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Enhancing the Efficacy of Mechanochemical Dehalogenation for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) In Contaminated Soils Using Ball Milling: Unveiling Rapid and Sustainable PFAS Remediation Pathways

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Abstract: Per- and polyfluoroalkyl substances (PFAS) contamination poses significant environmental and health risks due to their persistence and adverse effects. This study examines the efficacy of a special method, that is, dehalogenation by mechanochemical reaction (DMCR), comprising the application of a base metal in combination with a slightly acidic hydrogen source to dehalogenate per and/or polyhalogenated pollutants in different matrices in a ball mill, as a potential approach for remediating PFAS-contaminated soil. Laboratory-scale experiments were conducted using a planetary ball mill under controlled conditions to investigate the degradation of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in sand serving as a contaminated model soil. The experiments were carried out in two stages: initially, with sand alone, and subsequently, with the addition of milling agents. Sodium (Na) metal, Na with butylamine (BA), Na with ethylenediamine (EDA), and Na with bis(3-aminopropyl)amine (APA) were employed as the co-milling agents in specific ratios. The results demonstrated remarkably high degradation efficacy of PFOA and PFOS (approximately 100%) following ultra-high-performance liquid chromatography (UHPLC) coupled with a high-resolution mass spectrometer (LC-MS Orbitrap), as well as fluoride recovery employing a fluoride sensitive electrode (around 100%, within the experimental error), achieved within a strikingly short reaction time of just 5 min using Na in combination with EDA. Regarding Na with BA and APA, complete PFOA and PFOS removal was achieved after 10 min of milling, while complete fluoride recovery was achieved after 30 min. Na acted as a strong reductively defluorinating agent, enhancing the degradation process by facilitating the formation of reactive intermediates and promoting the breakdown of PFAS molecules. The amines, EDA, BA, and APA, simultaneously acted possibly as hydrogen sources as well as catalysts that could be providing solvated electrons, thus significantly enhancing the reactivity of the system under DMCR conditions, promoting PFOA and PFOS degradation, and facilitating complete fluoride recovery. Further experiments with sodium hydride (NaH), boron nitride (BN), and potassium hydroxide (KOH) were also performed for comparative analysis, following the same experimental conditions. In contrast,

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NaH, KOH, and BN systems showed comparatively lower fluoride mineralization despite moderate PFAS degradation, indicating kinetic limitations and incomplete defluorination under short milling durations. The enhanced degradation performance observed in Na–amine systems is attributed to synergistic mechanochemical interactions involving reactive intermediate formation, improved energy transfer, sustained thermal activity, and possible solvated electron generation that collectively accelerate PFAS defluorination. Overall, the findings of this study highlight the promising potential of DMCR or specially designed mechanochemical dehalogenation (MCD) for efficient and rapid remediation of PFAS-contaminated soil and open up new pathways for rapid and sustainable tackling of PFAS-contaminated soils and other toxic and hazardous contaminated matter, thus providing opportunities for more sustainable and expedient remediation strategies.

Keywords: dehalogenation by mechanochemical reaction (DMCR); mechanochemical dehalogenation (MCD); reductive defluorination; Grignard; PFAS; planetary ball mill; remediation

1. Introduction

Soil contamination is a critical environmental concern worldwide, particularly when it comes to the presence of persistent per- and polyhalogenated organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and per- and polyfluoroalkyl substances (PFAS) [1–5]. These pollutants pose significant challenges due to their persistence, bioaccumulation, and potential adverse effects on ecosystems and human health [6,7]. POPs such as PCBs, dioxins (PCDD), and furans (PCDF) have been extensively studied and recognized as persistent, toxic, and capable of long-range transport [1,4,8]. Some of them have a history of use in various industrial and agricultural applications and tend to accumulate in soils over time (though PCDD and PCDF have never been synthesized/produced, for instance, they are formed during combustion of materials comprising carbon and chloride in the presence of oxygen from 200 °C upwards called “Denovo synthesis”) or during chemical synthesis of polychlorophenols as byproducts. The presence of these pollutants in soil can disrupt natural processes, harm organisms in different environmental compartments such as soils, groundwater etc., and therefore potentially contaminate food and water supplies, subsequently jeopardizing human health through the food chain [9–13].

In recent years, PFAS have emerged as a significant concern due to their widespread use in various consumer and industrial purposes, as well as their resistance to degradation [6,14,15]. PFAS compounds, including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), have been detected in soils globally, often due to uncontrolled dumping of firefighting foams (AFFF—Aqueous Film Forming Foam), food paper impregnating agents, contaminated wastewater, lubricants, surfactants, industrial discharges, and solid biomass [12,16–18]. The extremely high persistence of PFAS is attributed to the high dissociation energy between carbon and fluorine atoms [19,20]. This characteristic poses significant challenges in the remediation of PFAS-contaminated soil and emphasizes the urgent requirement for the development of effective strategies to address this issue [20].

Conventional treatment methods, such as incineration, photolysis, and chemical oxidation, have limitations in terms of their efficacy and cost-effectiveness for PFAS degradation [21]. Consequently, researchers have explored alternative approaches such as photo-catalysis, sonochemical degradation, oxidation, electrochemical degradation, and mechanochemical dehalogenation (MCD) to address the remediation challenges posed by PFAS-contaminated environments [7,22–26]. Among these technologies, MCD, which combines mechanical energy and chemical reagents, has emerged as a promising technique for the rapid and efficient degradation of persistent and recalcitrant organic compounds [1–5,27–31].

There are different MCD approaches, that is, employing different co-milling reagents. One of them is also known as DMCR (Dehalogenation by Mechanochemical Reaction) and is employed for the degradation of persistent pollutants, specifically per- and polyhalogenated compounds [1]. This methodology involves the utilization of fine particles of base metals such as iron, zinc, aluminium, alkaline earth metals, or alkali metals. These metals are combined with optimal acidic hydrogen donors that contain functional groups such as hydroxyl, amino, ether, polyethers and/or alcohol groups, serving as co-reagents [27,28]. The presence of both metal and hydrogen donor reagents is crucial for the process. DMCR involves the additional use of mechanical energy to initiate, promote and/or implement highly selective chemical dehalogenation reactions of per- and polyhalogenated pollutants in complex matter such as soils, typically using ball milling as a means of applying mechanical stress, which utilizes high-energy collisions between grinding media and reactants [1,2,32].

Birke et al. [1] outlined three key steps of the DMCR approach, which primarily aims to enhance the dehalogenation reaction through the application of mechanical energy to the metal substrate—(i) the continuous production of small metal particles, typically ranging in size from micro- to nanometers. This ensures a plentiful supply of fresh metal surfaces that are highly accessible for reaction, (ii) the continuous renewal of surface layers by removing impurities such as oxides, reaction intermediates, and degradation products that may be adsorbed on the metal's surface for the readily availability of the surface metal atoms for interaction with reactants, and (iii) activating the surface metal atoms for reaction through continuous impact. This activation process sets the stage for subsequent chemical transformations. Regarding DMCR, it was proven in kinetic studies that the mechanically activated metal acts as a reducing agent. This role involves several aspects. Firstly, the activated metal delivers electrons to facilitate the breakdown of carbon-halogen bonds during the initial mechanistic step. This electron transfer can occur via single-electron transfer (SET) or double-electron transfer (DET), resulting in the formation of either a radical plus an inorganic halide or a carbanion plus an inorganic halide, respectively. Importantly, these transfer reactions take place at the metal's surface while the halogenated molecule is adsorbed onto the activated surface. In a subsequent mechanistic step, a hydrogen donor comes into play, which transfers hydrogen atoms or protons to replace the removed halogen atom. This step is crucial for the overall degradation process. Studies have demonstrated that the addition of a suitable, slightly acidic hydrogen donor plays a decisive role in achieving fast and well-defined degradation at room temperature in a second step. These findings emphasize the importance of selecting an appropriate hydrogen donor for effective DMCR processes [1,2,32].

In recent years, few studies have focused on investigating the MCD of PFAS using various co-milling agents [5,12,19,20,33–36]. Shintani et al. [35] elucidated the MCD of PFOS and PFOA by employing calcium oxide (CaO) as a co-milling agent within a small-scale planetary ball mill. The outcomes unveiled that under precise conditions encompassing a certain molar ratio of Ca/F and a very high mill rotation speed, an effective degradation yield exceeding 80% was attained for PFOS and PFOA within a constrained treatment span of three hours. Zhang et al. [5] highlighted the MCD of PFOS and PFOA applying potassium hydroxide (KOH) as a potentially more efficient and effective co-milling reagent, resulting in nearly complete destruction of PFOS and PFOA, however, in a treatment duration exceeding four hours. The mass ratio between PFOS and KOH was found to significantly impact fluoride recovery, while it did not affect PFOS destruction or sulfate recovery. Turner et al. [36] also investigated the MCD treatment of PFOS- and PFOA-amended sand in a planetary ball mill utilizing KOH as a co-milling reagent. Factors such as sand mass, the presence of different KOH proportions, and water saturation were evaluated for their impact on the degradation of PFOA and PFOS. Results showed that after four hours of milling, concentrations of PFOS and PFOA were reduced by up to 98% and 99%, respectively, in dry sand without the addition of a co-milling reagent, with very minimal fluoride recovery. Contrarily, up to 89% of fluoride was recovered from PFOS-amended sand in the presence of KOH. However, water saturation was found to impede the MCD process of PFOS and PFOA. Very recently, Yang et al. [37] also demonstrated the complete destruction of PFAS in contaminated soil using boron nitride (BN) as a co-milling agent within the milling time of 2 h, and the fluoride recovery was also defined as near quantitative (≈100%). These studies explored the effects of different milling conditions, additive concentrations, and PFAS structures on the degradation efficacy. However, it is crucial to undertake further evaluations in optimizing the conditions for MCD, exploring the development of novel co-milling agents to facilitate rapid PFAS degradation regarding enhancing the remediation scalability of PFAS, and acquiring a more comprehensive understanding of the intricate mechanistic aspects to gain profound insight into the observed phenomenon.

Therefore, the objectives of this study are to investigate the efficacy of MCD of PFOA and PFOS using Na—amine interactions as novel co-milling agents, the underlying mechanisms involved in the degradation process, and to shed light on the role of Na as a strong reducing agent and the enhanced reactivity conferred in association with different amines. The choice of amines is also critical, as different types of amines can influence the degradation efficacy and reaction kinetics [2,27,28,32,38]. Understanding the mechanisms underlying Na-amine interactions and their impact on PFOA degradation is essential for optimizing the remediation process.

2. Material and Methodology

2.1. Materials

All chemicals utilized in this study were obtained from various commercial suppliers. Potassium perfluorooctane sulfonate (PFOSK, potassium salt, ≥98% purity), perfluorooctanoic acid (PFOA, 97% purity), bis(3-aminopropyl)amine (APA > 99% purity), sodium hydride (NaH—90% purity), and boron nitride (BN ≥ 98% purity) were procured from Sigma-Aldrich Chemie GmbH, Germany. Na metal, butylamine (BA ≥ 99% purity), and solvents, including HPLC-grade water and methanol, were supplied by Merck KGaA, Darmstadt, Germany. Ethylenediamine (EDA > 98% purity) and potassium hydroxide (KOH ≥ 85% purity) were procured from Th.

Geyer GmbH & Co. KG, Germany. Glacial acetic acid (≥99% purity) and formic acid (98% purity) were acquired from Carl Roth GmbH + Co. KG and PanReac AppliChem ITW Reagents, Darmstadt, Germany, respectively. The sand used in this study consisted of filter sand with a particle size range of 0.7–1.2 mm, procured from "Toom Baumarkt", Wismar, Germany.

2.2. Mechanochemical Experimental Design

Three planetary ball mills (model "Retsch PM 100 CM", Retsch GmbH, Haan, Germany), each fitted with a 50 mL stainless steel grinding jar containing three 2 cm diameter steel balls, were employed for bench-scale degradation experiments of PFAS. Each jar was loaded with 15 g of sand, comprising high PFAS-contaminated spiked sand to achieve a final PFAS concentration of approximately 25 mg/kg in the mixture (PFAS concentration equivalent to 25 mg PFAS/kg of sand, comprising PFOA and PFOSK, was added to sand to prepare a total of 15 g of spiked sand. The spiked sand was then pre-milled at a constant rotational speed of 580 revolutions per minute (rpm) for 2 min to ensure homogeneous distribution of the PFAS throughout the sand matrix prior to initiating the ball milling experiments with the reactive agents). Co-milling agents, including Na, NaH, BN, and KOH, were added to the jars at a molar ratio of approximately 500:1 (co-milling agent to fluorine). In experiments involving sodium and amines, a fixed volume (250 µL) of each amine, namely BA, EDA, and APA, was added separately in combination with Na metal, what was applied in small pieces cut in n-hexane under an argon blanket. This volume was determined based on preliminary trials designed to optimize milling efficiency while preserving PFAS degradation performance.

Milling was conducted at four distinct time intervals—5, 10, 15, and 30 min—at a constant speed of 580 rpm, the maximum achievable with the equipment used. The workflow of the experimental procedure is represented in Figure 1. Each experiment was conducted in duplicate or triplicate. The milling jars were temperature-controlled via continuous cooling using a cooling jacket, water, and a thermostat. Despite this, temperature increases exceeding +5 °C were commonly observed, and in cases involving Na combined with amines, temperature differences between the start and end of milling exceeded 30 °C. These observations indicate that maintaining strict isothermal conditions was not feasible under the rapid, short-duration milling conditions employed with the reactive co-milling agents.

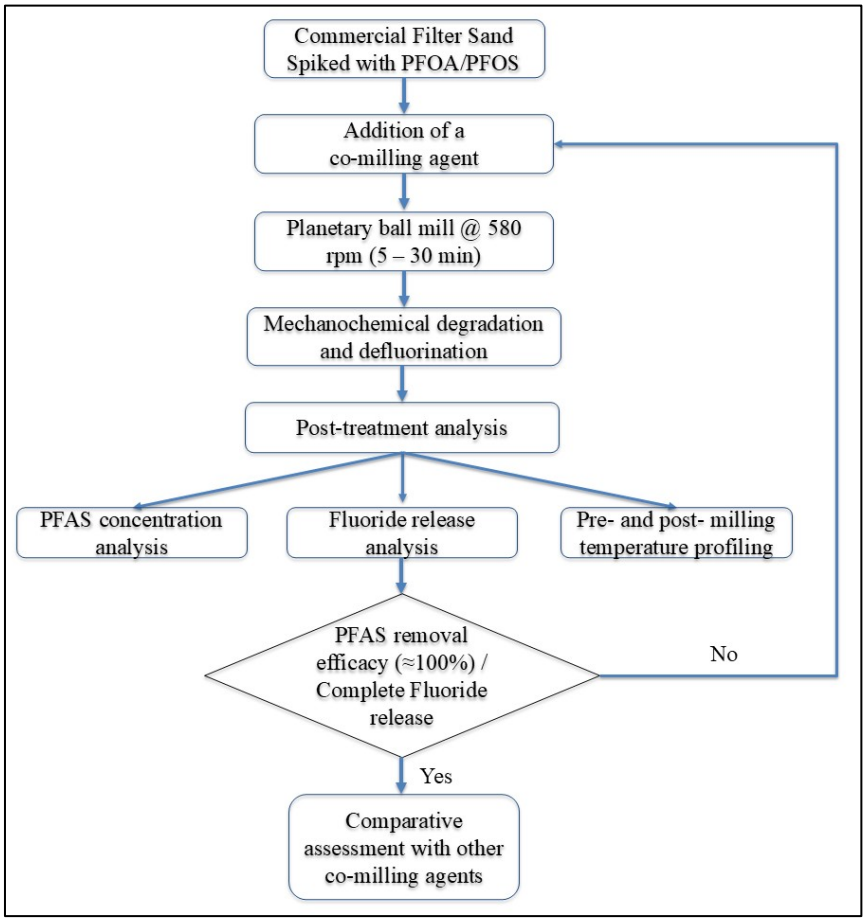


Figure 1. Workflow representation of the mechanochemical experimental design employed for PFAS degradation in contaminated sand matrices.

2.3. PFAS Extraction from Soil Samples

PFAS extraction was performed by collecting 2 g of the treated sample from the grinding jar post-experiment and transferring it into a centrifuge tube. Subsequently, 7.5 mL of extraction solvent—methanol containing 0.1% (*v*/*v*) acetic acid—was added to the tube. The mixture was then subjected to horizontal shaking for 2 h at ambient temperature using a shaker supplied by IKA®-Werke GmbH & Co. KG, Staufen im Breisgau, Germany. Following extraction, the samples were centrifuged for 20 min at 4000 rpm using a Heraeus Megafuge 16 centrifuge (ThermoFisher GmbH, Dreieich, Germany). The resulting supernatant was carefully filtered through 0.22 µm polytetrafluoroethylene (PTFE) syringe filters (LABSOLUTE, Th. Geyer GmbH & Co. KG, Renningen, Germany) into a clean centrifuge tube. The filtrate samples were then diluted as necessary with the same extraction solvent and transferred into vials for subsequent analysis. It was checked that, at the high PFAS concentrations investigated, virtually no significant adsorption and/or PFAS release occurred to or from any material, resp., during the sample workup.

2.4. Quantitative Analysis

2.4.1. PFAS Analysis Using LC-MS Orbitrap

Extracted PFAS samples were analyzed using an ultra-high-performance liquid chromatography (UHPLC) system (ThermoFisher Scientific GmbH, Dreieich, Germany) coupled with an LC-MS Ultimate 3000 and Q Exactive Focus Orbitrap mass spectrometer. Chromatographic separation was achieved using a ZORBAX Eclipse Plus C18 reversed-phase column (100 × 2.1 mm, 3.5 µm particle size), protected by a guard column (12.5 mm × 2.1 mm, 5 µm particle size), both sourced from Agilent Technologies Deutschland GmbH, Germany. The column assembly was housed in a temperature-controlled oven maintained at 30 °C, with a constant flow rate of 0.4 mL/min.

The mobile phase consisted of 10 mM ammonium acetate in HPLC-grade water (Phase A) and methanol (Phase B). The gradient elution program was as follows: 0–0.5 min (10% B), ramping to 60% B at 2.5 min, reaching 100% B at 6.5 min, and held until 10 min, followed by a return to 10% B at 10.5 min, and re-equilibration for 2.5 min before subsequent injections. Electrospray ionization (ESI) in negative ion mode was employed for analyte ionization.

The Q Exactive Focus Orbitrap was equipped with a heated electrospray ionization (HESI) source, with the following optimized parameters: sheath gas flow rate 50 arbitrary units (a.u.), auxiliary gas flow rate 13 a.u., sweep gas flow rate 3 a.u., spray voltage ±3.0 kV, capillary temperature 262 °C, S-lens RF level 50, and auxiliary gas heater temperature 425 °C.

Mass spectrometric data were acquired in Full MS. Full-scan spectra were collected over the *m*/*z* range of 50–600 at a resolution of 35,000 in negative polarity mode. Instrument control and data acquisition were performed using Xcalibur 1.7 software, while data processing and quantification were carried out using TraceFinder 5.1 (ThermoFisher Scientific GmbH, Dreieich, Germany).

2.4.2. Fluoride Analysis Using Ion-Selective Electrodes (ISE)

Fluoride analysis was conducted by transferring 5 g of the treated sample from the grinding jar into a 100 mL Erlenmeyer flask for extraction. Subsequently, 25 mL of deionized water was added, and the mixture was subjected to ultrasonic extraction for 1 h using a Bandelin SONOREX™ Digital ultrasonic bath (Berlin, Germany). The resulting extract was filtered through Whatman 41 filter paper, and the filtrate was then diluted in a 1:1 ratio (*v*/*v*) with Total Ionic Strength Adjustment Buffer (TISAB II, PanReac AppliChem ITW Reagents, Darmstadt, Germany) to ensure consistent ionic strength for accurate measurement. Fluoride concentrations were determined using a calibrated PerfectION™ ISE obtained from Mettler Toledo AG, Greifensee, Switzerland.

3. Results and Discussions

3.1. PFOA and PFOS Degradation Only in Sand

Figure 2 illustrates the degradation profiles of PFOA (Figure 2a) and PFOS (Figure 2b), along with the corresponding fluoride ion recovery, during MC treatment of PFAS-contaminated dry sand using a ball milling process. Within 30 min of milling, the concentration of PFOA declined to approximately 20% and 15% of its initial value, respectively. Notably, PFOA exhibited a rapid initial degradation phase, with approximately 17% of the total reduction occurring within the first 5 min. Beyond this point, the degradation rate significantly diminished, suggesting a decelerating reaction mechanism as milling progressed.

In contrast, PFOS degradation followed a markedly slower kinetic pathway. Negligible degradation was observed within the initial 5 min, followed by a gradual but sustained decrease in concentration over the 30 min milling period. This disparity in degradation kinetics can likely be attributed to the inherent differences in chemical stability between the two compounds. Specifically, PFOA, which contains a carboxylic acid functional group, is generally less chemically stable than PFOS, which contains a sulfonic acid group. This aligns with prior findings indicating that the chemical property of PFOS confers relatively higher resistance compared to PFOA, therefore, not easily destructible [5,39].

Despite the observed reduction in parent compound concentrations, fluoride ion recovery in both cases remained below 10%, indicating limited defluorination under the applied MCD conditions. This suggests that although initial bond cleavage involving functional groups (e.g., –COOH in PFOA and $–SO_3H$ in PFOS) occurs relatively readily due to weaker bonding, subsequent cleavage of the highly stable carbon–fluorine (C–F) bonds is largely ineffective in the absence of a chemical co-reactant. The low defluorination efficiency implies that the ball milling of PFAS-spiked dry sand alone does not provide sufficient energy or reactive species to facilitate significant mineralization of PFAS molecules, thereby limiting the overall efficacy of the MCD process for complete fluoride release.

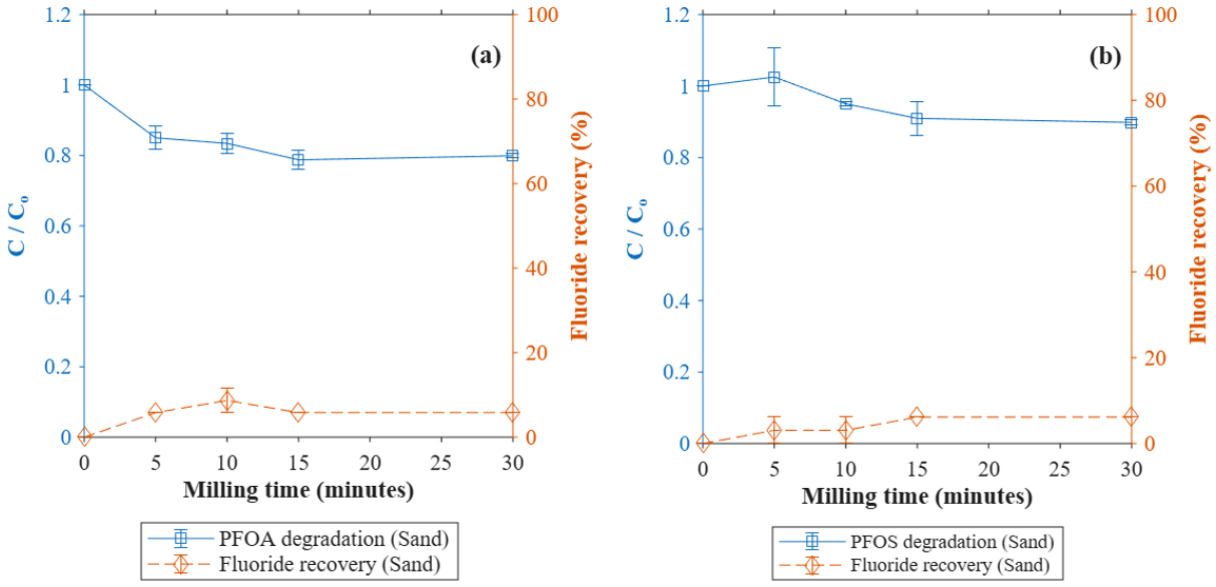


Figure 2. Degradation of (**a**) PFOA and (**b**) PFOS along with assessment of potential respective fluoride recovery in dry sand without any co-milling agent.

3.2. Enhanced Degradation of PFOA and PFOS with Na and Amines as Co-Milling Agents

The limitations of dry sand in facilitating C–F bond cleavage can be overcome through subsequent experiments incorporating reactive co-milling agents aimed at promoting defluorination of PFOA and PFOS. Na, a known strong electron donor and therefore strong reducing agent, was selected to assist in the MCD process by facilitating reductive defluorination pathways. Additionally, three amines—BA, EDA, and APA—were introduced individually in combination with Na to investigate the synergistic effects on the degradation kinetics of PFOA and PFOS degradation efficacy. These amines were selected based on their differing molecular geometries, basicities, nucleophilicities, or serving as weak acids as well (as amphoteric acid-base reagents), which can influence their interaction with PFAS molecules and their potential to stabilize transition states or facilitate radical and/or reactions involving carbanions on polyhalogenated molecules such as PFAS during the milling process. In combination with Na, these amines are hypothesized to enhance electron transfer processes and potentially serve as scavengers for intermediate radicals or reactive fluorinated fragments such as carbanions.

Figure 3a and Figure 3b depict the degradation behavior of PFOA and PFOS, respectively, in the presence of sodium alone. A progressive degradation of PFOA was observed, with approximately 50% removal achieved within the first 5 min and complete degradation (100%) by 30 min. Concurrently, fluoride ion recovery increased from 35% in 5 min to approximately 60% in 30 min, indicating a moderate degree of defluorination. In contrast, PFOS exhibited slower degradation kinetics under identical conditions, with only 20% removal at 5 min and a maximum of approx. 60% degradation after 30 min. Corresponding fluoride recovery/release remained relatively low, increasing from 10% to 30% over the same time frame. These results are consistent with the higher chemical

stability of PFOS due to the strong electron-withdrawing nature of the sulfonic acid group, which makes its C–F bonds more resistant to cleavage compared to those in PFOA [5].

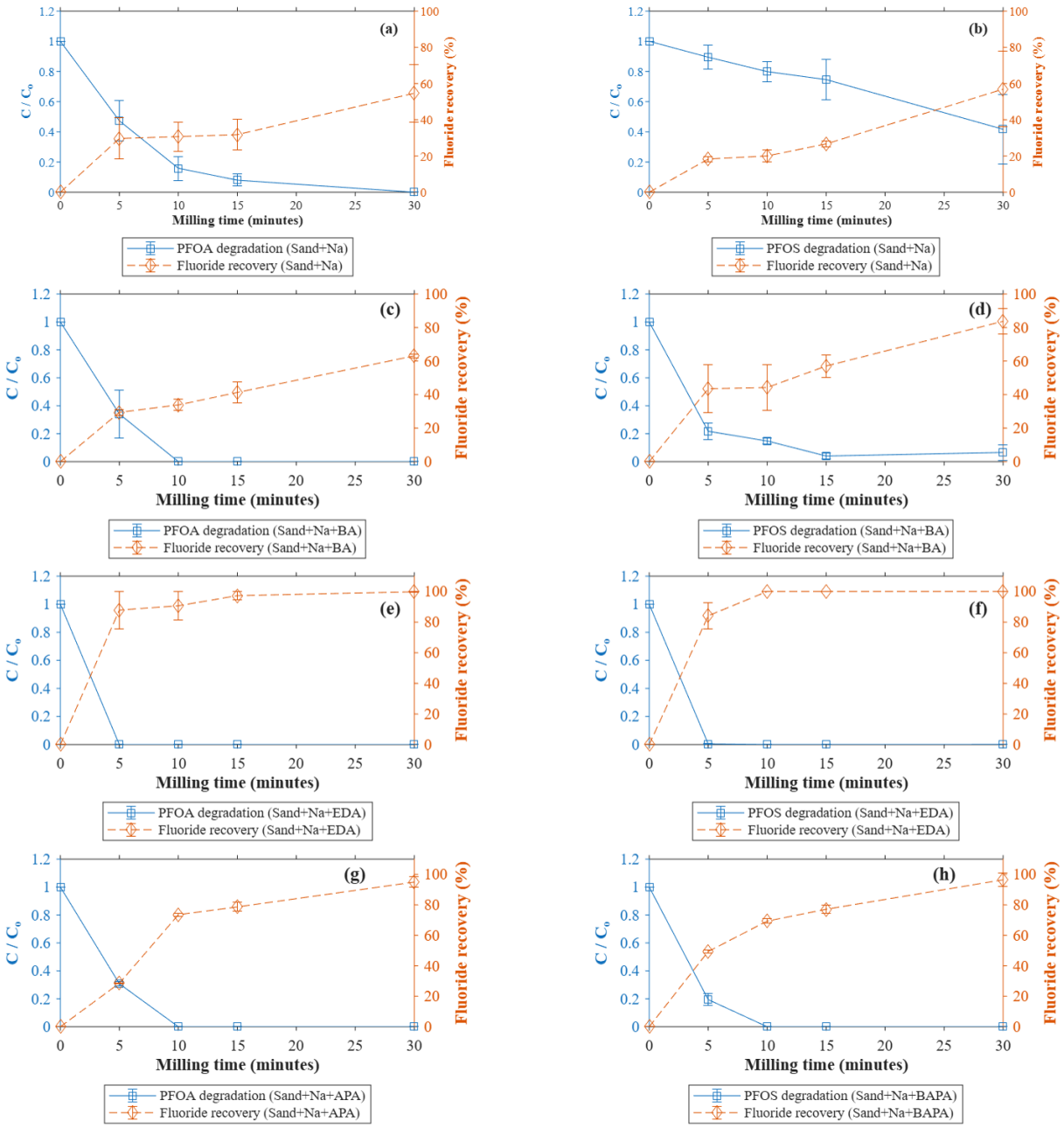


Figure 3. Degradation of (**a**) PFOA and (**b**) PFOS in dry sand with Na as a co-milling agent, (**c**) PFOA and (**d**) PFOS in dry sand with Na and BA as co-milling agents, (**e**) PFOA and (**f**) PFOS in dry sand with Na and EDA as co-milling agents, (**g**) PFOA and (**h**) PFOS in dry sand with Na and APA as co-milling agents, along with the respective fluoride recovery.

The introduction of BA as a co-milling agent with Na significantly accelerated the degradation of both PFOA and PFOS, Figure 3c and Figure 3d, respectively. In the presence of Na + BA, PFOA was completely degraded within just 10 min, while PFOS achieved near-complete degradation (≈100%) by 15 min. This rapid destruction was accompanied by enhanced fluoride ion recovery/release: approximately 60% for PFOA and up to 80% for PFOS by 30 min.

Figure 3e and Figure 3f highlight the most effective PFOA and PFOS destruction, respectively, observed in this study. The combination of Na and EDA exhibited complete degradation (100%) of both PFOA and PFOS within just 5 min of MC reaction. Notably, fluoride recovery was also substantially improved, reaching approximately 75% at 5 min and progressing to nearly 100% by 30 min for both compounds.

These findings suggest that EDA not only enhances the rate of PFAS degradation but also significantly improves the extent of defluorination. The dual amine groups in EDA may allow for better stabilization of reaction intermediates and facilitate more effective C–F bond cleavage through both chemical and physical interactions within the reaction matrix. This highlights the importance of this special amine structure in optimizing MCD processes.

Figure 3g and Figure 3h demonstrate that while the Na + APA system also achieved complete degradation of PFOA and PFOS, respectively, the reaction kinetics were comparatively slower than with EDA. Both compounds were fully degraded within 10 min, indicating a high reactivity profile. However, fluoride recovery was lower in the early stages: for PFOS, ≈50% fluoride release was recorded at 5 min, and for PFOA, ≈70%. These values gradually increased, reaching nearly 100% by 30 min.

Despite APA's tridentate structure and high nitrogen content, which theoretically provide multiple nucleophilic centers and coordination possibilities, its slightly slower regarding initial fluoride release, possibly due to the increased molecular size of APA, can introduce steric hindrance, reducing the efficacy of close-range interactions with PFAS molecules. Moreover, the longer propyl linkers between amine groups increase the spatial distance between reactive centers, which may affect the cooperative engagement with PFAS or reduce the probability of stabilizing short-lived radical intermediates efficiently during milling.

Overall, the mechanochemical system involving Na + EDA emerged as the most efficient configuration, achieving both rapid degradation and near-complete fluoride recovery. This underscores the critical role of amine structure in determining the reactivity and defluorination potential during DMCR. While Na provides a strong reducing environment essential for initial PFAS breakdown of its end groups, the presence of amines enhances the system's ability to disrupt the resilient C–F bonds, probably by solvated electrons in combination with sodium as a very strong reducing (reductive defluorination) system (compared to the system of Na dissolved in liquid ammonia).

The observed trends further suggest that bidentate and highly nucleophilic amines, such as EDA, are particularly effective in facilitating multi-pathway degradation mechanisms, likely involving both radical and ionic species. These findings demonstrate the potential of tailored co-milling agents to drastically improve PFAS destruction efficacy in solvent-free mechanochemical systems at ambient temperature.

3.3. Comparative Assessment of PFAS Degradation with NaH, KOH, and BN Co-Milling Agents

Regarding the performance of Na-amine systems, additional comparative experiments were designed by employing alternative co-milling agents: NaH, KOH, and BN. KOH and BN were selected based on prior research work of their mechanochemical reactivity and relevance in PFAS degradation [5,36,37], however, metal hydride was selected based on its distinct physicochemical properties and possible energy transfer behavior during high-energy milling, what was used for PCB dichlorination [40].

3.3.1. NaH

NaH was selected due to its trifunctional role, simultaneously offering a strong base, a nucleophilic, but also a relatively strong reducing agent (due to its hydride anion, H^-). As shown in Figure 4a, PFOA degradation reached approximately 90% within 30 min, increasing from 30% at 5 min, while PFOS showed degradation from ≈40% to 80% over the same period (Figure 4b). However, the corresponding fluoride recovery was limited to ≈50% in both cases, originating from an initial ≈15% at 5 min.

This disparity between degradation and fluoride release possibly suggests the presence of a mechanochemical induction period, during which PFAS molecules undergo preliminary transformations or partial defluorination before complete C–F bond cleavage occurs. Such behavior is consistent with prior observations in metal-mediated ball milling reactions [1,2,38].

Interestingly, temperature profiles recorded during and post-milling revealed that NaH reactions exhibited a sharp temperature rise, peaking significantly by the end of the 30-min milling cycle. However, after milling stopped, the temperature decreased rapidly while the jar remained sealed. In contrast, reactions employing Na with multidentate amine systems exhibited a more gradual cooling profile, indicating that heat dissipated more slowly under these conditions. The origin of these differences is not yet clearly understood but may reflect differences in the reaction mixture and the associated heat generation and transfer during milling.

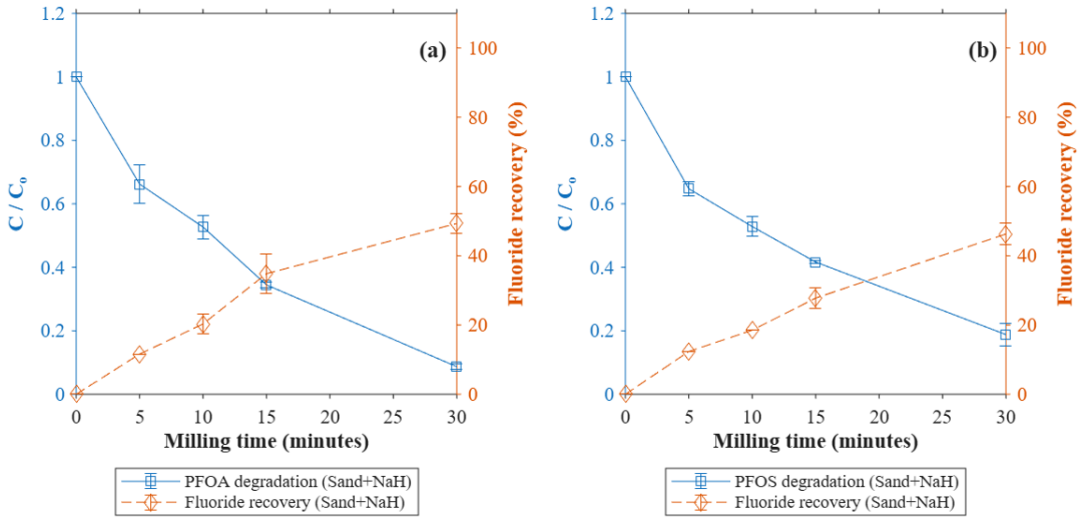


Figure 4. Degradation of (**a**) PFOA and (**b**) PFOS along with assessment of potential respective fluoride recovery in dry sand with NaH as a co-milling agent.

3.3.2. KOH

Subsequent trials were conducted using KOH as a co-milling agent, given its prior successful use in PFAS degradation studies and its availability as a strong co-milling agent [5,36]. As depicted in Figure 5a and Figure 5b, both PFOA and PFOS degradation plateaued at ≈60% and 50%, respectively, over 30 min. Notably, fluoride recovery remained below 20%, indicating limited C–F bond scission despite moderate apparent removal of PFAS.

These results suggest that KOH, under rapid milling conditions, lacks the reductive or nucleophilic strength required to achieve efficient defluorination in short timescales. While prior studies reported improved results with KOH, those systems typically employed significantly longer milling durations (4–6 h) and often relied on synergistic co-reagents, emphasizing the critical role of reaction time and system complexity in these base-mediated degradation processes.

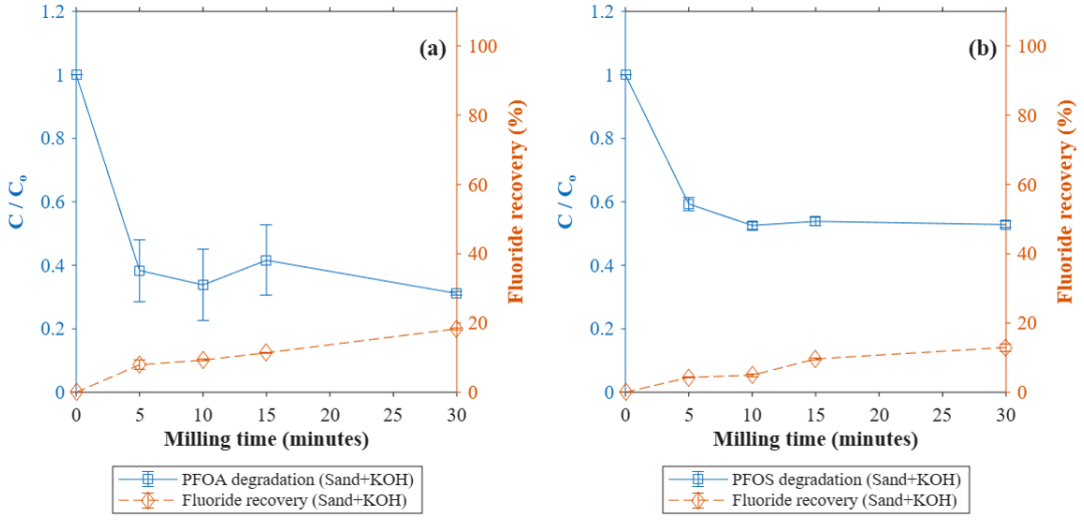


Figure 5. Degradation of (**a**) PFOA and (**b**) PFOS along with assessment of potential respective fluoride recovery in dry sand with KOH as a co-milling agent.

3.3.3. BN

In a recent successful mechanochemical PFAS degradation study, BN, a piezoelectric material (PZM), has been reported to enhance the defluorination process through the PZM-BM approach in a ball mill [37]. In this study, when applied as a co-milling agent, BN yielded better PFAS degradation performance than KOH. As observed, PFOA removal increased from 50% to ≈80% (Figure 6a), and PFOS removal from 40% to ≈70% (Figure 6b) from 5 to 30 min. However, fluoride recovery remained unexpectedly low (<10%) in both cases. This low defluorination efficiency, despite apparent PFAS degradation, indicates that BN may primarily assist in physical breakdown or partial transformation of PFAS molecules rather than complete mineralization or C–F bond cleavage.

Comparative evaluation with previously reported mechanochemical PFAS degradation studies indicates that PFAS destruction in contaminated solid matrices through high-energy ball milling remains a relatively emerging research area with limited available literature. Despite the use of a high stoichiometric excess (molar ratio ([PFAS]/[F]) = 500) in this study, compared to previous studies with these respective co-milling agents, the low fluoride recoveries with KOH and BN suggest that the molar ratio alone does not govern defluorination efficacy. On the other hand, it could be taken into consideration that milling time is a significant factor in achieving full PFAS degradation. The short 30 min milling window, in this study, may not be sufficient for KOH and BN-based co-milling agent MCD systems to reach full defluorination, especially considering previous reports utilized 4–6 h [36]. This reinforces the idea that kinetic limitations are significant in systems relying solely on physical or base-driven pathways.

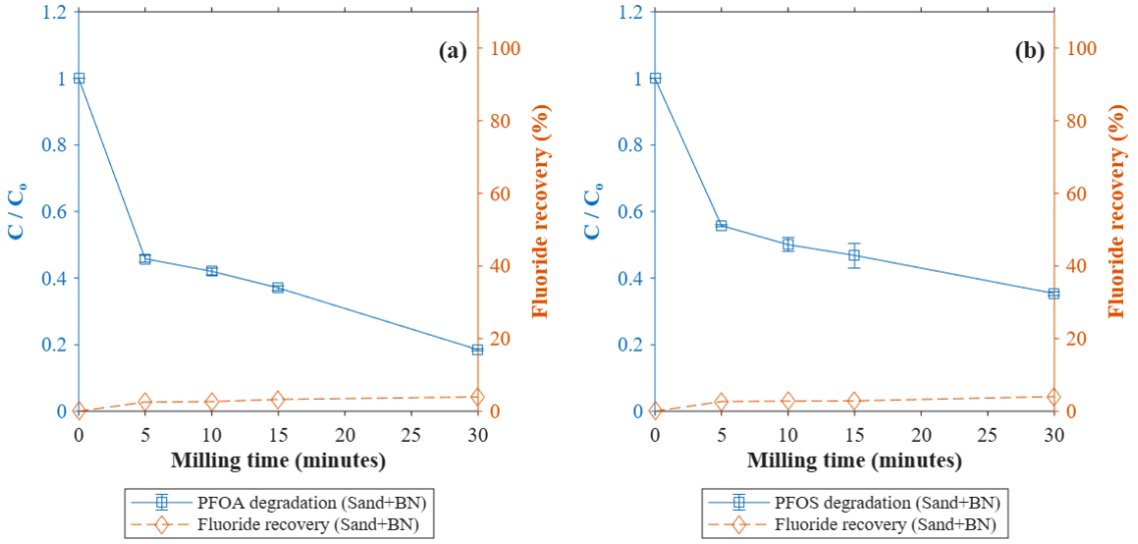


Figure 6. Degradation of (**a**) PFOA and (**b**) PFOS along with assessment of potential respective fluoride recovery in dry sand with BN as a co-milling agent.

Similarly, Yang et al. [37] emphasized the role of mechanochemically induced electron transfer and energy-transfer-assisted degradation pathways. Consistent with these observations, the BN-assisted system in the present study also showed improved PFAS degradation compared with KOH. However, defluorination remained limited, indicating incomplete mineralization under short milling durations.

Although strict isothermal conditions were not maintained during milling, temperature monitoring before and after treatment demonstrated notable differences among the investigated co-milling systems. In particular, Na─amine systems exhibited comparatively sustained thermal profiles, while NaH systems showed transient heat spikes, and KOH/BN systems exhibited relatively limited thermal activity. These observations suggest that localized temperature generation and exothermic mechanochemical interactions may contribute significantly to PFAS degradation efficiency by promoting enhanced electron transfer, increased molecular activation, reactive intermediate formation, and accelerated C–F bond cleavage reactions. These points further highlight the possible role of localized high-energy collision zones and thermal effects in facilitating mechanochemical PFAS defluorination.

Overall, the present study significantly demonstrates that additive chemistry significantly influences mechanochemical PFAS degradation behavior, thermal evolution, and fluoride mineralization efficacy. In particular, a base metal such as sodium in combination with multidentate amine systems or NaH exhibited comparatively enhanced degradation and sustained thermal activity, suggesting more favorable mechanochemical conditions for electron transfer and successive C–F bond cleavage. These findings contribute to the limited but growing body of research on additive-assisted mechanochemical PFAS remediation technologies.

3.4. Probable Degradation Pathways: Influence of Amine Structure on PFAS Degradation and Defluorination Efficacy

The observed variations in defluorination efficacy across Na-based systems supplemented with BA, EDA, and APA can be partially explained through mechanistic analogies drawn from prior mechanochemical studies involving organohalide degradation. In particular, Birke et al. [1,2,38] provided a mechanistic model for the reductive dechlorination of chlorinated aromatics using magnesium (Mg) and primary amines, as shown in Figure 7a, which may offer a parallel framework applicable to PFAS degradation under similar mechanochemical conditions as shown in Figure 7b.

According to [1,2,38], the formation of Grignard-type intermediates in ball milling systems involving zero-valent metals (e.g., Mg) and halogenated compounds often exhibits an induction period, consistent with the slow initiation phase observed in certain PFAS systems. Once formed, these organometallic intermediates readily undergo protonation by primary amines, even in the solid state, due to the highly basic nature of the metal–carbon bonds. Additionally, complex formation between the amine and the organometallic species was shown to stabilize or promote intermediate reactivity, accelerating subsequent degradation pathways.

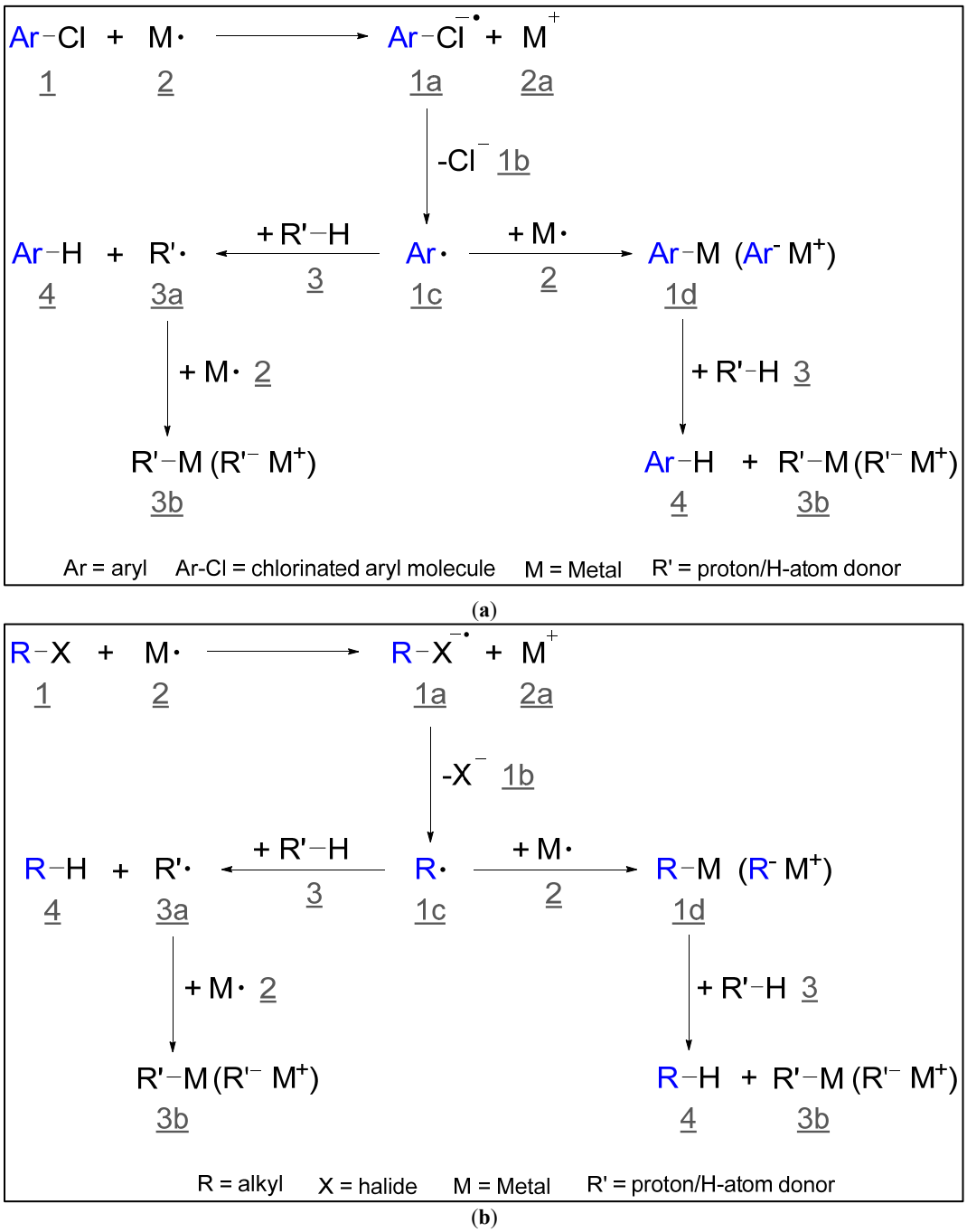


Figure 7. (**a**) Validated dehalogenation mechanism for chlorinated aryl compounds, adapted with permission from [41]. (**b**) proposed analogous defluorination pathways illustrating hypothetical PFAS degradation mechanisms following the cleavage of carboxylic and sulfonic acid functional groups from PFOA and PFOS, respectively.

Following the degradation mechanism of the current PFAS system, it is plausible that Na interacts with PFAS molecules, particularly the perfluoroalkyl chains, to generate partially defluorinated alkyl-Na intermediates step-by-step up finally leading to a full defluorination (release of fluoride), that is, probably surface-activated species (such as carbanions) or even in amine solutions during the milling process (mechanochemical activation). The introduction of various amines, such as BA, EDA, or APA, may then serve two primary roles:

(1) Protonation or stabilization of reactive intermediates: Similar to the protonation of Grignard compounds by BA described by [1,2,38], primary amines in this system may quench intermediate carbon-centered radicals or organometallic species (carbanions), with Na, facilitating C–F bond cleavage and promoting fluoride release.

(2) Formation of coordination complexes: Amines, particularly multidentate ones like EDA and APA, may transiently coordinate with Na or PFAS intermediates, enhancing the electron density at the reaction site and promoting nucleophilic attack or chain scission. In line with those findings [1,2,38], this interaction may help overcome activation energy barriers, thereby accelerating degradation.

Among the three amines, EDA showed the most rapid and complete defluorination, likely due to its compact structure and chelating ability, allowing efficient complex formation and fast proton transfer. BA, while effective, offered slightly delayed fluoride recovery, possibly due to limited interaction with intermediate species. APA, although rich in nitrogen sites, showed slower initial fluoride release, which may stem from steric bulk and longer chain flexibility, reducing the probability of effective protonation or complexation in the early stages.

The proposed mechanism for the PFAS degradation is given in Figure 8. This mechanistic analogy reinforces that amine-assisted Na-mediated PFAS degradation likely involves more than just reductive defluorination. The concerted role of electron transfers, complexation, and protonation steps, as observed in analogous polychlorinated compound systems such as polychlorbenzenes or PCBs, should be considered in the kinetic modeling and optimization of this DMCR process applied to PFAS as well.

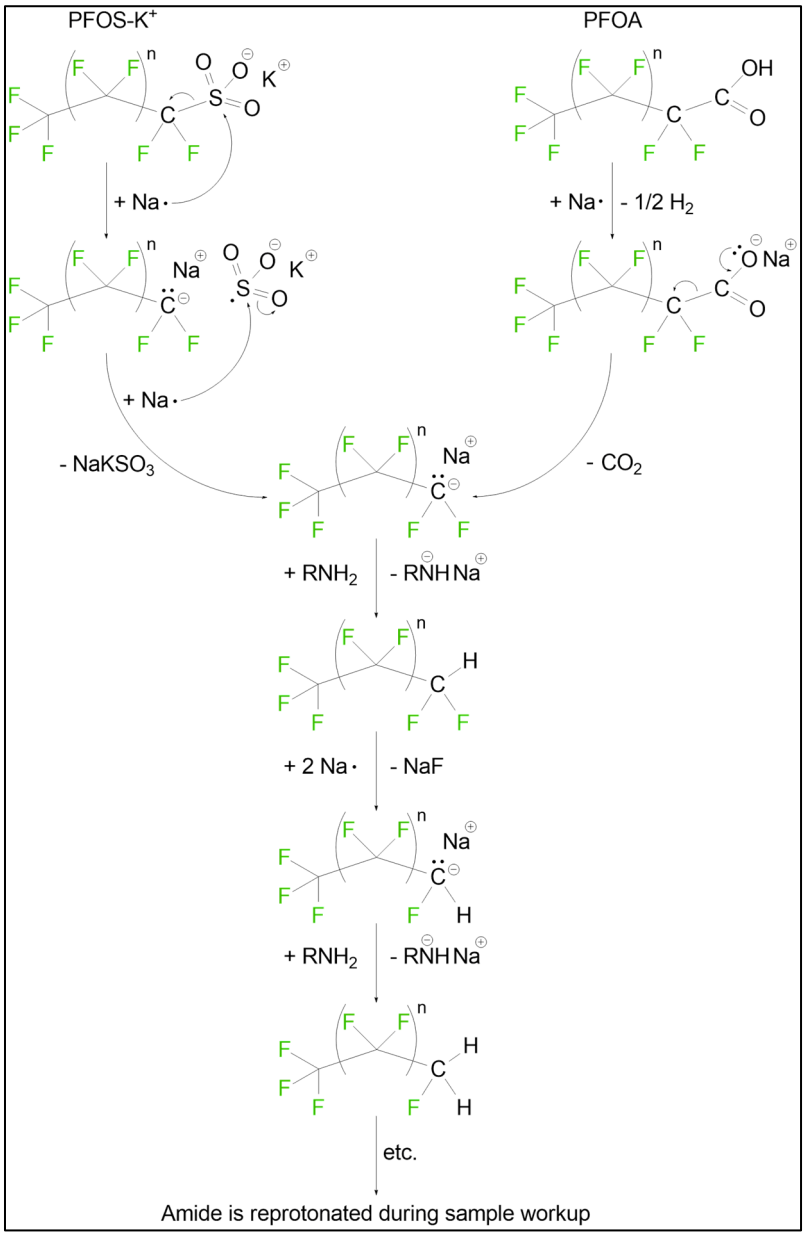


Figure 8. Proposed mechanism for the rapid defluorination and mineralization pathways of PFOS and PFOA via mechanochemically induced reactions using Na metal and amines under high-energy planetary ball milling conditions.

4. Conclusions

This study establishes a rapid and effective mechanochemical platform for PFAS degradation using Na in combination with selected amine-based co-milling agents. Among the systems tested, Na with EDA and APA demonstrated near-complete degradation and fluoride recovery of both PFOA and PFOS within 30 min, significantly outperforming recently tested agents such as KOH and BN. The results demonstrate that additive chemistry plays a critical role in governing mechanochemical degradation efficiency, thermal behavior, and defluorination pathways. The superior performance of Na-amine systems is likely associated with synergistic interactions promoting reactive intermediate formation, enhanced electron transfer, sustained thermal activity, and accelerated successive C–F bond cleavage reactions. In contrast, KOH- and BN-assisted systems appeared to rely more strongly on physical transformation and slower base-mediated degradation pathways, requiring extended milling durations for effective mineralization. Comparative evaluation with previously published mechanochemical PFAS remediation studies further confirms that the degradation efficacy achieved in the present work is highly competitive, particularly considering the remarkably short milling durations employed.

Importantly, this work highlights the significant potential of additive-assisted mechanochemical treatment as a scalable, solvent-free, and non-combustion remediation technology for PFAS-contaminated soils and other hazardous solid matrices contaminated by PFAS or other poly- or perhalogenated environmental pollutants. The reagent combinations, rapid kinetics, and minimal operational footprint make this approach particularly attractive for field-deployable or modular treatment units. These findings indicate the promising potential of the DMCR process involving base metals and special weak acidic hydrogen sources such as amines (serving as catalysts in addition) for efficient and rapid new pathways for tackling on-site PFAS-contaminated soils worldwide by effective MC defluorination reactions in ball mills, thus providing potentially great opportunities for more sustainable and expedient non-combustion remediation strategies for PFAS-contaminated soils in the 21 century.

To translate this work toward real-world applications, that is, sustainable future work/remediation processes applying ball milling should focus on: (i) mechanistic validation of PFAS and degradation pathways using in situ diagnostics, (ii) process scale-up using continuous milling systems and energy-optimized reactor designs, (iii) matrix adaptability across diverse environmental media and co-contaminant conditions, (iv) reagent innovation leveraging multifunctional organic or hybrid systems for enhanced defluorination, (v) cost parameter estimations regarding ball milling/mechanochemical dehalogenation in comparison with incineration, soil washing, depositing at specialized landfills etc. These directions, in combination, can enable a next-generation PFAS treatment technology that is fast, efficient, and environmentally sustainable.

Author Contributions

V.B.: conceptualization, methodology, resource procurement, writing—reviewing and editing; R.S.: conceptualization, methodology, visualization, investigation, data curation, writing—original draft preparation; K.B. and D.E.: visualization, writing—reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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Not applicable.

Data Availability Statement

The data that support the findings of this study are available upon reasonable request.

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Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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