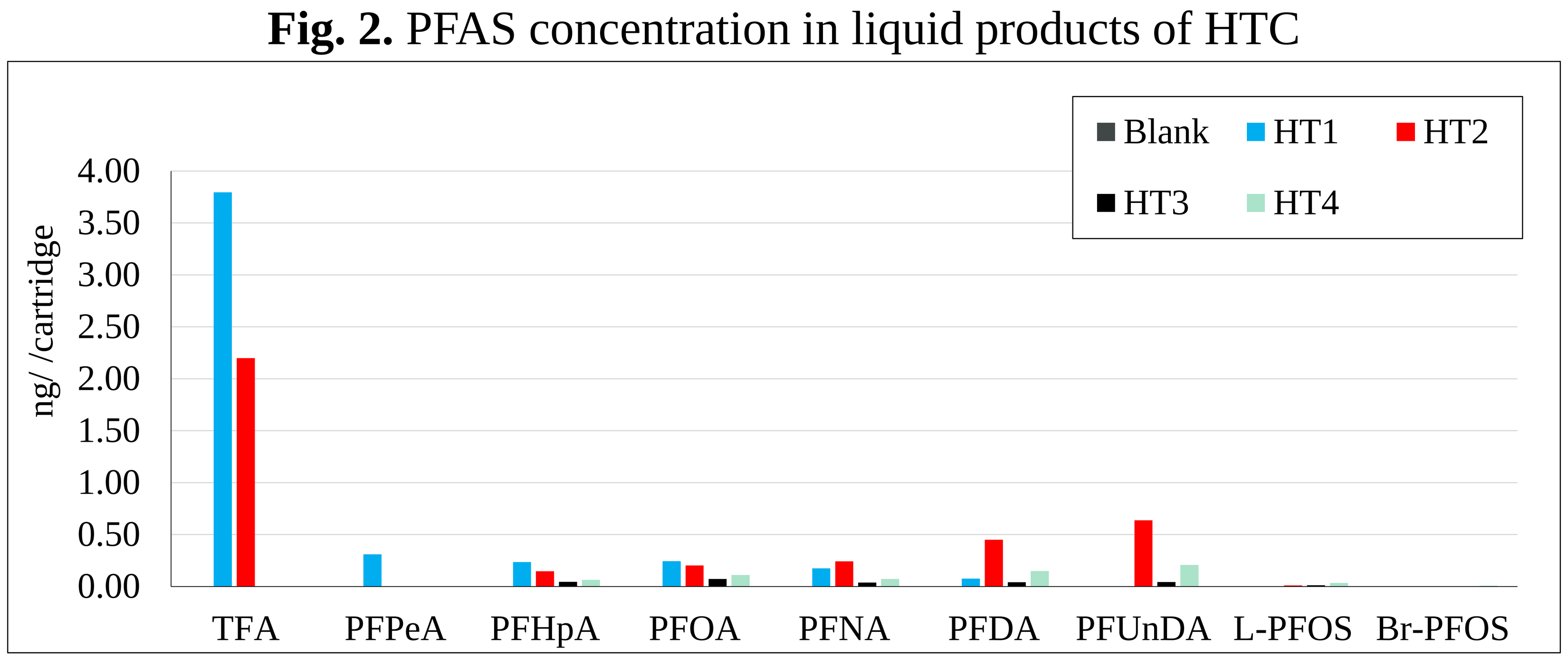

Fig. 3. PFAS concentration in gaseous products of HTC

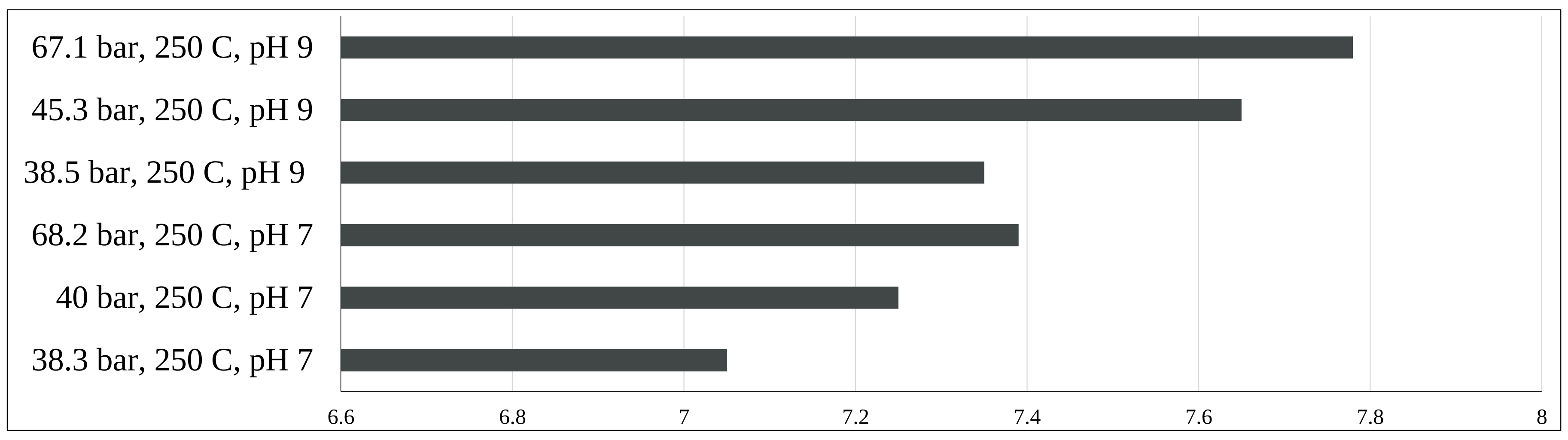

Fig. 4. pH values of liquid products of HTC

- PFAS in liquid products. The results suggest that the different pressures employed during HTC processing do not seem to have an effect on PFAS removal (Fig. 3). Five out of seven PFAS were removed at a percentage higher than 94% in all experiments, while PFUdA and PFOS were removed at percentages ranging between 55 and 75%.
- PFAS in gaseous products. Mass balance calculations indicated that less than 0.001% of the target PFAS transferred to the gas phase (Fig. 4). The tar trap condensate showed no detectable levels of PFAS.
- pH values after treatment. The pH levels observed were affected by the increasing pressures during the treatment (Fig. 5). Previous research highlights that the pH in the liquid phase is complexly determined by the interaction of acidic and basic functional groups.

CONCLUSIONS

- A novel PFAS-free gaseous sampling set-up has been introduced and applied in this study.
- In addition, PFAS were assessed in the liquid and gaseous HTC products from hydrothermal carbonization of anaerobic sludge.
- Alkaline pH value (with KOH) tended to influence positively the destruction of PFAS in all HTC products
- Secondarily, elevated pressures seem to influence positively the destruction of PFAS in HTC gaseous products

References:

Arvaniti, O.S., Ventouri, E.I., Stasinakis, A.S. and Thomaidis, N.S., 2012. Occurrence of different classes of perfluorinated compounds in Greek wastewater treatment plants and determination of their solid–water distribution coefficients. Journal of Hazardous Materials, 239-240, pp.24-31.

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