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PFAS removal from landfill leachate by ozone foam fractionation: System optimization and adsorption quantification

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ABSTRACT

Landfills are the primary endpoint for the disposal of PFAS-laden waste, which subsequently releases PFAS to the surrounding environments through landfill leachate. Ozone foam fractionation emerges as a promising technology for PFAS removal to address the issue. This study aims to (i) assess the effectiveness of the ozone foam fractionation system to remove PFAS from landfill leachate, and (ii) quantify equilibrium PFAS adsorption onto the gas-water interface of ozone bubbles, followed by a comparison with air foam fractionation. The results show that ozone foam fractionation is effective for PFAS removal from landfill leachate, with more than 90 % long-chain PFAS removed. The identified operating conditions provide valuable insights for industrial applications, guiding the optimization of ozone flow rates (1 L/min), dosing (43 mg/L) and minimizing foamate production (4 % wettability). The equilibrium modelling reveals that the surface excess of air bubbles exceeds that of ozone bubbles by 20–40 % at a corresponding PFAS concentration. However, the overall removal of PFAS from landfill leachate by ozone foam fractionation remains substantial. Notably, ozone foam fractionation generates foamate volumes 2 – 4 times less, resulting in significant cost savings for the final disposal of waste products and reduced site storage requirements.

1. Introduction

Per- and poly-fluoroalkyl substances (PFAS) constitute a diverse set of synthetic chemicals renowned for their superior in water and oil repelling and have high thermal stability. Owing to these unique characteristics, PFAS have been used for a wide range of surface-active applications in construction materials, paper and packaging products, textile, metal finishing, and plating; and aqueous film foaming foams (AFFFs) (Barzen-Hanson et al., 2017). Landfills represent the primary endpoint for disposal of PFAS-laden waste, where, several years after landfilling, PFAS have leached and dissipated to the surrounding environments via landfill leachate (Li et al., 2023). Numerous reports have highlighted the association between PFAS and health effects such as elevated cholesterol levels, increased cancer risks, diminished organ functions, and reproduction issues (Sunderland et al., 2019). It leads to a range of regulations imposed on landfill leachate to restrict PFAS discharge into the environment.

Foam fractionation stands out as a promising technology for removing PFAS from aqueous media (e.g. groundwater, wastewater, landfill leachate) (Smith et al., 2022). The fundamental concept of foam fractionation revolves around the hydrophobic sorption of PFAS molecules into the gas-water interface of bubbles. Hence, PFAS can be recovered by stripping the bubble foam on the top of the foam fractionation system. The advantages of foam fractionation lie in its substantial reduction of PFAS waste volume from hundreds to thousands of times (Ebersbach et al., 2016; Meng et al., 2018). On that basis, foam fractionation technology has been developed for pilot and full-scale implementations, with the removal efficiency of long-chain PFAS higher than 99 % (Burns et al., 2022; Smith et al., 2022).

Ozone is a strong oxidation agent that has been widely used for water treatment and to some extent, wastewater treatment. Ozone can be incorporated in ozonated bubbles for an effective water treatment, for

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example, Hu and Xia (2018) reported an efficient removal of organic contaminants, up to 99 %. Hence, ozone foam fractionation emerges as a promising technology for PFAS removal (Dai et al., 2019). However, a knowledge gap persists regarding performance of ozone foam fractionation system for PFAS removal, the mechanism of PFAS adsorption onto ozone bubbles; and how its effectiveness compares to the traditional foam fractionation system using air bubbles.

Despite extensive studies on foam fractionation, the knowledge of PFAS thermodynamic and thermophysical is not fully investigated (Damião et al., 2023). The sorption of PFAS in water and wastewater at the microscopic level needs to be further elucidated. While equilibrium sorption of PFAS onto the gas-water interface of air bubbles has been studied well in literature (Costanza et al., 2019; Schaefer et al., 2019), limited attention has been given to ozone bubbles. Therefore, a insightful investigation into the mechanism of PFAS sorption onto the gas-water interface of the ozone bubble under equilibrium conditions is imperative.

This study aims to (i) evaluate the performance of the ozone foam fractionation system in removing PFAS from landfill leachate under varying operating conditions, and (ii) elucidate the mechanism of PFAS equilibrium sorption onto the gas-water interface of the ozone bubbles. A comparison of ozone foam fractionation and air foam fractionation is also conducted. The foam fractionation systems are operated using different inlet gas flow rates and ozone doses to assess removal efficiency of PFAS. The wettability (volume ratio of recovered foam and remaining leachate) and PFAS composition of foam influenced by the operating conditions are also assessed. Lastly, the equilibrium sorption models and quantification of PFAS sorption are developed based on the Langmuir and Frumkin isotherms.

2. Quantification of PFAS adsorption onto bubbles

The adsorption of PFAS molecules at the gas bubbles is critical to the effectiveness of PFAS removal from landfill leachate. To quantify the adsorption, the available theories were employed including the Gibbs adsorption theory and the Langmuir or Frumkin adsorption isotherms (Adamson and Gast, 1997). The Langmuir adsorption isotherm is described as follows:

$$CK = \frac{\Gamma}{\Gamma_m - \Gamma} \tag{1}$$

where *C* is PFAS concentration in the bulk (g/L), *K* is the adsorption constant (L/g), Γ is equilibrium surface excess of adsorbed PFAS species (µmol/m²), and Γ_m is the maximum surface excess (µmol/m²). Surface excess is the area-related concentration of a surfactant at the surface or interface. The Frumkin isotherm advances the Langmuir theory by considering the lateral intermolecular interaction at the adsorption layer as below (Fainerman et al., 2001):

$$CK = \frac{\Gamma}{\Gamma_m - \Gamma} \exp\left\{-A\frac{\Gamma}{\Gamma_m}\right\}$$
(2)

where *A* is a constant which accounts for the lateral intermolecular interaction. The adsorption of PFAS molecules at the gas-water interface reduces the water surface tension, γ (mN/m), which can be linked with the surface excess as follows (Fainerman et al., 2001):

$$\gamma = \gamma_0 + 2RT\Gamma_m \ln\left\{1 - \frac{\Gamma}{\Gamma_m}\right\} + RT\Gamma_m A\left\{\frac{\Gamma}{\Gamma_m}\right\}^2 \tag{3}$$

where γ_0 is the surface tension of water in the absence of PFAS molecules (mN/m), *R* is the gas constant, *T* is the absolute temperature (K).

The surface tension as a function of PFAS concentration can be measured in conjunction with the above-described adsorption theory to determine the molecular characteristics of PFAS molecules. The adsorption quantification can be performed using the regression analysis by the best fit of the measured surface tension with the predicted surface tension by Eq. (3). In the case of the Langmuir adsorption isotherm, expressing as Γ (a function of C) using Eq. (1) and inserting the result into Eq. (3) yields the following equation (Eq. (4)) for surface tension as a function of the bulk concentration. It is noted that the last term on the right-hand side of Eq. (3), which represents the lateral intermolecular interaction, was discarded in the case of the Langmuir adsorption isotherm.

$$\gamma = \gamma_0 - 2RT\Gamma_m \ln\{1 + CK\} \tag{4}$$

Eq. (4) is similar to the empirical equation of von Szyszkowski. Eq. (4) is first used to best fit the measured surface tension to determine the maximum surface excess and the adsorption constant. Then the Frumkin isotherm is used to check if the best fit can be improved by changing the model parameter *A*. In this case, Eq. (2) is nonlinear and can be solved by iteration, starting from the initial guess obtained by the Langmuir isotherm.

A Matlab code was written to perform these numerical computational tasks. Specifically, the regression analysis provides the most accurate numerical predictions for surface tension when compared to the experimental data. It is achieved by numerically minimizing the sum of squared differences between the model values and measured values for surface tension. The sum of residual squares was minimized by changing the model parameters: K, Γ_m , and A by applying the Levenberg–Marquardt method (Press et al., 1992).

3. Materials and methods

3.1. Chemical and leachate

The native and isotopically labelled standards of PFAS were purchased from Wellington Laboratories (Canada). More details of the studied PFAS are provided in Table S1. All the chemicals used were warranted analytical grade. Ammonium acetate (>97 %, C₂H₇NO₂) and acetic acid were purchased from ChemSupply (Gillman, SA, Australia). Methanol (99.8 %, LiChrosolv®) were purchased from Merck (Darmstadt, Germany).

The leachate was collected from a landfill in Queensland (Australia). To warrant the consistency of leachate used for the experiment, the leachate was collected in bulk volume. Concentrations of prevalent PFAS in the leachate such as perfluorobutanoic acid (PFBA) (C₃), perfluoropentanoic acid (PFPeA) (C₄), perfluorobutane sulfonate (PFBS) (C₄), perfluorohexanoic acid (PFHxA) (C₅), 5:3 fluorotelomer carboxylic acid (5:3 FTCA) (C₅), perfluoropentane sulfonic acid (PFPeS) (C₆), perfluorohexanesulfonic acid (PFHxA) (C₆), perfluorohexanesulfonic acid (PFHxS) (C₆), perfluorooctanoic acid (PFOA) (C₇), 6:2 fluorotelomer sulfonate (6:2 FTS) (C₆), perfluorooctane sulfonate (PFOS) (C₈) are 1.65 \pm 0.11 µg/L, 0.87 \pm 0.17 µg/L, 3.36 \pm 0.17 µg/L, 2.23 \pm 0.06 µg/L, 3.12 \pm 0.33 µg/L, 0.14 \pm 0.02 µg/L, 0.45 \pm 0.06 µg/L, 1.84 \pm 0.16 µg/L, 0.95 \pm 0.1 µg/L, 0.21 \pm 0.09 µg/L, respectively (*n* = 15). The total PFAS concentration in the original leachate is approximately 15 µg/L.

The leachate also contained dissolved salts, characterized by the total metal load including Na (883.3 \pm 12.7 mg/L), K (144.7 \pm 2.6 mg/L), Ca (6.2 \pm 0.2 mg/L), Mg (163.2 \pm 3.5 mg/L). pH of the leachate was 7.8 \pm 0.1 (n = 3).

3.2. Foam fractionation system setup

The foam fractionation system was set up in semi-continuous mode. The system apparatus consisted of a cylindrical reactor body connected with an acrylic column on the top, an overflow tray, a collector tank, and a sparger (Bibby Sterilin 120 mm Pyrex sintered disc with porosity number 3) mounted at the base of the column (Fig. S1). The leachate in the reactor was processed as a batch with respect to PFAS, while the air and ozone were sparged continuously to the system to generate bubbles. The foam was extracted by an overflow tray on top of the foam column. The foam was driven by gravity flow to a collector tank next to the foam column. The collected foam was left until all the bubbles collapsed (foamate), which contained highly concentrated PFAS.

3.3. Foam fractionation experiment

Each experiment was operated with a set of feeding gas flow rates (i. e., 0.5 L/min, 0.8 L/min, 1 L/min) for both air and ozone. All the experiments were operated in 5 min to ensure sufficient foaming by the leachate itself. The ozone used for the experiment was generated by an ozone generator (Triogen ® Lab2B model) using pure oxygen as feed. Three ozone doses (i.e., 43 mg/L, 57 mg/L, 65 mg/L) were created by adjusting the feed flow rate and ozonation output control. The details of the ozone dose (mg O_3/L) with the corresponding feed flow rate and output control are provided in Table S2.

The experimental leachate samples were collected at the following experimental time points: 0 min, 0.5 min, 1 min, 2 min, 3 min, 4 min, and 5 min. The foamate samples were only collected at the end of the experiments. The removal efficiency (%) of PFAS removal was calculated as follows:

Removal Efficiency (%) =
$$\frac{C_0 - C_e}{C_e} \times 100$$
 (5)

where C_0 and C_e represent the concentrations of PFAS in the feed solution before starting the experiment, and the processed liquid after the experiment at 5 min. If C_e at 5 min is less than limit of detection (LOD) then C_e = LOD/2 is used for the calculation of removal efficiency.

3.4. PFAS analysis and QA/QC

Total 20 PFAS compounds were studied comprising of 7 perfluoroalkyl carboxylic acids (PFCAs) (e.g., PFBA (C₃), PFPeA (C₄), PFHxA (C₅), PFHpA (C₆), PFOA (C₇), PFNA (C₈), PFDA (C₉)) and 5 perfluoroalkyl sulfonic acids (PFSAs) (e.g., PFBS (C₄), PFPeS (C₅), PFHxS (C₆), PFHpS (C₇), PFOS (C₈)) and 4 perfluoroalkyl acids (PFAAs) precursor (6:2 FTS (C₆), 8:2 FTS (C₈), 6:2 FTCA (C₆), 5:3 FTCA (C₅)), 3 perfluoroalkane sulfonamide (FOSA (C₈), FBSA (C₄), N-MeFOSAA (C₈)), and 1 cyclic PFAS (PFECHS (C₈)). For internal standards, 9 mass labelled PFAS including 13C₃-PFBS, 13C₂-PFHxA, 18O₂-PFHxS, 13C₃-PFHpA, 13C₂-6:2 FTS, 13C₄-PFOA, 13C₄-PFOS were used for quantification (Table S1). The QA/QC results are provided in Table S3.

3.5. Measurements of surface tension of PFAS solutions

The surface tensions of three popular PFAS (i.e., PFOA (C7), PFHxS (C₆), PFBS (C₄)) at a wide range of concentrations (i.e., $10^{-3} - 50$ g/L) were measured using PAT-1 M bubble profile analysis tensiometer from SINTERFACE, Germany. The concentrations of PFAS were chosen to cover from low bulk-water concentration to near-micelle and micelle levels of the three PFAS studied. To ensure the cleanliness, all devices were double-checked by comparing the standard sum frequency generation (SFG) spectroscopy spectra of DI water with the SFG spectra of DI water in the sample holder. The tensiometer was calibrated once per month using the reference liquid method (e.g., Milli-Q water) with a thermometer temperature gun. All measurements were conducted using the buoyant bubble method. The PFAS solution was saturated by air or ozone prior to the measurement. Air and ozone bubbles were created in the cell by connecting the inlet pipe with ambient air and ozone generator, respectively. The measurement of dynamic surface tension measurement responds by a quick decrease in the first 10-15 min, following by a slower reduction in the next 90 min without reaching equilibrium. The gradual decline suggests a slow restructuring of PFASs at the interface (Rojas et al., 2010). Therefore, in our study, we define the equilibrium point when the reduction rate of surface tension is less than 0.1 mN/s per min. The equilibrium surface tensions were retrieved

from the surface tension curve. The measurements were calibrated using the measured data with DI water and the National Institute of Standards and Technology (NIST) tabulated data for the surface tension of DI water as a function of ambient (room) temperature. The final surface tension was normalized to the surface tension of water at 22 °C. All tests were performed in triplicates to warrant the reproducibility of data.

4. Results and discussion

4.1. Effects of air flow rates on PFAS removal

The effects of air flow rates on PFAS removal are shown in Fig. 1. Foam fractionation using air demonstrated its appreciable effectiveness by removing more than 90 % of long-chain PFAS (i.e., PFOA (C_7) and PFOS (C_8)). The removal of short-chain PFAS (i.e., PFBS (C_4), PFHxA (C_5), 5:3 FTCA (C_5), PFHpA (C_6), PFHxS (C_6), 6:2 FTS (C_6)) ranged from 8 % to 95 %. The recoveries of below 10 % were observed for some short-chain PFAS, which have less than four perfluorinated carbons. Increasing the air flow rates improved the efficiency of PFAS removal. Pertaining to short-chain PFAS, by increasing the air flow rates from 0.5 L/min to 1 L/min, the removal of the short-chain PFAS (e.g., PFHxA (C_5), PFPeS (C_5)) was upwarded by 10 % – 30 %. The removal efficiency of PFOA (C7) was also increased by 20 %. It took 2 min to 6 min to remove long-chain PFAS to the level below LOD in the bulk liquid (0.03–0.05 µg/L) while a complete removal of short-chain PFAS is unlikely to be achieved within the studied timeframe (Table S4).

The removal rate of long-chain PFAS is higher than the short-chain PFAS due to the higher surface activity of the longer fluorinated tail (Buckley et al., 2023). It indicates that the air flow rates used (e.g., 1 L/min) are sufficient for equilibrium between PFAS in leachate and the surface area flux provided by the air flow rates. The results confirm the importance of proper air flow rates to PFAS removal using foam fractionation. Most studies concurred that increasing the air flow rate, thereby providing more bubbles surface area for PFAS adsorption, improves the total PFAS removal efficiency (Dai et al., 2019; McCleaf et al., 2021; Wang et al., 2023). Those findings are in good agreement with our findings. There is a wide variation in the configuration settings and operation modes of the foam fractionation system in practice (Dai et al., 2019; Smith et al., 2022). However, the gas-water surface area of the bubbles produced by different types of bubble spargers (e.g., air diffuser, glass frit, venturi) is the key one (Movahed and Sarmah, 2021). Increasing the gas flow rate does mean providing more bubbles and gas-water surface area for PFAS adsorption. However, achieving optimal gas flow rates is crucial to make a balance with the volume of foamate generated. Excessive gas flowrate can lead to the production of a significant amount of foamate, posing a challenge for downstream processing.

4.2. Effects of ozone flow rates on PFAS removal

The effects of ozone flow rates on PFAS removal are demonstrated in Fig. 2. Most long-chain PFAS were recovered more than 90 % at all ozone flow rates so it is equivalent to using air foam fractionation.

However, ozone bubbles recovered PFAS (e.g., PFOS (C₈), 6:2 FTS (C₆)) in slower rates than air bubbles by 0.5–1 min (Table S4). Similar to using air, a higher ozone flow rate resulted in an increase of short-chain PFAS removal, while using ozone was 10 %–30 % less effective in short-chain PFAS removal than using air at the same gas flow rate. This finding reveals one critical difference between ozone and air foam fractionations. Another significant difference was the formation of short-chain PFAS (i.e. FBSA (C₄) – Fig. 2A) induced by ozone foam fractionation, which was not observed in air foam fractionation. FBSA (C₄) formation ranged from 20 % to 50%. This finding confirms the hypothesis that ozone can transform PFAS precursors in leachates into terminal/stable PFAS. However, it is worth to notice that there is also a possibility that ozone can transform long-chain PFAS or PFAS precursors into short-



Fig. 1. Removal efficiency of PFAS during foam fractionation process by air using different air flow rates (Panel A). Kinetics of PFAS removal using gas flow rate 1 L/ min (Panel B), 0.8 L/min (Panel C), and 0.5 L/min (Panel D) in both dash and continuous lines. Error bars represent minimum/maximum values from triplicate experiments (n = 3). C represents the concentrations of PFAS at time t, C₀ represents the concentrations of PFAS at the initial time.

chain ones, which are not included in the analytical list of this study.

4.3. Effects of ozone doses on PFAS removal

The effects of ozone doses to PFAS removal are shown in Fig. 3. It was observed that at all ozone doses, the removal of long-chain PFAS was higher than 90 %. The removal of short-chain PFAS (e.g., PFBS (C₄) and PFHxA (C₅)) were negligible (less than 10 %). Interestingly, our results suggested that increasing ozone doses led to the decrease of PFAS removal by 10 %–20 % (Fig. 3A). The scientific understanding of this phenomenon requires further eluciation in the future works. However, the finding indicates that optimization of ozone dose is important for achieving the highest PFAS removal efficiency. In practice, calibrating the ozone dose for each specific leachate might be essential due to a complex matrix of organic matter presented in the leachate. The organic matter can potentially compete with PFAS sorption onto ozone bubble and impede the oxidation of PFAS precursors (Wu et al., 2019).

Ozone and its products (•OH, $O_2 \bullet^-$, 1O_2) are the driving factor to oxidize PFAS precursors in the leachate. The higher concentration of FBSA (C₄) at ozone dose 43 mg/L than the others (i.e., 57 mg/L and 65 mg/L) indicates that some PFAS precursors were transformed in a greater extent than in lower ozone doses. However, we did not observe the transformation of other PFAS precursors such as 6:2 FTS (C₆) and 5:3 FTCA (C₅). Theoretically, the possible products of 5:3 FTCA (C₅) transformation are PFHxA (C₅), PFPeA (C₄), PFBA (C₃) (Abada et al., 2018), however in our case their concentrations were not observed increasing at the end of the experiments. A possible reason for the formation of FBSA is the selective oxidation of a PFAS precursor(s) by a specific reactive oxygen species to form FBSA. It was previously reported that •OH, $O_2 \bullet^-$ is highly reactive but 1O_2 is the most selective one for oxytetracycline, which might be a similar case for PFAS precursors (Tang et al., 2022).

4.4. Wettability of foamate and PFAS presented

The wettability and PFAS concentrations of the recovered foamate are shown in Fig. 4. The foam wettability was influenced by both increasing ozone doses and air/ozone flow rates; however, the magnitude of influence by ozone dose was less than the flow rates. The wettability of foam increased proportionally with the increasing flow rates for either air or ozone fractionation. The reason was the increase of flow rates leading to the higher rise velocity of a liquid-containing bubble than the drainage velocity of free water in the foam. The finding is well supported by others experiments and modelling studies (Nguyen et al., 2003; Stevenson et al., 2003). The wettability of the foam recovered using air foam fractionation ranged from 7 % to 13 %; in turn, the wettability of foamate recovered by ozone fractionation is below 4 %. Another notable difference between ozone foam fractionation and air foam fractionation lies in the finding that the foamate produced by the ozone system is 2-4 times drier compared to that generated by air system. This phenomenon is attributable to the stronger hydrophobicity of the ozonated bubbles. It results in a lesser extent of boundary water on the surface of bubbles which be carried out to the reservoir tank. The amount of boundary water surrounding the bubble strongly affects the wettability of the foam recovered (Nguyen et al., 2003). In addition, the higher foam hydrophobicity results in lower surface water density, making it easier for the liquid film between two bubbles to thin and undergo coalescence. Foam hydrophobicity also promotes the rupture of liquid films by increasing the attractive hydrophobic force, so called non-DLVO force, alongside the attractive van der Waals forces and



Fig. 2. Removal efficiency of PFAS during foam fractionation process by ozone using different ozone flow rates – similar dose 43 mg/L (Panel A). Kinetics of PFAS removal using ozone flow rate 1 L/min (Panel B), 0.8 L/min (Panel C), and 0.5 L/min (Panel D) in both dash and continuous lines. Error bars represent minimum/ maximum values from triplicate experiments (n = 3). C represents the concentrations of PFAS at time t, C₀ represents the concentrations of PFAS at the initial time. The negative removal efficiency means formation of the studied PFAS.



Fig. 3. Removal efficiency of PFAS during foam fractionation process by ozone (flow rate 0.5 L/min) using different ozone doses (Panel A). Kinetics of PFAS removal using ozone dose 57 mg/L (Panel B), 65 mg/L (Panel C), 43 mg/L (Panel D of Fig. 1) in both dash and continuous lines. Error bars represent minimum/maximum values from triplicate experiments (n = 3). C represents the concentrations of PFAS at time t, C₀ represents the concentrations of PFAS at the initial time. The negative removal efficiency means formation of the studied PFAS.

repulsive electrostatic forces in the disjoining pressure of liquid films (Ghosh, 2004; Langevin, 2020; Pereira et al., 2014). Another reason for the difference is the heavier mass of ozone than air in which resulted in slower rise of ozone bubbles, hence forming drier foamate.

The concentrated foamate showed a significantly increasing number

of PFAS detected compared to the original leachate, such as 6:2 FTCA, PFECHS, FOSA, 8:2 FTS, and N-MeFOSAA. The total concentration of PFAS in the foamate reached up to 800 μ g/L. It again indicates the occurrence of substantial PFAS compounds in landfill leachate that need to be removed (Smith et al., 2022; Vo et al., 2023).



Fig. 4. Wettability of foam in% (Panel A), and concentrations of PFAS found in foamate (Panel B).

4.5. Equilibrium adsorption and quantification of PFAS onto gas-water interface

The measured surface tensions of PFAS solutions and quantification of PFAS adsorption after sparging with air and ozone are shown in Fig. 5 and Fig. 6, respectively. As expected, the surface tension decreases with increasing PFAS concentration. However, the rates of change in surface tension are different amongst PFAS: the PFAS with higher molecular weights and more perfluorinated carbon decrease surface tension faster. It is noted that the critical micelle concentration (CMC) of PFOA and K-PFHxS are 4 g/L and 3 g/L, respectively, which correspond with surface tension around 15 mN/m and 22 mN/m as shown in the flat region of the surface tension. The critical micelle concentrations of PFBS however is higher than 50 g/L. The data of micelle concentration by using air bubble agree well with the literature (Costanza et al., 2019). Within the studied concentration, the equilibrium surface tension of K-PFHxS is higher than PFOA at an equivalent concentration when using air bubbles (2–50 g/L); in turn, using ozone bubbles shows that the equilibrium surface tension of K-PFHxS is much lower than PFOA (0.1–50 g/L) (Fig. S2). The reason could be due to the interaction of K-PFHxS counterion and ozone molecules that ultimately decrease the surface tension. Ions such as K^+ reduce the electrostatic repulsion force of the PFAS headgroup and ozone/hydroxyl radical groups resulting in an increase of PFAS sorption into the interface (Brusseau and Van Glubt, 2021).

The correlation of surface excess and concentration of PFAS is nonlinear which agrees with the previous study (Costanza et al., 2019). The results of surface excess suggest air bubbles have higher PFAS adsorption capacity than ozone bubbles. The Γ_m values of all studied



Fig. 5. Comparison between the measured (points) and model surface tension (lines), and sorption quantification for PFOA, PFHxS, and PFBS solutions in contact with air. Their molecular weights are 414, 400, and 300 g/mol, respectively.



Fig. 6. Comparison between the measured (points) and model surface tension (lines), and sorption quantification for PFOA, PFHxS, and PFBS solutions in contact with ozone. Their molecular weights are 414, 400, and 300 g/mol, respectively.

PFAS (except K-PFHxS) of air are higher than the corresponding ones of ozone by 20–40 % (Table 1). For example, surface excess of PFOA adsorbed in air bubbles are beyond 3 μ mol/m², at concentration higher 1 g/L, whereas ozone bubble demonstrates a lower surface excess value at the corresponding concentration. The fitting results of Frumkin model indicates that the lateral intermolecular interactions at both air and ozone bubble surface is also negligible as *A* fluctuates around 0. The finding in equilibrium sorption confirms the results of the previous sections, which air foam fractionation shows a better PFAS removal than ozone foam fractionation, regardless effects of complex matrices in landfill leachates. However, the adsorption quantification obtained in this study does not reflect the real values in landfill leachate because the surface excess of PFAS in leachate is known to be higher extent due to the presence of dissolved solids (Buckley et al., 2022; Costanza et al., 2019).

Foam fractionation using air purely depends on the interaction of PFAS molecules and the gas-water interface of air bubbles. In turn, ozone fractionation is driven by O_3 and its products (e.g., •OH, O_2 •⁻ and 1O_2), which affect the sorption of PFAS molecules to gas-water interface of ozone bubbles through an O_3 -rich layer surrounded the interface of

Table 1

Molecular parameters of PFAS adsorption at gas-water interface using air and ozone sparging.

	AIR			OZONE		
Parameter	PFOA	PFHxS	PFBS	PFOA	PFHxS	PFBS
g _o (mN/m)	72.5	72.5	72.5	72.5	72.5	72.5
K (L/g)	5.36	7.07	0.16	3.62	11.06	1.03
$G_{\rm m} \ ({\rm mmol}/{\rm m}^2)$	3.74	3.16	2.42	2.97	3.02	1.55
A (-)	0.006	0.015	0.012	-0.006	0.041	-0.046

ozone bubbles (Dai et al., 2019). Previous study hypothesized that ozone and its products act as a binder to attract the negatively charged head groups of PFAS molecules such as SO_3^- and COO^- , hence improving the removal of PFAS. Ozone fractionation was known to recover long-chain PFAS better using over-the-air fractionation given the comparison of short-chain PFAS removal was missing (Dai et al., 2019). However, in this study, our results and model showed that adsorption of PFAS onto air bubbles was higher than ozone bubbles. The underlying mechanism for the phenomenon needs further investigation.

4.6. Implications

Using a rigorous ozone dose as shown in this study, PFAS precursors will be transformed to a terminal/stable PFAS in a relatively short time. In practice, the ozone doses used in this study is producible because a commercial ozone generator system can produce up to 26 kg/hr. A more insightful investigation in the chemistry of ozone also needs to be conducted in the context of quantifying the reaction rate, selective oxidation of ozone and its products for end-point engineering applications. In addition, by-products formation such as bromate during the ozone fractionation process requires a consideration due to its detrimental effects to human and ecological health (Morrison et al., 2023). A one-size-fits-all approach unlikely exist in this case, hence reduction of bromide discharged to the waste stream or minimization of bromide formation by chemical controls are highly encouraged to leverage the purpose of PFAS removal. Practically in Australia, the treated wastewater after ozone fractionation is discharged as trade waste, which is all non-human liquid waste generated on commercial properties discharged to our sewerage system. The trade waste is subject to further treatment at the wastewater treatment plant according to the requirement of each water utility.

The removal of PFAS using ozone bubble can be beneficial from improving the delivery of O_3 into the bulk liquid via micro-nano bubbles. The smaller the bubble size is, the more concentration of O_3 was acquired at the gas-water interface due to the increase of pressure and gas density inside the bubble according to the Young-Laplace equation. The solubility of O_3 is increased up to 1.7 times (Fan et al., 2021). The micro-nano ozone bubbles can also produce less innoxious by-products in leachate and wastewater than the conventional ozonation (Rojas et al., 2010). Characteristics of the wastewater (e.g., pH) also pose impact on the performance of ozone foam fractionation. Though the production of \bullet OH, $O_2\bullet^-$ and 1O_2 works well in both acidic and alkaline wastewater, the acidic condition is reported to deliver the best performance (Tang et al., 2022).

Another area for future work is the microscopic investigation of PFAS sorption onto ozone bubbles and the foam phenomenon. The production of reactive oxygen species plays an important role to what extent PFAS are recovered and PFAS precursors are transformed. However, the interaction of PFAS and reactive oxygen species is not fully understood such as effect of reactive oxygen species to the orientation of PFAS molecules onto ozone bubble, and thickness of sorption layer. The underlying science for the less foam production induced by ozone foam fractionation also needs to be investigated.

5. Conclusions

The overall treatment performance indicates total PFAS removed by ozone foam fractionation is significant with more than 90 % long-chain PFAS removed. The greatest advantage of ozone foam fractionation is a higher reduction in foamate generated than air foam fractionation. It results in substantial benefit for final disposal costs and reduces site storage requirements of hazardous materials. The subsequent technology for PFAS destruction such as plasma, thermal and electrochemical oxidation also receive a corresponding reduction in workload with lower volume of foamate for degradation. These results demonstrate the promising applicability of ozone foam fractionation for treatment of PFAS-laden landfill leachate. In a broader scale, ozone foam fractionation can also be incorporated with the aeration stage in wastewater treatment plants by developing a foam collection system and an ozone generator. Further research is required to validate the operation mode (e.g., continuous, enriching, stripping) and system configuration (e.g., multistage treatment) to comprehensively elucidate the technoeconomic viability of this technology.

Supporting information

Quantification of PFAS, QA/QC, Data analysis, PFAS study, Experimental Design, Foam Fractionation System, Measured Surface Tension of PFAS.

CRediT authorship contribution statement

Phong H.N. Vo: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. Thao T.P. Nguyen: Writing – review & editing, Investigation, Formal analysis. Hong T.M. Nguyen: Writing – review & editing, Investigation, Formal analysis. Justin Baulch: Methodology, Conceptualization. Simon Dong: Writing – review & editing, Methodology, Conceptualization. Cuong V. Nguyen: Writing – review & editing. Phong K. Thai: Writing – review & editing. Anh V. Nguyen: Writing – review & editing, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Justin Baulch and Simon Dong report a relationship with Evocra Pty Ltd that includes: employment.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.121300.

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