Hydrothermal liquefaction of sewage sludge – effect of four reagents on relevant parameters related to biocrude and PFAS

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Abstract

Catalytic hydrothermal liquefaction (HTL) can convert wet biomass into crude-like oil and has potential to degrade pollutants during the thermal depolymerization process. To avoid negative environmental impacts from per- and polyfluoroalkyl substances (PFAS) in sewage sludge after its final disposal, we comprehensively evaluated catalytic destruction of PFAS in sludge through HTL. The results showed that adding red mud to HTL was beneficial for the biocrude yield and significantly increased the carbon conversion efficiency and energy recovery of the hydrothermal process. HTL at 300 °C for 2 h degraded > 96% of spiked perfluorooctanoic acid (PFOA). The mass of spiked perfluorobutanesulfonic acid (PFBS) and perfluorooctanesulfonic acid (PFOS) and pre-existing perfluorohexanoic acid (PFHxA) and perfluoroheptanoic acid (PFHpA), however, increased in the HTL product streams. The remaining PFAS after HTL mainly stayed in the biocrude phase. Our findings indicated that HTL under the studied condition was not able to degrade all PFAS existed in sewage sludge. Although adding red mud could improve the HTL performance with respect to biocrude, this reagent did not improve the removal of perfluoroalkyl acids (PFAAs). As a matter of fact, the hydrothermal process amended with the selected reagents resulted in increased mass of PFBS, PFHxA, and PFHpA in the HTL products due to degradation of PFAA precursors. Thus, other treatment approaches for PFAS removal from sewage sludge need to be identified to prevent possible contamination of environments receiving PFAS-containing sludge.

Keywords: sewage sludge, hydrothermal liquefaction, biocrude, per- and polyfluoroalkyl substances, energy content.

Abbreviations

HTL, hydrothermal liquefaction; GAC, granular activated carbon; SPE, solid phase extraction; DCM, dichloromethane; TOP, total oxidizable precursor; PFAS, per- and polyfluoroalkyl substances; PFAAs, perfluoroalkyl acids; PFCAs, perfluorocarboxylic acids; PFSAs, perfluoroalkane sulfonates; 7:3 FTCA, 7:3 fluorotelomer carboxylic acid; 8:2 FTUCA, 8:2 fluorotelomer unsaturated carboxylic acid; 8:2 FTS, 8:2 fluorotelomer sulfonate; ^{13}C-PFOA, perfluoro-n-[1,2-^{13}C2]octanoic acid; ^{13}C-PFOS, sodium perfluoro-1[1,2,3,4-^{13}C4]octanesulfonate; ^{13}C-PFHxA, perfluoro-n-[1,2,3,4,6-13C5]hexanoic acid; PFBA, perfluorobutanoic acid; PFHxA, perfluorohexanoic acid; PFHpA, perfluoroheptanoic acid; PFOA, perfluorooctanoic acid; PFBS, perfluorobutanesulfonic acid; PFHxS, perfluorohexane sulfonate; PFOS, perfluorooctanesulfonic acid; HHV, higher heating value; CCE, carbon conversion efficiency; ER, energy recovery.

1. Introduction

In 2016, the US generated approximately 14.82 million dry tons (MDT) of wastewater residuals or sewage sludge. Traditionally, sewage sludge has been handled through landfilling, land application and incineration. During recent years, all these practices have faced scrutiny due to detection of PFAS in sewage sludge. Based on a 2001 National Sewage Sludge Survey conducted in the US, it was estimated that the mean annual load of total PFAS in sludge was 2,749-3,450 kg, of which around 1,375-2,070 kg could reach agricultural land through biosolids land application (Venkatesan and Halden, 2013). PFAS concentrations in domestic sludge were reported to range from 55 to 3,370 ug/kg in the US (Higgins et al., 2005). In Switzerland, PFAS were detected at 28-637 ug/kg in digested sludge. This was mainly contributed by PFOS at 15-

600 ug/kg (Sun et al., 2011). In Sweden, the concentration of PFOA and PFOS in domestic sludge was found to be 0.6-23.9 and 1.6-54.8 ug/kg, respectively (Bolan et al., 2021).

PFAS in sewage sludge can be grouped into PFAAs and PFAA precursors. PFAAs include both long chain and short chain PFCAs and PFSAs. These PFAAs, owing to their stability and recalcitrant to degradation, are commonly regarded as PFAS degradation end products (Remde and Debus, 1996). The precursors include any PFAS that can be transformed into PFAAs. During conventional wastewater treatment processes, some precursors are converted to PFAAs as evidenced by higher concentrations of PFAAs in wastewater effluents than those in influents. For example, Gallen et al. (2018) reported that the total PFAS concentrations in the effluents were 9.8 times higher than those in the influents. Treatments of sludge for generating biosolids, such as heat drying, composting, alkaline stabilization, and aerobic/anaerobic digestion, are reported to be incapable of destructing PFAS. Regarding heating and composting, PFAS concentrations increased after these treatments due to breakdown of PFAA precursors (Kim Lazcano et al., 2019). As a result of PFAS in biosolids, PFOS and PFOA were detected in biosolids applied soil at 408 and 312 ug/kg, respectively (Washington et al., 2010). These PFAS potentially could be translocated to plants and enter the food chain. Therefore, given the ubiquitous presence of PFAS in sludge and biosolids, direct land application of biosolids needs to be carefully re-evaluated to avoid any potential dire consequences. These consequences could include increased distribution of PFAS to groundwater, surface water through PFAS leaching from soil, contamination of crops, animals and human exposure to PFAS through consuming products from the biosolids land-applied soil.

To avoid such negative impacts, PFAS in sludge must be destroyed using methods beyond those historically recommended by regulatory agencies and those practiced at different

facilities. Toward this end, we have demonstrated that ultrasonication of sludge for the purpose of increasing sludge digestibility for anaerobic digestion is ineffective for PFAS destruction (Zhang et al., 2022). Sonication at 20 kHz for longer than 15 min led to increased concentrations of PFOA, PFHpA, and PFHxA in the liquid phase. Adding permanganate at 10 mM resulted in higher concentrations of PFOA and PFHxA in the solid phase and PFOA, PFHpA, PFHxA, and PFBS in the liquid phase compared to those in untreated sludge. These increases could be due to increased release of PFAS from sludge due to the effect of sonication. Similar to sonication, thermal hydrolysis, such as CambiTHP operated at 165-170 °C for 20-30 min has been used at commercial scales for pretreating sludge for anaerobic digestion (Cano et al., 2014). Our studies have shown that the CambiTHP process itself did not lead to significant PFAS removal. With the addition of $Ca(OH)_2$, thermal hydrolysis performed at 165 or 300 °C for 2 h completely removed PFAA precursors (Zhang and Liang, 2021). Additionally, when the temperature was increased to 300 °C, either with or without $Ca(OH)_2$, thermal hydrolysis degraded PFOA, PFHxA, and PFHpA completely after 2 h. The same conditions, however, led to significantly increased concentrations of PFOS, PFBS and PFHxS in the product streams compared to the untreated sludge. The presence of $Ca(OH)_2$, especially resulted in higher concentration of PFBS and PFHxS than those without this base (Zhang and Liang, 2021) although $Ca(OH)_2$ was demonstrated to assist in complete degradation of PFOS accumulated in biomass of *Thypha latifolia* (Zhang et al., 2021; Zhang et al., 2020). The increase of PFSAs in the final products correlated with undetectable concentration of PFAA precursors when $Ca(OH)_2$ was added. Thus, it was concluded that $Ca(OH)_2$ assisted degradation of PFAA precursors to PFSAs.

Thermal hydrolysis, when conducted at 300 °C in a closed vessel, is referred to as hydrothermal liquefaction (HTL) and this Waste-to-Energy process improves sustainability

(Chen and Quinn, 2021; Chiaramonti et al., 2017; Li et al., 2021). To our best knowledge, there are only two studies that have evaluated fate of PFAS in sludge before and after HTL. In a report presented by Mitroshkov et al. (2019), 15 PFAS were quantified in five sludge samples before HTL. After HTL, concentrations of the majority of these PFAS were below detection limit of the GC/MS/MS. However, the authors did not report the HTL operating conditions used in this study. In addition, PFSAs including PFOS, the commonly recognized most recalcitrant PFAS, were not targeted in this work. In another study, degradation of five PFAS (i.e., PFOA, 7:3 FTCA, 8:2 FTUCA, 8:2 FTS, PFOS) in sludge by HTL was conducted (Yu et al., 2020). Among the five, each spiked at 1,000 µg/kg, the first three were degraded > 99% at 350°C for 90 min. Degradation of 8:2 FTS and PFOS was 34% and 67%, respectively. It was found that undegraded PFAS partitioned to the biocrude phase, which may negatively impact the quality and use of these biocrude in the real world. Compared to PFAS in water only, more degradation was observed when these PFAS were spiked to sludge. It was speculated that metal ions and mineral solids in the sludge might have contributed to enhanced PFAS degradation (Yu et al., 2020).

These results are encouraging, but they also point to the need for further research to identify HTL conditions that could lead to complete degradation of PFAS, especially PFSAs. Considering the recalcitrance of PFSAs, catalytic HTL is a must. However, although a wide range of catalysts have been tested so far, all of these investigations did not evaluate how PFAS change as a result of HTL. Thus, it is largely unknown whether the catalysts beneficial for biocrude yield and quality are effective in degrading PFAS. In addition, due to the high concentrations used in the study conducted by Yu et al. (2020), it is unclear whether PFAS at concentrations of low ends of ppb (µg/kg) in sludge could be removed by HTL. Furthermore,

although 24 h was allowed for sorption of the spiked PFAS to sludge solids (Yu et al., 2020), it is unknown how much sorption actually took place and whether PFAS originally sorbed or bound to sludge solid particles could be destroyed.

Given all these knowledge gaps, the reported study here was designed to assess effect of catalytic HTL toward PFAS destruction. For this purpose, PFOS, PFOA and PFBS were spiked at 150 µg/kg sludge given the relatively low concentrations of PFAS in the original sludge. In particular, the effect of each of four reagents (i.e., $Ca(OH)_2$, GAC, zeolite, red mud) on biocrude yield and quality and distribution of PFAAs and precursors in the three product streams (the biochar, the biocrude and the aqueous phase) were evaluated in detail. To date, this is the first comprehensive study evaluating catalytic destruction of PFAS in sludge through HTL.

2. Materials and Methods

2.1 Chemical reagents and sewage sludge

Table S1 listed the chemicals used in this study. The combined primary and secondary sewage sludge was collected from a wastewater treatment plant close to the University at Albany, State University of New York. The total solid (TS), total volatile solid content (TVS), and ash content were 4.20 ± 0.02%, 78.24 ± 0.25%, and 21.76 ± 0.25%, respectively. The original combined sludge was first centrifuged at 3,000 ×g for 10 min. After discarding the supernatant and spiking PFBS, PFOS, and PFOA at 150 µg/kg dry sludge, the semi-solid pellet with a TS of 13.08 ± 0.18% was then homogenized with four different reagents (i.e. $Ca(OH)_2$, GAC, zeolite, or red mud) at 5 wt.% and aged for 10 days. The particle size of the reagents added to the sludge was less than 63 µm. Afterwards, the mixture was used for hydrothermal processing.

2.2 Hydrothermal processing

Hydrothermal liquefaction of sewage sludge spiked with PFBS, PFOS, and PFOA was performed in 15-mL reactors (MS-15 Micro Reactor, High Pressure Equipment Co. Erie, PA, USA). Around 10 g of the prepared sewage sludge with or without a reagent was injected into the 15-mL reactor using a 60-mL syringe. The reactor was then sealed and heated at 300 °C for 2 hours. After cooling down to room temperature, the whole content in the reactor was flushed out using 10 mL of dichloromethane (DCM). Then, the reactor was rinsed with another 10 mL of DCM and the rinsing solution was combined with the mixture of the HTL products. The liquid phase and solid phase (biochar with added reagent) in the mixture were then separated through vacuum filtration. The solid phase was freeze-dried and weighed. The liquid phase was further divided into an aqueous phase and a biocrude phase by separating the aqueous layer and the DCM layer after centrifugation. The volume of the aqueous phase was measured. The DCM fraction was evaporated under nitrogen and the remaining DCM-free portion was weighed and recorded as biocrude. All experiments were run in triplicates.

2.3 Elemental analysis and energy content calculation for biocrude

The determination of carbon, hydrogen, nitrogen, and sulfur content (wt.%) in sewage sludge before HTL and biocrude oil after HTL was performed using a PerkinElmer 2400 CHNS Organic Elemental Analyzer (PerkinElmer, Waltham, MA). The oxygen content was estimated by difference. The higher heating value (HHV, MJ/kg) of the sample was then calculated using Dulong's formula (Valdez et al., 2012) (Equation 1). The carbon conversion efficiency (CCE, %) was calculated based on the ratio of carbon wt.% in the biocrude to carbon wt.% in the sewage sludge (Equation 2). Energy recovery (ER, %) was calculated by using Equation 3 (Mishra and Mohanty, 2020).

$$HHV = 0.338\ C + 1.428\ (H - O/8) + 0.095\ S \quad (1)$$

$$CCE = C_{biocrude} \times Y_{biocrude} / C_{sludge} * 100\% \quad (2)$$

$$ER = HHV_{biocrude} \times Y_{biocrude} / HHV_{sludge} * 100\% \quad (3)$$

where C, H, O, and S are the mass percentages of carbon, hydrogen, oxygen, and sulfur, respectively; $Y_{biocrude}$ is the biocrude yield.

2.4 PFAA extraction and analysis

Before PFAA extraction, 10 ng of surrogate (^{13}C-PFHxA) was spiked to each sample of different phases (i.e., aqueous phase, solid phase, biocrude phase). PFAAs in the aqueous phase were extracted through SPE using HyperSep C18 cartridges (Thermo Scientific, Waltham, MA, USA). PFAAs retained in the C18 cartridges were eluted with 2 mL of methanol, followed by 2 mL of 0.1% NH_4OH in methanol. PFAAs in the freeze-dried solid phase were extracted following the method published by Houtz et al. (2013) and Nickerson et al. (2020) with slight modifications. Briefly, 4 mL of methanol with 0.1 M ammonium hydroxide were added to the solids, followed by vortexing for 30 seconds, sonicating at 35 ˚C for 30 min. The mixture was then centrifuged at 4,500 rpm for 10 min and the supernatant was collected. The extraction steps were repeated twice and the extracts from the three rounds were combined. Afterwards, the combined extract was passed through a Supelclean ENVI-Carb cartridge (250 mg, Millipore Sigma, Burlington, MA, USA) before analysis. PFAAs in the biocrude phase were extracted following the method developed by Yu et al. (2020). In short, the biocrude was mixed with 3 mL of DCM and 3 mL of 50% methanol in water containing 0.5% NH_4OH. The mixture was vortexed for 1 min, shaken for 1 hour, and centrifuged at 4,500 rpm for 10 min. The supernatant of the mixture was diluted two times with methanol containing 1% acetic acid. Then, the extract was passed through an Envi-Carb cartridge for cleanup.

Afterwards, the extract of each sample from different phases was separated into two portions evenly. One portion was analyzed for PFAA concentrations directly. The other portion was further processed with a total oxidizable precursor (TOP) assay, which converts PFAS precursors to PFCAs (Houtz et al., 2013; Houtz and Sedlak, 2012). Briefly, the extract was evaporated to dryness under N_2 and resuspended in 6 mL of deionized water containing 60 mM potassium persulfate ($K_2S_2O_8$) and 150 mM NaOH. Then, the mixture was heated at 85 °C for 6 hours. After reaction, the sample was neutralized with HCl and passed through a HyperSep C18 cartridge. PFAAs retained in the C18 cartridge were eluted with 2 mL of methanol, followed by 2 mL of 0.1% NH_4OH in methanol. The concentration of precursors was calculated by subtracting the total PFCA concentrations in the sample before TOP assay from the total PFCA concentrations after TOP assay.

PFAAs in the extracts were quantified using a 6470 Triple Quad Mass Spectrometer coupled with a 1290 Infinity II LC system (Agilent Technologies, Santa Clara, CA, USA). Internal standards (i.e., ^{13}C-PFOA, ^{13}C-PFOS) were spiked to each sample before analysis. Analytes were separated in an Agilent ZORBAX Eclipse Plus C18 (3.0 × 50 mm, 1.8 μm) analytical column with an Agilent Eclipse Plus C18 (4.6 × 50 mm, 3.5 μm) delay column at 50 °C. The sample injection volume was 5 μL and the flow rate of the mobile phase was 0.5 mL/min. The mobile phase was a mixture of solvent A (water with 5 mM ammonium acetate) and solvent B (95% methanol with 5 mM ammonium acetate). The gradient profile started with 70% A, decreased to 0% A at 8 min and held for 4 min before reverting to original conditions. Agilent Jet Stream electrospray negative ionization mode and dynamic multiple reaction monitoring (dMRM) mode were used for quantifying PFAAs in the mass spectrometer.

2.5 Data analysis

The statistical analysis of the results was conducted using IBM SPSS Statistics 22. One-way ANOVA with post-hoc Duncan's test was conducted to determine the significance of differences. Statistical significance was accepted when $p < 0.05$.

3. Results and discussion

3.1 HTL reagent selection

Four different reagents were selected in this study for the following reasons. $Ca(OH)_2$ as a base was reported to help reduce char formation and improve the properties of the biocrude by promoting water-gas shift, dehydration, and deoxygenation reactions (Remón et al., 2019). It also demonstrated great potential in defluorination of PFAS (Wu et al., 2019; Zhang et al., 2021; Zhang et al., 2020; Zhang and Liang, 2021). GAC has been used commercially to remove PFAS from water through sorption (Zhang et al., 2019a; Zhang et al., 2019b). Its effect on PFAS removal during HTL, however, is unknown. Sludge derived activated carbon was also reported to enhance yield and energy density of biocrude obtained from HTL of sludge (Zhai et al., 2014). Zeolite which is aluminosilicate facilitates cracking reactions and may convert the heavier components of the biocrude into smaller fuel-range molecules (Saber et al., 2016). It was reported to lead to increased biocrude yield from *Nannochloropsis* sp. without H_2 in the headspace (Duan and Savage, 2011). Red mud was shown to increase biocrude yield from synthetic food waste (Maag et al., 2018a; Maag et al., 2018b).

3.2 Biocrude yield, elemental composition, and energy content

HTL is a depolymerization process that can convert wet biomass into energy-dense biocrude oil and other by-products (Bi et al., 2018; Chand et al., 2019; Nazari et al., 2017; Qian et al., 2020). Qian et al. (2017) found that HTL of sewage sludge at 400 °C for 60 min achieved a

biocrude yield of around 25 – 30 wt.%. The HHV of the produced biocrude and ER were 38 MJ/kg and 52%, respectively. Similarly, Xu et al. (2018) studied the HTL products of secondary sewage sludge treated at 260 – 350 °C for 20 min. Their results showed a maximum biocrude yield of 22.9 wt.% at 340 °C and the HHV of produced biocrude and ER were 35.41 MJ/kg and 50.2%, respectively. More recently, Mishra et al. (2020) reported that the domestic sewage sludge collected in India had an HHV of 18 ± 0.27 MJ/kg. The produced biocrude after HTL under optimum condition (340 °C for 30 min) had a yield of 23 wt.% and an HHV of 37.76 ± 1.1 MJ/kg. Higher biocrude yield (40 ± 1.1%) was reported for HTL of municipal sludge performed at 350 °C for 30 min in a stirred reactor (Prestigiacomo et al., 2020). The HHV and ER of the biocrude were 39.9 MJ/kg and 74%, respectively.

As shown in Fig. 1, the biocrude yield of 33.3 – 42.65% after HTL treatment of the combined sludge with or without a chosen reagent was at the higher end of the reported range in the previous publications. The presence of red mud during HTL resulted in a significantly higher biocrude yield of 42.65 ± 3.88% compared to 36.93 ± 1.28% derived from the controls. The addition of zeolite led to a biocrude yield of 41.19 ± 2.74%. Regarding GAC, the yield of biocrude was 33.30 ± 2.08%. The positive and negative effect on the biocrude yield as a result of zeolite and GAC amendment, however, was not statistically significant. With respect to $Ca(OH)_2$, no effect on biocrude yield was observed.

In terms of biocrude quality, the biocrude from the HTL treatment with $Ca(OH)_2$ had significantly lower carbon content and higher oxygen content than those from HTL treatments with other reagents and control, resulting in a significantly lower higher heating value (HHV) and carbon conversion efficiency (CCE) (Table 1). The corresponding energy recovery (ER) of the treatment with $Ca(OH)_2$ was also significantly lower than those of other treatments and the

controls. The biocrude from the treatment with red mud had similar elemental composition and HHV to those of the controls. Due to higher biocrude yield of the treatment with red mud, significantly higher CCE and ER were observed for those with red mud. Red mud is an alumina refining waste and mainly composed of metallic oxides, including Fe_2O_3, Al_2O_3, TiO_2, CaO_2, SiO_2, and Na_2O (Ayres et al., 2001). Apparently, these metallic oxides enhanced the biocrude yield and carbon conversion during HTL, hence increased the energy recovery.

3.3 Changes of spiked PFAAs after HTL

In this study, PFBS, PFOS, and PFOA were initially spiked at 150 µg/kg sludge. After 10 days of aging, the extractable concentrations of the three PFAAs in the spiked sludge were 182.41 ± 41.75 µg/kg, 36.87 ± 17.30 µg/kg, and 221.31 ± 7.45 µg/kg, respectively. Thus, a significant amount of PFOS was adsorbed by the sludge and became non-extractable as a result of aging. After HTL at 300 °C for 2 h, around 3 – 10% of the total residual PFBS were in the aqueous phase (Fig. 2). PFBS after HTL with $Ca(OH)_2$ or red mud had the lowest (2.86%) and highest (10.33%) mass fraction in the aqueous phase, respectively. Regarding PFOS, only less than 1% of the remaining after HTL stayed in the aqueous phase. Remaining PFOA in the aqueous phase had a mass fraction ranging from 8.91% to 14.14%. Detailed concentrations of the spiked PFAAs in the aqueous phase were shown in Fig. 3. Zeolite and red mud significantly increased the concentration of remaining PFBS in the aqueous phase. The concentrations of remaining PFOS and PFOA in the aqueous phase were at a very low level (< 0.16 µg/kg) and not affected by any of the four reagents.

In the solid phase, the HTL treatment with GAC resulted in significantly higher mass percentages and concentrations of PFOS and PFOA compared to other HTL treatments (Fig. 2 & 3). The high adsorption performance of GAC for removing long chain PFAS could lead to this

relatively higher retention of PFOS and PFOA in the solid phase (Zhang et al., 2019b). In addition, $Ca(OH)_2$ led to significantly higher concentration of remaining PFBS in the solid phase.

The majority of all remaining PFAAs after HTL treatment were in the biocrude phase (Fig. 2). This could be due to the higher affinity of PFAAs to biocrude oil than to aqueous solution and solid surface. The four reagents tested did not lead to any effects on the removal of the three PFAAs in the biocrude phase, except that $Ca(OH)_2$ resulted in a significantly higher concentration of remaining PFBS than the other reagents and the controls.

The removal (%) of the spiked PFAAs was then calculated by dividing the total removal mass of PFAAs in the three product streams by the total extractable mass of the corresponding PFAAs (Fig. 4). Our previous research indicated that the pre-existing PFCAs (0.6 – 3 μg/kg) in the treated sludge without any PFAS spiking can be completely removed after HTL at 300 °C for 2 h, while the concentrations of pre-existing PFBS (5.15 μg/kg) and PFOS (7.53 μg/kg) were increased to 67.58 μg/kg and 14.65 μg/kg, respectively (Zhang and Liang, 2021). We proposed that the non-extractable PFSAs that were strongly bound to the sludge particles could be released when the sludge underwent hydrolysis and depolymerization processes in subcritical water, hence contributing to the increase of PFSAs in the extracts (Zhang and Liang, 2021). The degradation of PFAA precursors in the sludge to PFSAs could be another reason causing the mass increase of PFSAs. Although extra PFBS, PFOS, and PFOA were spiked in this study and their extractable concentrations were around 5 - 35 times higher than their pre-existing concentrations, the results of PFAA removal were still consistent with our previous findings. Over 96% of the spiked PFOA were degraded (Fig. 4), indicating the chemical instability of PFOA under the studied HTL conditions. Moreover, adding different reagents did not cause any

negative effects on the PFOA removal. Similar to our previous report, HTL treatments caused a mass increase of PFBS and PFOS in the HTL product streams, leading to their negative removal efficiencies. Thus, the concentration increase (%) of PFBS and PFOS was calculated instead. As shown in Fig. 4, PFBS had the highest increase in the HTL treatments with $Ca(OH)_2$, while PFBS in the control treatment without any reagents had the lowest increase. PFOS had a 200 – 230% mass increase after HTL treatments (the controls) and adding different reagents did not affect the PFOS increase.

3.4 Changes of pre-existing PFAAs and PFAA precursors

Besides the spiked PFAAs, we also investigated the changes of pre-existing PFBA, PFHxA, PFHpA, PFHxS, and PFAA precursors in the sludge after HTL. As shown in Fig. 5, the concentration of PFHxS was negligible in all three phases. Similar to the three spiked PFAAs, the majority of remaining PFBA, PFHxA, and PFHpA after HTL was in the biocrude phase (Fig. 5). Ca(OH) significantly increased the concentration of remaining PFHxA and PFHpA in the biocrude phase, while GAC significantly increased the remaining PFHpA concentration in the solid phase. In terms of PFAA mass removal, over 70% of PFBA was removed after HTL (Fig. 6). $Ca(OH)_2$ and zeolite significantly improved the PFBA removal. The mass of PFHxA and PFHpA, however, was significantly increased after HTL (Fig. 6). This was contradictory to our previous finding that the pre-existing PFCAs, including PFHxA and PFHpA, can be completely removed after HTL at 300 °C for 2 h. The mass increase could be due to at least two reasons.

First, HTL may convert PFAA precursors to PFHxA and PFHpA. Sewage sludge was reported to be a sink for various PFAA precursors, such as 5:3 fluorotelomer carboxylic acid (5:3 FTCA), 6:2 fluorotelomer sulfonate (6:2 FTSA), 8:2 FTSA, 6:2/6:2 disubstituted polyfluoroalkyl phosphates (6:2/6:2 diPAPs), 6:2/8:2 diPAPs, and 8:2/8:2 diPAPs (Kim Lazcano et al., 2019).

Some PFAA precursors are convertible to PFAAs through heat-activated chemical oxidation (Park et al., 2016). Lazcano et al. (2019) also found that thermal treatment at 480 °C – 650 °C for 45 min led to an increase of total PFAA concentrations by 53% and the increase was attributed to PFAA precursor conversion. In this study, the pre-existing PFAA precursors in the sewage sludge was 5.38 ± 1.39 μg/kg (9.18 ± 0.44 ng/reactor). Due to the extremely high variance of PFAA precursor mass in the aqueous and biocrude phase (Fig. S1), it is nearly impossible to confirm PFAA precursor conversion. However, according to our previous research, HTL at 300 °C for 2 h with $Ca(OH)_2$ significantly decreased pre-existing PFAA precursors in the sewage sludge (Zhang and Liang, 2021). Thus, the increase of PFHxA and PFHpA could be very likely due to conversion of PFAA precursors. Unlike complete disappearance as what we observed in our previous study with un-spiked sludge, the newly generated PFHxA and PFHpA might not have enough time to be degraded further.

Second, the degradation of spiked PFOA at an extractable concentration of 221.31 ± 7.45 μg/kg may produce significant amount of degradation intermediates, such as PFHxA and PFHpA and the sludge may prevent the intermediates from further decomposition. The total mass of the spiked PFOA in the sludge loaded in each reactor before HTL was around 350 – 390 ng/reactor, while the total mass of PFHxA and PFHpA in the HTL products was around 250 – 410 ng/reactor. Considering the pre-existing mass of extractable PFHxA and PFHpA (36 – 44 ng/reactor), the total mass of PFOA, PFHxA, and PFHpA in the sludge before HTL was larger than or close to the total mass of PFHxA and PFHpA in the HTL product streams (Fig. S2). Thus, it is reasonable to speculate that the majority of the increased PFHxA and PFHpA could be from degradation of the spiked PFOA.

4. Conclusions

In this study, we evaluated $Ca(OH)_2$, GAC, zeolite, and red mud with regard to their effects on biocrude yield and quality and PFAS destruction during HTL of sewage sludge. Among the four reagents, red mud showed beneficial effect on biocrude yield and significantly increased the CCE and ER of the hydrothermal process. $Ca(OH)_2$, however, had negative effects on biocrude yield, quality, CCE and ER. Regarding PFAS removal, HTL at 300 °C for 2 h degraded > 96% of the spiked PFOA. The mass of PFBS and PFOS, however, increased after HTL, possibly due to the conversion of PFAA precursors and the release of non-extractable PFSAs from sludge particles during HTL. The remaining PFAAs after HTL mainly stayed in the biocrude phase. Among the four tested reagents, HTL with $Ca(OH)_2$ resulted in a significantly higher concentration of the remaining PFBS in this phase. Zeolite and red mud increased the concentration of the remaining PFBS in the aqueous phase, while GAC led to significantly higher retention of PFOS and PFOA in the solid phase than those of the controls. The mass of PFHxA and PFHpA was significantly increased after HTL. This increase could be a result of degradation of spiked PFOA and conversion of PFAA precursors. Overall, HTL under the studied conditions was highly effective toward removal of PFOA but was unable to destruct all PFAS in the sewage sludge, regardless of addition of a chosen reagent. The catalytic HTL in this study even increased the total detectable mass of PFBS, PFHxA, and PFHpA in the reaction products. Results from this study pointed to the difficulty in removing and degrading PFAS in sludge, the need to profile and quantify PFAA precursors in sludge and the need to understand potential transformations and reactions of precursors during HTL.

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Table 1. Elemental composition, higher heating value (HHV), carbon conversion efficiency (CCE), and energy recovery (ER) of sewage sludge before HTL and produced biocrude after HTL. Different letters indicate significant differences among HTL treatments with or without different reagents ($p < 0.05$).

	Carbon wt.%	Hydrogen wt.%	Nitrogen wt.%	Sulfur wt.%
Sludge	42.65 ± 0.76	7.02 ± 0.10	6.81 ± 1.57	1.93 ± 0.00
Control	75.84 ± 0.18 ^{a}	9.97 ± 0.07 ^{b}	4.48 ± 0.03 ^{a}	2.37 ± 0.08 ^{ab}
$Ca(OH)_2$	68.56 ± 1.43 ^{b}	9.11 ± 0.23 ^{c}	3.71 ± 0.09 ^{c}	2.23 ± 0.06 ^{b}
GAC	76.17 ± 0.11 ^{a}	10.35 ± 0.04 ^{a}	3.60 ± 0.26 ^{c}	2.49 ± 0.06 ^{a}
Zeolite	75.25 ± 0.20 ^{a}	9.73 ± 0.04 ^{b}	4.12 ± 0.18 ^{b}	2.36 ± 0.03 ^{ab}
Red mud	76.56 ± 0.81 ^{a}	9.80 ± 0.11 ^{b}	4.46 ± 0.18 ^{a}	2.33 ± 0.01 ^{b}
	Oxygen wt.%	HHV MJ/kg	CCE %	ER %
Sludge	19.83 ± 0.84	21.09 ± 0.18	-	-
Control	7.34 ± 0.31 ^{b}	38.78 ± 0.18 ^{ab}	65.66 ± 2.42 ^{b}	67.90 ± 2.50 ^{bc}
$Ca(OH)_2$	16.39 ± 1.64 ^{a}	33.47 ± 1.11 ^{c}	57.13 ± 2.50 ^{c}	56.39 ± 2.09 ^{d}
GAC	7.39 ± 0.45 ^{b}	39.44 ± 0.16 ^{a}	59.47 ± 3.62 ^{bc}	62.27 ± 3.70 ^{cd}
Zeolite	8.54 ± 0.32 ^{b}	38.03 ± 0.07 ^{b}	72.66 ± 4.82 ^{ab}	74.27 ± 4.91 ^{ab}
Red mud	6.85 ± 0.78 ^{b}	38.88 ± 0.57 ^{ab}	76.59 ± 7.58 ^{a}	78.66 ± 8.03 ^{a}

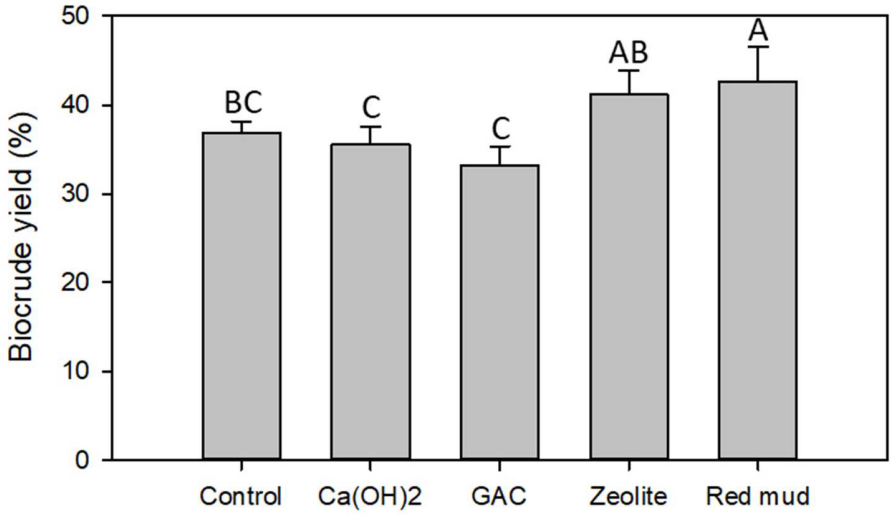

Fig. 1. Yields of biocrude from HTL of sewage sludge with different reagents. Different letters indicate significant differences among the biocrude yields from different treatments ($p < 0.05$).

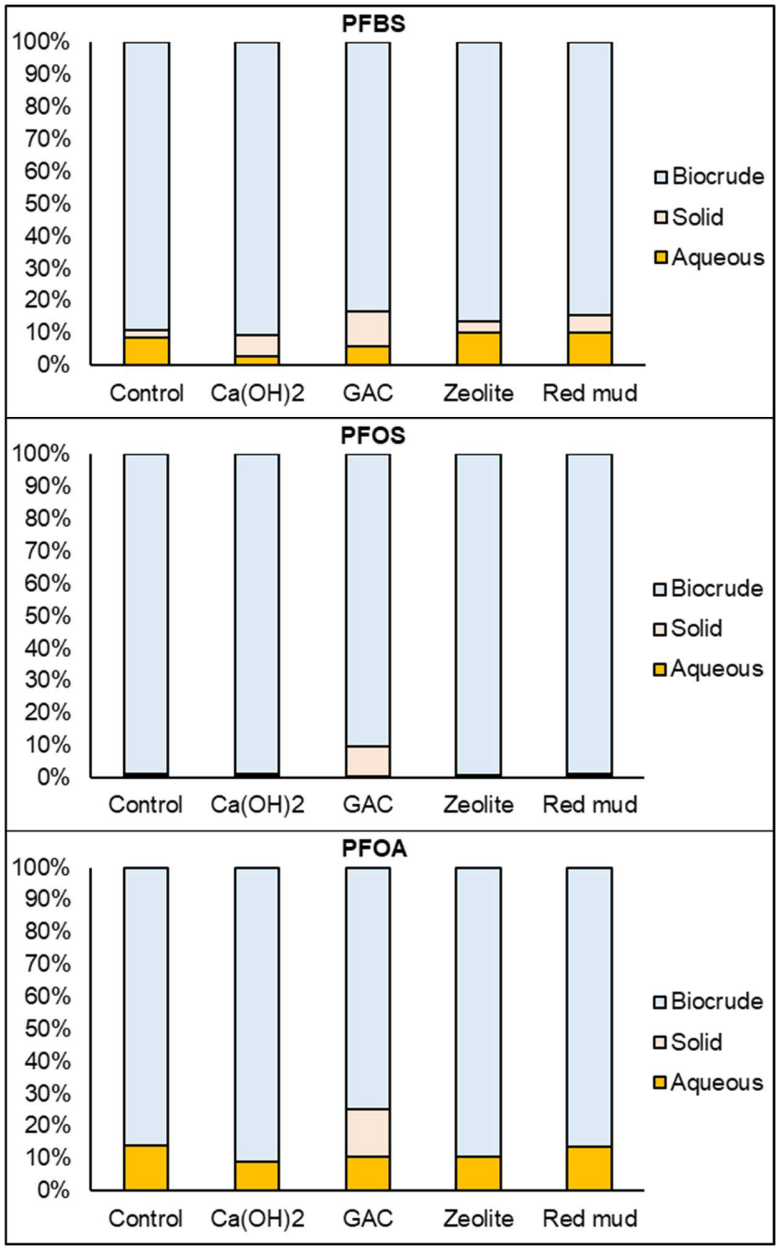

Fig. 2. Fractionation of normalized PFAA mass in HTL products.

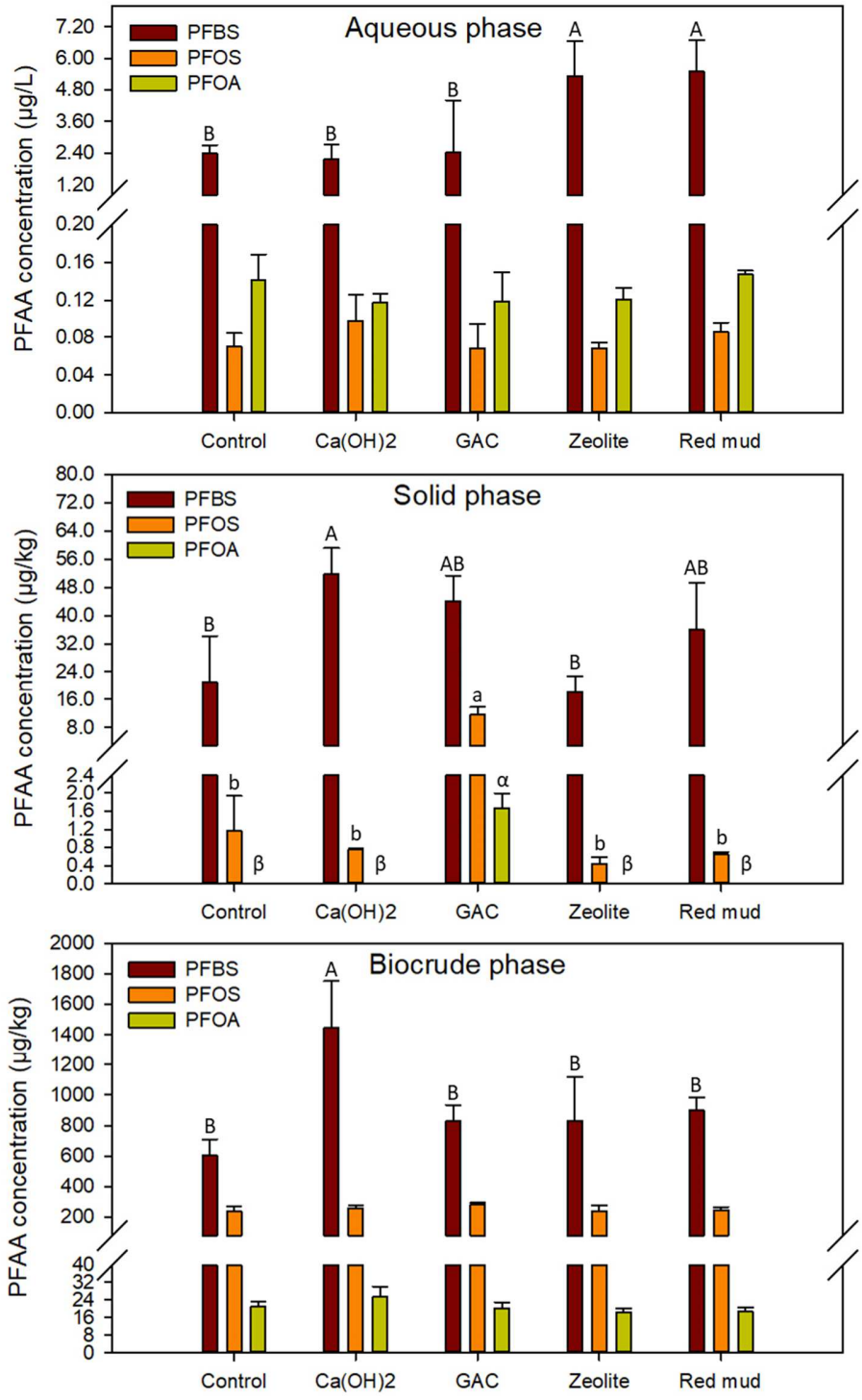

Fig. 3. Concentration of PFBS, PFOS, and PFOA in aqueous phase, solid phase, and biocrude phase after HTL. Different Latin letters in upper case and lower case and Greek letters indicate significant differences among HTL treatments with or without different reagents ($p < 0.05$).

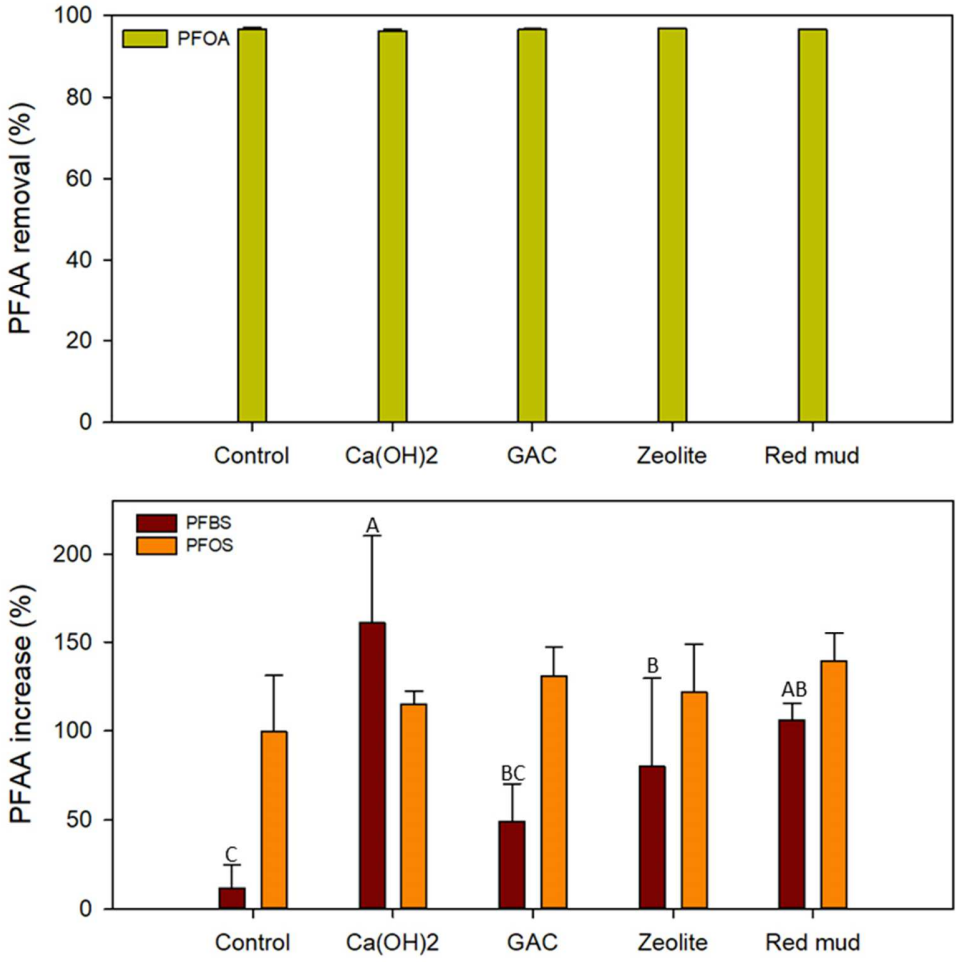

Fig. 4. Mass removal of PFOA and mass increase of PFBS and PFOS after HTL. Different letters indicate significant differences among HTL treatments with or without different reagents ($p < 0.05$).

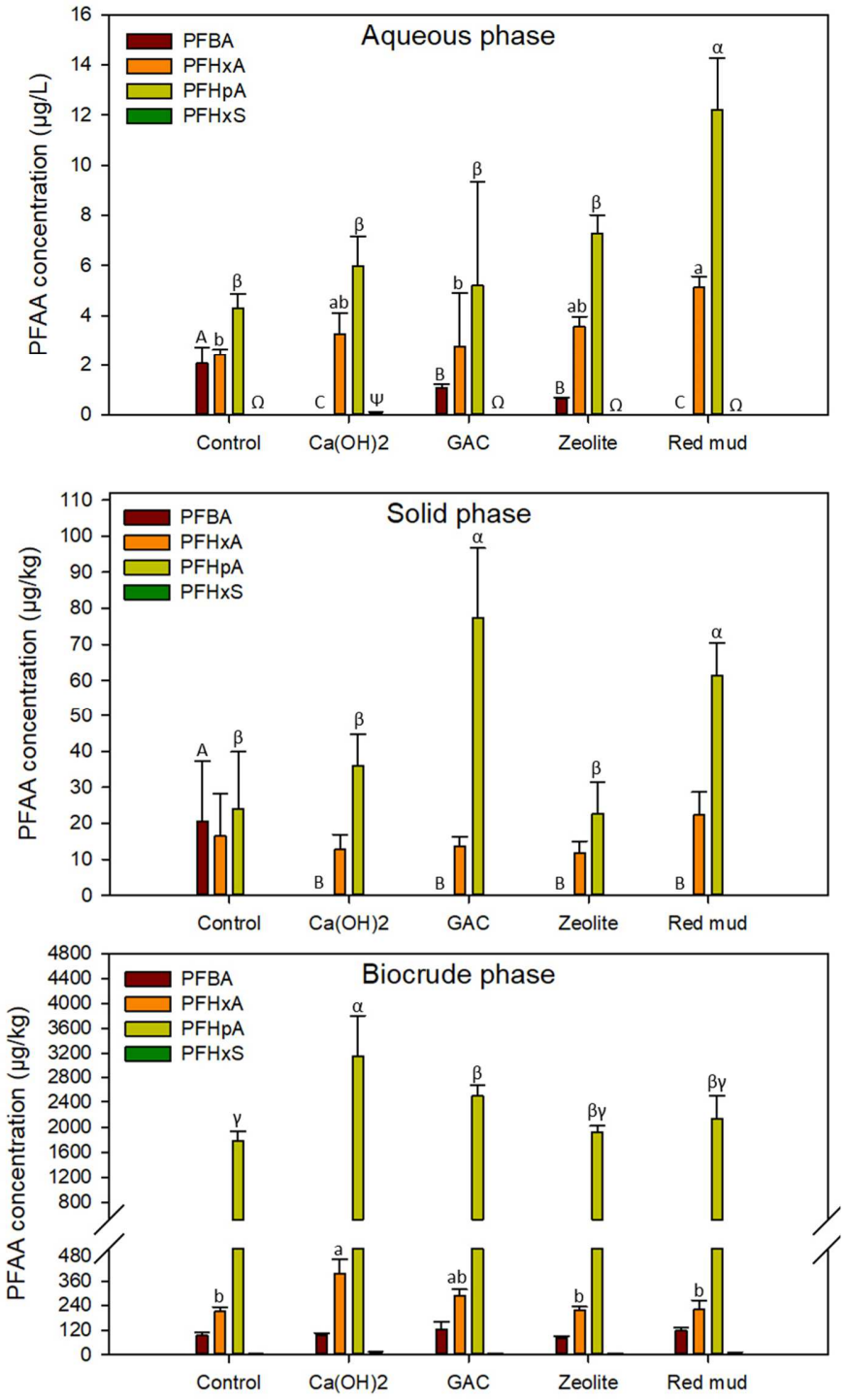

Fig. 5. Concentration of PFBA, PFHxA, PFHpA and PFHxS in aqueous phase, solid phase, and biocrude phase after HTL. Different Latin letters in upper case and lower case and Greek letters indicate significant differences among HTL treatments with or without different reagents ($p < 0.05$).

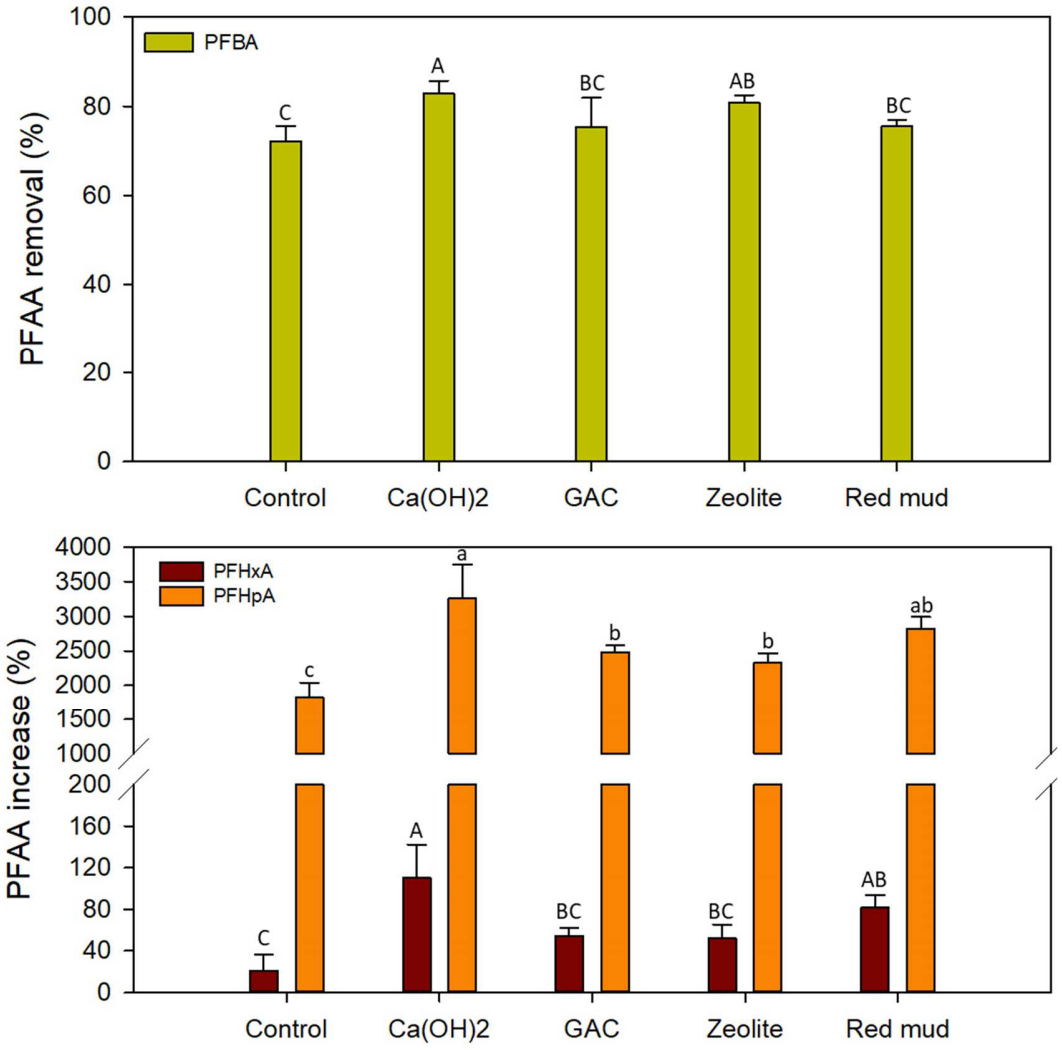

Fig. 6. Mass removal of PFBA and mass increase of PFHxA and PFHpA after HTL. Different letters in upper case and lower case indicate significant differences among HTL treatments with or without different reagents ($p < 0.05$).

Graphical abstract