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Nonthermal Mechanochemical Destruction of POPs

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Abstract

The present chapter is dedicated to all relevant theoretical and application aspects of mechanochemical destruction technology for mineralization of POPs, both stockpiled ones and as contaminants in environmental and waste matrices. It will show that such solid-state technology, realized by high energy milling of POPs with a co-milling solid reagent, can achieve complete mineralization of haloorganics into graphitic/amorphous carbon, carbon oxides, and halides; it takes place at near environmental temperature, thus limiting unintentional formation of dioxins (if treatment conditions are selected carefully); and, in some cases, it can be used to produce useful materials instead of just detoxified waste. The chapter will also give a comprehensive picture of complex mechanochemical destruction mechanism, including mechanochemical activation of the co-milling reagent and the cascade of radical reactions that cause POP molecules mineralization. Finally, technological and economic considerations will be provided, which corroborate the validity and feasibility of the mechanochemical destruction as an effective and safe technology to treat POPs.

Keywords: mechanochemistry, high energy milling, POPs mineralization, nonthermal technology, waste detoxification

1. Introduction

As a consequence of their classification as POPs by the Stockholm Convention and prohibition of their use, a number of already manufactured toxic chemicals have become obsolete. Many countries, especially developing ones, do not have the economic and/or technological capacity to dispose such waste materials in proper manner, that is, ensuring their mineralization to non-toxic form. Hence, obsolete chemicals are just stockpiled, often in poor conditions that cannot avert secondary contamination.

Currently, (high temperature) incineration is the sole largely available technology for efficient and economic POPs destruction. However, during combustion notable amounts of hydrogen halide gases are generated, which corrode facility structural elements and, therefore, heighten maintenance cost. Most importantly, risk of unintentional formation of dioxins is never null for such kind of plants. Consequently, new technologies alternative to combustion are highly needed. They must insure complete mineralization of POPs, even at high concentrations, and prevent secondary formation of new POPs [1]. Among the nonthermal alternatives, mechanochemical treatment is considered a valid option for POPs destruction.

1.1 Fundamentals of mechanochemistry

Mechanochemistry is a branch of chemistry that deals with physical and chemical transformations undergone by materials (eminently solids) that are induced during the action of mechanical forces (shear and compression), or are triggered by them [2]. The earliest known example of mechanochemical reaction is friction of two flints that originates sparks. Flint is a variety of quartz, so its scraped surfaces expose radicals that violently react with air producing sparkling plasma. The first mechanochemical experiments are acknowledged to Walthère-Victor Spring (1880–1911), who obtained barium carbonate by solid-state reaction between barium sulfate and sodium carbonate under high pressure; and Mathew Carey Lea (1823–1897), who demonstrated that heating and friction can induce, in some cases, diverse chemical transformations [3]. Today knowledge on mechanochemical phenomena is rather advanced, as well as development of special mechanochemical reactors that can be used to provide high mechanical energy input to solid systems.

A number of physicochemical phenomena may occur to solids under the action of mechanical forces. Some of them are quite unique, like emission of electrons [4] and light [5], while others are commonly experienced such as particle breakage and heating [6]. In truth, a complete classification of the various mechanochemical phenomena is hardly compilable (although some attempts were done [2]). The reason is that often it is not facile to distinguish properly said mechanochemical phenomena (those that occur while the mechanical force acts on the solids) from those that are triggered and/or facilitated by mechanical forces. In addition, it should be noted that every phase transition or emergence of new phases with diverse specific volume (due, for example, to chemical reactions) causes mechanical stress in the solid, thus possibly having mechanochemical effects on the system [7].

Currently, the “mechanochemical activation” theory is considered a reliable explanation of the evolution of solid systems under the action of (sufficiently intense) mechanical forces. Briefly, it hypothesizes that atoms or molecules are shifted from their equilibrium crystal lattice positions by mechanical stress, thus accumulating potential energy (**Figure 1**). This brings the solid in a high-energy metastable state that must release exceeding energy. Common relaxation pathways are heating and particle fracture. But, when particles reach a critical size, solid materials begin to build up crystal defects, develop amorphous phases or other crystalline morphologies, and chemical reactions might take place. Such processes are jointly named “mechanochemical (or mechanical) activation” of solids [8]. Mechanochemically activated solids are more prone to react with other chemicals and can give origin to reactive species.

1.2 Mechanochemical reactors

Action of mechanical forces on solid materials is realized in special mechanochemical reactors. In general, the main effect of these forces is particle breakage and, therefore, the large majority of such machines were originally designed to comminute particles. Consequently, high energy mill is usually considered synonym of mechanochemical reactor. A large number of milling machine typologies is available on the market that can apply mechanical forces with different intensities and by diverse means [9]. Principally, these machines can be classified according to the main type of action in three groups [10]:

1. Shocking mills, where the force derives from high speed impact of the material particles onto elements of the mill. In pin disintegrators, particle hits rotating

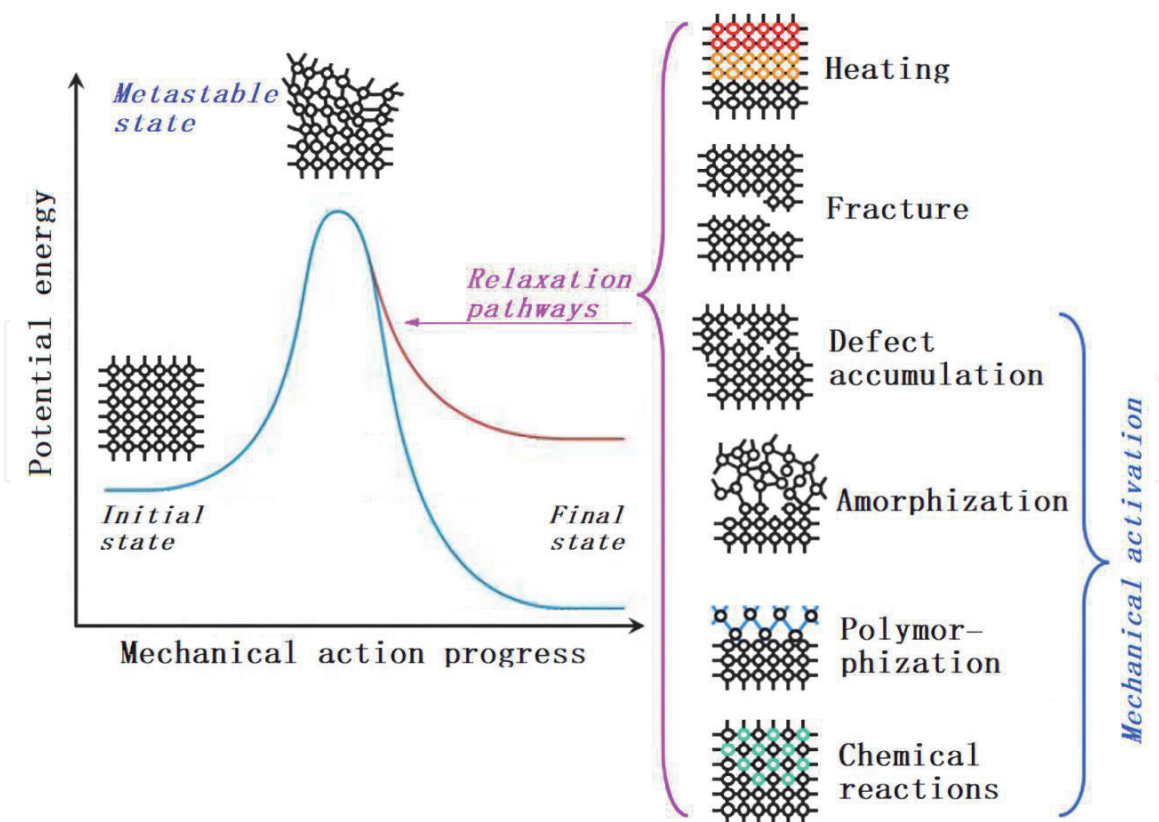


Figure 1.
 Main processes occurring during the action of mechanical forces on solids according to the “mechanochemical activation” theory.

blades; in jet mills, a fluid (air) accelerates the particles and throws them against a target.

2. Shear mills, where sliding surfaces of the mill produce friction on the particles, like in ring mills and roller mills.
3. Ball mills, where milling bodies (mostly balls) are accelerated into chambers and provide compression and shear to the material. Such kind of mills can accelerate the milling bodies by planetary, elliptical, etc. movements of the chamber, or by stirring with armed shaft.

Operating parameters of each type of mill mainly control the rate of provision of mechanical energy (i.e., milling intensity) to the milled material, as well as the efficiency of the energy transfer (i.e., the amount of energy that is effectively accumulated by the solid, compared to that dissipated by heat). The quantity of mechanical energy that is accumulated by a unitary mass of milled solid is often referred to as ‘specific energy dose’. It has been amply ascertained that transformation degree undergone by a mechanochemical system mainly depends on the total energy dose that is transferred to the system by the high-energy mill, independently from the milling intensity. In other words, the accumulated energy is invariant for a specific mechanochemical system [11]. Indeed, it was also proved that the modality of energy provision, that is, the type of high energy mill has, within certain tolerance ranges, limited influence on the transformation degree [12]. This fact points out that scaling up of mechanochemical processes is relatively facile and is not necessarily done just by trial and error. Taking advantage of the invariance of mechanochemical systems, provision of the same amount of energy dose in high

energy mills with diverse scale is a good starting point to achieve similar transformations and transfer the process from small scale to large one.

2. Mechanochemical destruction of POPs

In 1994, Rowlands et al. [13] demonstrated that high energy milling (HEM) can effectively destroy dichlorodiphenyldichloroethane (DDT) in presence of CaO as co-milling reagent. They obtained almost entire dechlorination of DDT, which, as ascertained in subsequent works, was transformed into halides and amorphous/graphitic carbon. Since that groundbreaking work, efficacy of mechanochemical destruction (MCD) obtained by HEM of many toxic organohalogenes, included all POPs, has been confirmed [14] (**Figure 2a** shows some examples with CaO as co-milling reagent). In particular, a number of other co-milling reagents and related optimal milling conditions have been investigated, as well as their mechanical activation. Moreover, key aspects of organics mineralization mechanism have been ascertained.

2.1 Treatment conditions of mechanochemical destruction

Co-milling reagent is certainly the most important component of MCD reactions. Theoretically, POPs can be degraded by the sole action of mechanical forces [22], but it would require a long time (i.e., high energy consumption) and could only achieve incomplete mineralization. Differently, co-milling reagent boosts the reaction rate and assures the complete transformation of POPs into inorganic form (usually, halides and carbon). HEM facilitates formation of fresh surfaces on reagent particle due to their breakage, as well as mixing and contact with POPs, thus accelerating the solid-state reaction. Moreover, reagents can be activated by the mechanical energy provided by the mechanochemical reactor, thus enabling or heightening their reactivity (see Section 2.2). Reagents can be classified in four groups:

1. Reducing reagents, like zero valent metals (e.g., Fe, Al, Zn, and Mg) and hydrides (e.g., CaH_2 , NaBH_4 , and LiAlH_4).
2. Oxidants, as manganese dioxide (MnO_2), persulfate ($\text{S}_2\text{O}_8^{2-}$), and ferrate (FeO_4^{2-}).

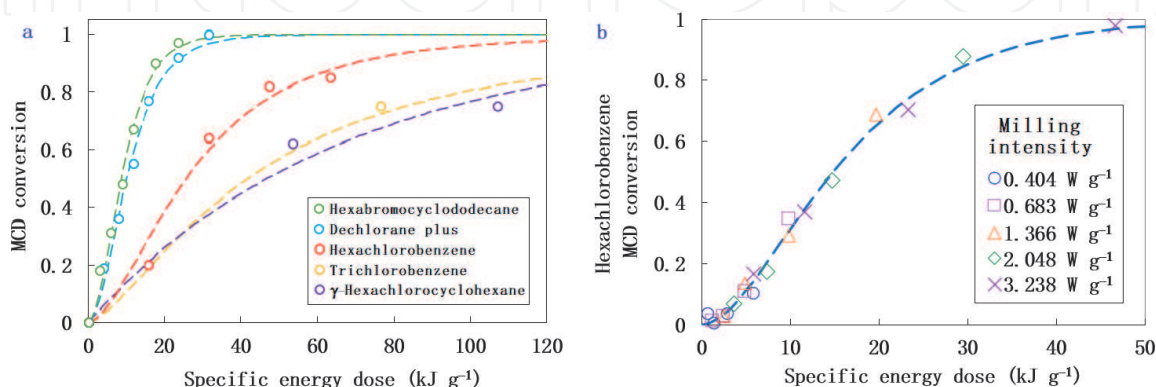


Figure 2. (a) MCD of some haloorganics (Hexabromocyclododecane [15], Dechlorane plus [16], Hexachlorobenzene [17], Trichlorobenzene [18], and γ -Hexachlorocyclohexane [19]) co-milled with CaO (dashed lines are obtained by interpolation of experimental data with the model of ref. [20]). (b) MCD kinetics invariance respect to milling intensity of hexachlorobenzene co-milled with CaO [21].

3. Lewis bases, such as metal oxides (e.g., CaO and MgO), and strong bases, like NaOH and KOH.
4. Plasma-former reagents, like silica (SiO₂) and alumina (Al₂O₃).

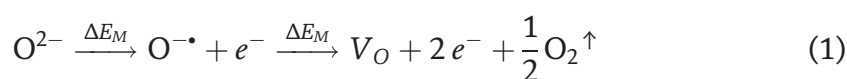
Reagent-to-pollutant ratio (often calculated as mass ratio) is one of the most critical parameters of MCD treatment. It governs the reaction kinetics: within certain ranges, the MCD kinetic constant for a specified POPs-reagent system is directly proportional to such ratio, that is, the higher is the ratio, the faster is the reaction [21]. An exceedingly high reagent ratio, however, decreases the energy efficiency (the amount energy spent to achieve a certain POPs dehalogenation/mineralization percentage) of the treatment, having a negative economic impact.

Milling operation parameters also have a notable influence on the reaction progress. Each HEM device has a number of such parameters that can be modified for the same equipment. In general, some of them are related to geometrical feature of the milling device such as milling chamber dimensions, milling tool (i.e., ball) dimension, and chamber filling ratio; and others are properly said operating parameters, like milling jar speed (e.g., rotation speed or vibration frequency) and ball-to-powder charge ratio. All of them control the amount of the mechanical energy that is inserted in the MCD system and, consequently, its kinetics, but the operating parameters have surely the most relevant effect. It was amply verified that each parameter has an optimal value that maximizes the reaction rate for a specified MCD system [14], which is due to the energetic efficiency of the milling tool impacts. Moreover, it was ascertained as well that MCD systems are invariant respect to the energy provided to the system. In other words, the pollutant degradation conversions are the same for the same amount of mechanical energy inserted, independently from the milling intensity (**Figure 2b**). Hence, MCD results, within certain ranges of tolerance, can be reproduced on any type of HEM device [21].

2.2 Mechanochemical activation of the co-milling reagent

Primary role of HEM is to ensure intimate contact among POPs molecules and the co-milling reagent. In particular, products of the mechanochemical reaction (e.g., carbon), in addition to side-products deriving from interaction with air, milling tools, etc. (e.g., passivating oxide layer on zero valent metals), are removed by the continuous particle fracture, thus exposing fresh surfaces available for further reaction. Such effect is sufficient for reactive materials, like zero valent metals, hydrides, and strong oxidants or bases, which, in some cases, can degrade haloorganics even by simple manual grinding [23].

Other kinds of reagent are efficient thanks to the physicochemical transformations they undergo during HEM. In these cases, the elevated energy input of HEM devices induces the formation of active species, mainly electrons and radicals, that are responsible for POPs mineralization. Metal oxides are known to be very efficacious co-milling reagents. The oxide anion on particle surfaces, thanks to the mechanical energy, generates in the crystal lattice an oxygen vacancy (V_O) with two trapped electrons and an oxygen atom that is released in gaseous form (Eq. (1)). This reaction passes through a step of electron release from the oxide anion to form an oxide radical ($O^{\cdot-}$):



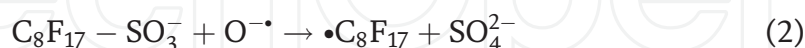
Generation of trapped and free electrons in CaO + chlorobiphenyl system, as well as the existence of the oxide radical, was ascertained by electron paramagnetic resonance [24]. Moreover, using the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) as probe, it was verified that electron generation on metal oxide surfaces under HEM is constant and follows a pseudo-zeroth order kinetics [25]. Electrons and oxide radicals are both responsible of haloorganics mineralization, as illustrated in subsection 2.3.

Another class of co-milling reagents that are remarkably reactive under HEM conditions is that of quartz (SiO₂), alumina (Al₂O₃) and silico-aluminates (including clays, etc.). Most of such minerals are known to be plasma-formers, that is, their new surfaces created by particle breakage are rich of electrons [26], which interact with the organic pollutant and mineralize it. For example, in silica-based minerals electrons come from the homolytic cleavage of Si–O bonds, producing silyl (Si•) and siloxyl (SiO•) radicals [17]. Experiments with DPPH probe suggest that generation kinetics of such species follows the pseudo-first order [27].

Persulfate, a strong oxidant that is being widely utilized for advanced oxidation of organic pollutants in solution, has been proficiently used as co-milling reagent for POPs destruction. As in solution, it is transformed in sulfate radicals (SO₄•[−]) by the mechanical energy, which then oxidize the haloorganics. In presence of strong bases or electron donors, such conversion is faster, thus increasing the overall mineralization rate [28, 29].

2.3 Mechanochemical mineralization of POPs

The active species generated by mechanochemical activation of co-milling reagent, or the reagent itself, interact with POPs molecules triggering and sustaining their degradation, eventually to mineral form. It was recently proposed that the mechanochemical activation of co-milling reagents and the mineralization of haloorganics are kinetically independent, which, in turn, suggests that both processes do not interfere significantly one with the other during HEM [20]. Since reactive species are of two types (i.e., electrons and radicals), their attack generally provokes expulsion of a halide and transformation of the haloorganics into radical form (**Figure 3**). For example, it was suggested that the first step of sulfonated perfluoroalkyl substances (e.g., perfluorooctane sulfonate) MCD with La₂O₃ is cleavage of the polar group by addition of oxide radical to form perfluorinated moiety radical and sulfate (Eq. (2)) [30]:



Then, the perfluorinated moiety could undergo further oxidation by reaction with the oxide radical through a so-called CF₂ flaking-off process to form CO_x (or carbonates) and fluorides (Eq. (3)); or it could be reduced by electron addition followed by fluoride expulsion and generation of graphitic/amorphous carbon (Eq. (4)).



Likewise, hexachlorobenzene dechlorination in presence of CaO might proceed by capture of an electron from the oxide surface to generate pentachlorobenzyl radical (Eq. (5)) or by substitution of one chlorine with oxide radical to form a pentachlorophenoxy radical (Eq. (6)) [31]:

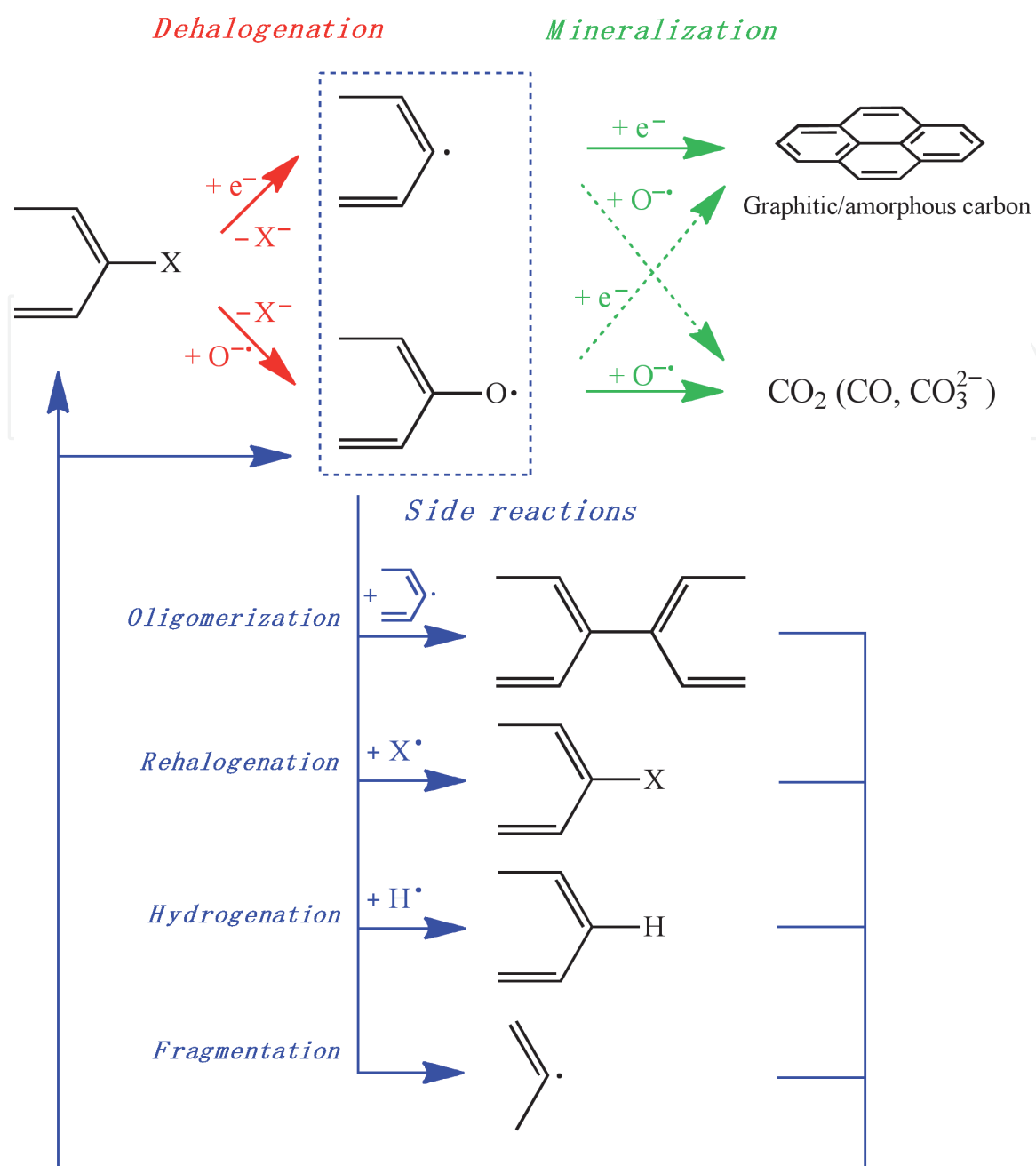


Figure 3.
 Generic reaction scheme of MCD process.



The mineralization process proceeds in similar fashion by addition of electrons to generate chlorides and graphitic/amorphous carbon, or by oxide radical attack to produce carbon oxides and chlorides.

It can be seen that generation of anion and organic radical as products of active species attack appears to be the general rule for MCD triggering processes. Then, the organic radicals are ultimately transformed into graphitic and amorphous carbon under the attack of electrons, or carbon oxides by addition of oxide radicals. Both redox processes occur at the same time, which is a distinct feature of mechanochemical reactions of organics [32]. Nevertheless, the mineralization process is not that plain (**Figure 3**). A number of secondary radical reactions have been observed in MCD systems, like de-/hydrogenation, oligomerization or radical addition, rehalogenation, etc. They are typical radical reaction that take place

among the organoradicals generated during the MCD process. Such by-products, however, are eventually destroyed following the mineralization pathways mentioned above.

Finally, it should be reminded that some types of reagent are per se highly reactive, so they do not necessitate of any mechanochemical activation and the effective mixing realized in the HEM is sufficient to induce the reaction. Obviously, the mineralization depends on the specific reagent. For instance, highly electropositive metals (Na, Mg, etc.) dehalogenate POPs, keeping their organic structure almost intact [33], while less electropositive zero valent metals such as iron produce graphitic/amorphous carbon, probably due to a less effective electron transfer rate, so that the original carbon skeleton is destroyed [17]. Another example is the notable efficacy of KOH to defluorinate perfluoroalkyl substances under HEM. After splitting the polar group, hydroxide anions sequentially substitute fluorides in the perfluorinated moiety, causing shortening of the organic chain by CF_2 flake-off to generate formate [34].

3. Application to stockpiled POPs

Laboratory results on MCD with various reagents can be easily applied to the disposal of stockpiled POPs, which often are a mixture of congeners and/or by-products of the manufacturing process. Anyway, such components have similar reactivity under HEM conditions. Preliminary scaling-up from laboratory-scale to large one can be done by taking advantage of the energetic invariance of mechanochemical reactions (as mentioned in subsection 1.2). Yet, pilot-scale testing could be necessary, especially if the experimental results are translated to a large milling equipment with different type of action, compared to the laboratory one. Choice of the reagent is a vital issue: it should be cheap, easily suppliable, durable, etc., but, its most important feature is efficacy. Efficacious reagent can be utilized with low reagent-to-pollutant ratio (which has a correlation of direct proportionality with MCD rate), so that the energy consumption per mass of treated POPs is contained. Unfortunately, most of the cheapest and largely available co-milling reagents (e.g., CaO , SiO_2 , Al_2O_3 , Fe, etc.) are not so efficacious and necessitate of large reagent ratios [14]. In order to obviate to this problem, two strategies have been proposed to dispose stockpiled POPs: multi-reagent approach and waste-to-materials one.

3.1 Multi-reagent approach

The multi-reagent approach is simply based on mixing two or more cheap co-milling reagents that, because of their specific physical or chemical properties, have a synergistic interaction that boosts the MCD rate. A typical example of taking advantage of physical properties is the case of mixing a soft reagent (e.g., zero valent metal, metal oxides) with a hard material (e.g., silica, alumina) to improve millability of the former. During HEM, soft material particles reach rapidly the critical size and cannot be further comminuted, therefore their specific surface remains unvaried during the MCD treatment. Moreover, if the reagent is plastic (like metals), the phenomenon of cold-welding hinders particle size reduction and thus the reactivity. Addition of a hard component to the mixture helps an effective fracture of the soft material particles, which are crushed on those of the hard component, forming smaller particles that cover the hard ones. An example is given by the case of zero valent iron (Mohs hardness of 4-5), which had a very poor effectiveness in destroying hexachlorobenzene (**Figure 4a**) [17]. Addition of quartz sand (Mohs hardness of 7), which itself performed better than iron in mineralizing

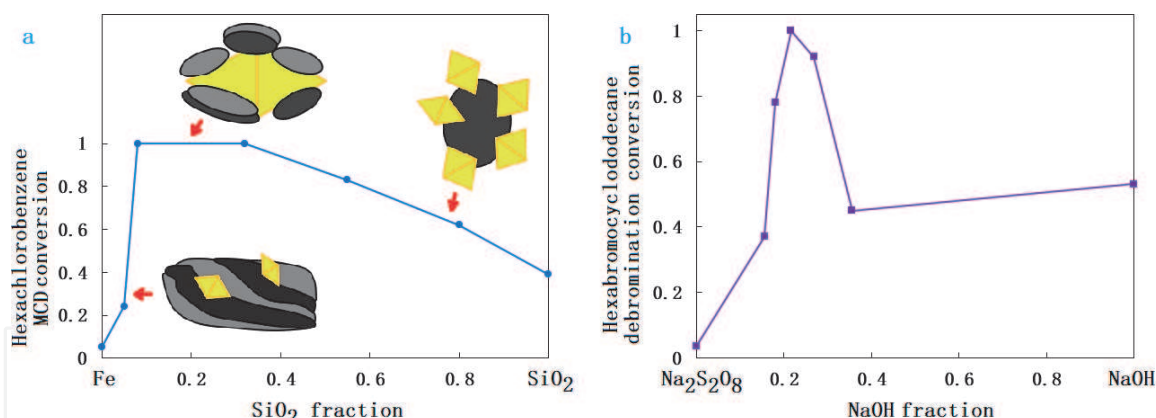


Figure 4. Influence of multi-reagent composition on two MCD systems: (a) hexachlorobenzene high-energy milled with Fe-SiO₂ [17], and (b) hexabromocyclododecane high-energy milled with Na₂S₂O₈-NaOH [35].

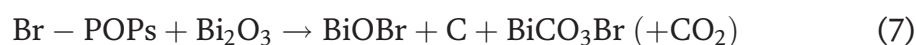
the haloorganic, enhanced notably degradation conversion of hexachlorobenzene. Varying the composition of the Fe-SiO₂ mixture, it can be seen that with low silica fractions, such mixture is still scantily effective, since the few SiO₂ crystals are incorporated into the iron cold-welded particles. Then, a range of maximum effectiveness is observed: within this interval, silica crystals are covered with tiny Fe particles, which are extremely reactive towards hexachlorobenzene. Further addition of silica has a negative effect because of redundant number of crystals that cover iron particles.

Additional component(s) can be used to activate or potentiate chemical reactivity of the main co-milling reagent. In this case the synergistic effect depends on the specific chemical properties of the components. For instance, persulfate (S₂O₈²⁻) can be directly activated by sole HEM to generate sulfate radicals (SO₄^{•-}) with strong oxidant power. Nevertheless, addition of strong bases or electron donors (e.g., Fe) has been proved to remarkably accelerate persulfate cleavage kinetics and, consequently, target organics mineralization rate. Experiments on hexabromocyclododecane MCD (**Figure 4b**) [35] revealed that the meager debromination capability of persulfate could be markedly improved by addition of ~20% NaOH. Then, excessive NaOH interfered with sulfate generation (likely by reacting with sulfate radical), reducing the debromination rate to levels close to those obtainable by treatment with sole NaOH.

3.2 Waste-to-materials approach

A serious issue of the MCD technology is production of large amounts of HEM residue. In general, the residue is mainly composed of unreacted reagent (since it is often employed in large excess to ensure a rapid and complete destruction of the treated POPs) and mineralization products (graphitic/amorphous carbon and halides). Although detoxified, such material is still an economic burden, because it must be disposed properly. The waste-to-materials approach is aimed to solve such problem by generating a useful material instead of waste. In fact, such method is based on the employment of highly reactive (and rather expensive, too) reagents in stoichiometric amounts that, however, can mineralize POPs and produce a value-added material at the same time.

So far, only two reagents have been ascertained to satisfy both such requirements, that is, bismuth oxide (Bi₂O₃) and lanthanum oxide (La₂O₃). These oxides were used in stoichiometric amount with some brominated and fluorinated POPs (i.e., metal-to-halogen atomic ratio of 1) to mechanosynthesize the corresponding oxyhalide [30, 36, 37]:



POPs were entirely mineralized in graphitic/amorphous carbon and CO_2 (mainly found as carbonate), thus ensuring detoxification. At the same time, an almost pure oxyhalide was obtained, after a short thermal treatment to remove C and reconvert the carbonate into the corresponding oxyhalide. Bismuth oxybromide is a material with excellent photocatalytic properties and the mechanosynthesized BiOBr was tested for removal of dye methyl orange in water under visible light irradiation. Lanthanum oxyhalides have excellent optical properties with actual application in X-ray imaging for medical devices (LaOBr) and potential one to produce doping host for transparent oxy-fluoride glass ceramics (LaOF). The production of such value-added materials could be a driving force to use toxic and obsolete POPs as source of halogens, achieving their detoxification.

4. Application to contaminated waste

MCD of POPs in contaminated waste is complicated by components of the waste matrix, making it almost unpredictable. Most of the components are mechanochemically activated by HEM, so they can interact with both POPs and co-milling reagent(s). Such interaction could be positive or negative. Components such as aluminosilicates, metal oxides, carbonates, etc. can be more or less activated, thus supporting the mineralization process. Moreover, some of these components are known to acquire improved catalytic properties during and after HEM, frequently facilitating POPs degradation [38]. On contrary, radical scavengers, like organic matter, hinder the degradation of haloorganics. In the following subsections, three examples are discussed: soils and sediments, fly ashes, and plastic waste.

4.1 Soils and sediments

In general, soils and sediments are suitable matrices to obtain effective mineralization of POPs by MCD. Providing an adequate amount of mechanical energy (e.g., prolonging HEM for sufficiently long time) ensures destruction of haloorganics due to a number of phenomena that might occur during the treatment [39]. In the first place, decrease of particle size and the consequent enlargement of specific surface enhance adsorption capacity of soils and sediments towards POPs. Clays play a key role in this: aside from particle breakage, HEM induces delamination of aluminosilicates, as well as partial amorphization of their surfaces, thus exposing more dangling bonds [40]. Hence, POPs can be adsorbed mainly by Van der Waals interactions, and possibly undergo catalytic degradation, thanks to surface acidity of clays [38].

More relevantly, aluminosilicates, metal oxides, carbonates, and other inorganic components of soil and sediments can be mechanochemically activated to generate active species (as elucidated in Section 2.2). These are deemed to be the major responsible of POPs mineralization in such kinds of waste [27, 39]. Organic matter, on the other hand, might facilitate adsorption and catalytic degradation of POPs onto particles, but surely scavenges radical species generated by the mechanical activation of inorganic components and co-milling reagent(s).

Since HEM can activate several mineral components of soil and sediments, MCD can be potentially realized by taking advantage of the “self-healing” properties of

these matrices. Indeed, mechanochemical treatment of such contaminated waste without addition of co-milling reagent suffices, in some cases, to achieve entire degradation of POPs [41]. Using a reagent, typically in large amount, insures complete mineralization of the haloorganics in a reasonable time and sensibly boosts the MCD rate [42], but usually transforms the contaminated matrix in a useless waste (whose amount is in general conspicuous). In order to avoid excessive usage of reagent, but to keep energy consumption contained, coupling of MCD with other technologies, such as thermal desorption [43] and biological treatment [44] was also experimented. Such approach is probably the most promising to avert extreme denaturation of the contaminated soils and sediments and allow their relocation in the original geological position.

4.2 Fly ashes

Fly ashes, with their high content of silicates, is another matrix that responds well to MCD treatment. However, because of the notable concentration of PCDD/Fs, such waste must be co-milled with a suitable amount of reagent to ensure entire mineralization of dioxins. Metal oxides (e.g., CaO, MgO), zero valent metals (e.g., Al), and their combination are inexpensive reagents that can efficaciously destroy PCDD/Fs, dioxin-like compounds, and their precursors [45, 46].

A key issue of fly ash detoxification by MCD is the compresence of carbon and chlorides, which determines a high potential for reformation of dioxins, also under low-temperature HEM conditions. In fact, de novo formation of PCDD/Fs was observed during the mechanochemical treatment [46, 47], in particular in presence of dioxin-formation catalysts, like copper compounds [45]. This might be caused by hits of the milling tools, which induce high local temperature increase, although for short time, on surfaces of the particle that are trapped between the hitting tools [45]. Despite such issue, it was proved that sufficiently long time milling, as well as temperature control, assures definitive dioxin removal and prevents their reformation [48]. This is owed to extensive amorphization of the fly ash components, especially carbonaceous matter, which averts de novo formation [45, 47].

4.3 Plastic waste

Some types of plastic waste contain high amounts of (brominated) flame retardants because of their utilization in electric and electronic devices. Removal of such chemicals from the polymeric matrix is a hard task. Nonetheless, it was realized by HEM with co-milling reagents such as zero valent metals (e.g., iron), metal oxides (e.g., CaO), plasma-formers (e.g., SiO₂), and their combination [49, 50]. Reagents with relatively high hardness (i.e., Fe and SiO₂) were found to be more efficacious to debrominate the plastic waste for the reason that they improve the mechanical and chemical degradation of the polymeric matrix, thus allowing a better contact between the reagent and the flame retardant.

Another relevant problem of brominated flame retardant MCD in plastic waste is the negative effect of the polymeric matrix, which slows down the degradation rate. Firstly, the impact energy is mainly absorbed by the matrix, and only a minor share is actually available for reagent activation and debromination of the POPs. Secondly, the mechanochemically activated radical species generated from the co-milling reagent are scavenged by the polymer, leading to chain shortening and other degradation phenomena of the plastic. In fact, it was verified experimentally that decabromodiphenyl ether mechanochemical degradation rate in polypropylene matrix co-milled with Fe-SiO₂ mixed reagent was 4.4 times slower than the rate observed for the pure flame retardant co-milled with the same reagent and under

similar HEM conditions [49]. Consequently, longer milling times and higher energy consumption are required for POPs mineralization in plastic waste, compared to the MCD of sole haloorganics.

5. Technological and economic considerations

The MCD technology can efficaciously destroy POPs, whether they are in almost pure form as (obsolete) chemicals, or they are present in environmental and waste matrices as contaminants. In both cases it is possible to transform the POPs in mineral form using HEM, often employing a co-milling reagent. Yet, effectiveness alone is not sufficient for large-scale application of this technology: greenness, safeness, and cost effectiveness are necessary requirements as well. Among non-thermal technologies, MCD is certainly one of the greenest, compared to other POPs destruction technologies. It does not require any solvent, since it is a solid-state treatment. And, it can be potentially utilized to prepare useful materials (instead of detoxified waste). More importantly, MCD phenomena occur only under the energy input provided by the HEM and can be terminated by simply turning off the milling device. Hence, in case of any non-mechanical accident (e.g., unintentional emission of toxic chemicals), the process can be interrupted immediately [37]. In addition, when treating hazardous waste with high potential of dioxin de novo formation, milling chamber temperature can be kept very close to environmental temperature to avert unintentional dioxin generation [48]. In sum, MCD is a safe and green technology.

Another substantial advantage of the MCD technology is the simplicity of the plant design and its versatility. **Figure 5** shows a block scheme of a mechanochemical plant for treatment of stockpiled POPs and POPs-contaminated waste. Stockpiled POPs are directly fed into the milling section, with a co-milling reagent. An air treatment section is included to prevent any emission due to volatilization of the POPs or their degradation by-products, as well as release of contaminated dust. MCD treatment of waste materials just includes (depending on the specific waste to be treated) a drying section to decrease humidity content, and a sieving section to remove debris that cannot be fed to the mill (e.g., stones in contaminated soil). Air deriving from each of these auxiliary sections is treated to avert possible POPs release in the environment. Obviously, such simple plant scheme can be used versatily to treat any type of POPs waste.

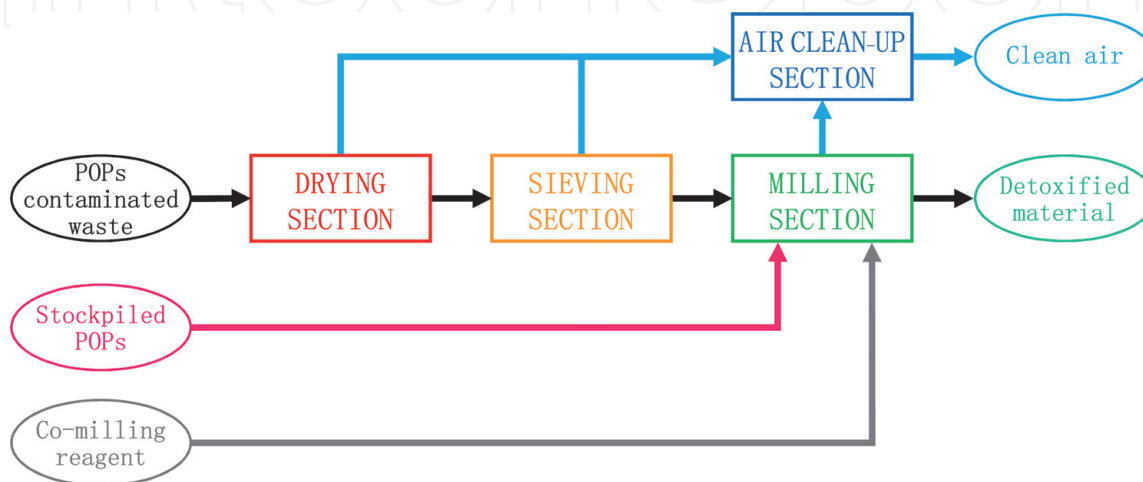


Figure 5.
Block scheme of a mechanochemical plant for stockpiled POPs and POPs contaminated waste treatment.

Despite the above-mentioned advantages, MCD technology is affected by two issues: noise and fine powder emission, which is related to worker and environmental safety, and high energy consumption, which is mainly an economic problem. The first one is easily overcome by constructing adequate containment facilities and utilizing individual protective devices inside such facilities. The issue of energy consumption can be managed by a few ways, which can be selected through an adequate economic assessment. Possible options comprise employment of large amounts of cheap and easily supplyable reagents to boost the MCD reaction rate, or, alternately, reduced quantities of strong/efficacious reagents; and coupling MCD with other non- or low-thermal technologies (e.g., biological treatment, thermal desorption, etc.).

Economic assessment is the sole way to evaluate effectively the various solutions for reduction of energy consumption, as well as other issues related to plant configuration. Typology of HEM device available on the market, electric energy cost, kind of the accessible reagent(s), and nature and concentration of the POPs waste are some of the major factors that have remarkable influence on the investment and operating cost of an MCD plant. Such factors depend more or less on the location, so it is not possible to execute a priori a generic economic assessment for this technology. But, a tentative economic feasibility study for MCD treatment for soil was carried out on the basis of data related to the US in 2016 [39]. This study highlighted that milling chamber volume is the key parameter that governs both investment and operating costs: the larger is the volume, the lower are the expenditures. Estimated operating costs were close to or less than those of the technologies currently available on the market for contaminated soil treatment. Actually, the chief economic issue of MCD technology is that most of HEM devices are relatively small, hence, it is for now more suitable to treat low volume waste, like stockpiled POPs. On the other hand, given the increasing interest in mechanochemical technology in various fields, it is expected that larger scale mills will be available on the market, so that MCD treatment of large volume waste such as contaminated matrices will become economical, too.

6. Conclusions

The present chapter illustrated that high energy ball milling of haloorganics in presence of co-milling reagent(s) can dismantle the structure of such organics to generate inorganic graphitic/amorphous carbon, carbon oxides, and halides. This transformation occurs at near-room temperature and pressure; therefore, the chance of unintentional formation of dioxins and dioxin-like compounds is almost null (if milling parameters are chosen judiciously). POPs can be efficaciously destroyed as both in almost pure form (e.g., stockpiled obsolete chemicals) and in contaminated matrices (e.g., soil, sediments, and hazardous waste). The high energy consumption and the lack of sufficiently large industrial high energy milling equipment hamper full-scale application of this technology. Nevertheless, specific approaches to reduce energy consumption, such as multireagent and waste-to-materials strategies, and the increasing interest for mechanochemical methods in other fields, which is pushing also the development of low-priced large-scale mills, will facilitate application of mechanochemical treatment to POPs destruction.

Conflict of interest

The authors declare no conflict of interest.

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References

- [1] USEPA. Reference Guide to Non-combustion Technologies for Remediation of Persistent Organic Pollutants in Soil, Second Edition – 2010. Available from: https://www.epa.gov/sites/production/files/2015-08/documents/pops_report_finalepa_sept2010.pdf [Accessed: 15 Nov 2021]
- [2] Boldyreva E. Mechanochemistry of inorganic and organic systems: What is similar, what is different? *Chemical Society Reviews*. 2013;**42**(18):7719
- [3] Takacs L. The historical development of mechanochemistry. *Chemical Society Reviews*. 2013;**42**(18):7649
- [4] Boldyrev V. Experimental methods in the mechanochemistry of inorganic solids. *Treatise on Materials Science & Technology*. 1983;**19**:185-223
- [5] Xie Y, Li Z. The development of mechanoluminescence from organic compounds: Breakthrough and deep insight. *Materials Chemistry Frontiers*. 2020;**4**(2):317-331
- [6] Baláž P, Achimovičová M, Baláž M, Billik P, Cherkezova-Zheleva Z, Criado JM, et al. Hallmarks of mechanochemistry: From nanoparticles to technology. *Chemical Society Reviews*. 2013;**42**(18):7571-7637
- [7] Boldyrev VV. Mechanochemical processes with the reaction-induced mechanical activation. Chemo-mechanochemical effect. *Russian Chemical Bulletin*. 2018;**67**(6):933-948
- [8] Boldyrev VV. Mechanochemistry and mechanical activation of solids. *Russian Chemical Reviews*. 2006;**75**(3):177-189
- [9] Lomovskiy I, Bychkov A, Lomovsky O, Skripkina T. Mechanochemical and size reduction machines for biorefining. *Molecules*. 2020;**25**(22):5345
- [10] Boldyrev VV, Tkačova K. Mechanochemistry of solids: Past, present, and prospects. *Journal of Materials Synthesis and Processing*. 2000;**8**(3/4):121-132
- [11] Delogu F, Deidda C, Mulas G, Schiffini L, Cocco G. A quantitative approach to mechanochemical processes. *Journal of Materials Science*. 2004;**39**(16/17):5121-5124
- [12] Santhanam PR, Dreizin EL. Predicting conditions for scaled-up manufacturing of materials prepared by ball milling. *Powder Technology*. 2012;**221**:403-411
- [13] Rowlands SA, Hall AK, McCormick PG, Street R, Hart RJ, Ebell GF, et al. Destruction of toxic materials. *Nature*. 1994;**367**(6460):223
- [14] Cagnetta G, Robertson J, Huang J, Zhang K, Yu G. Mechanochemical destruction of halogenated organic pollutants: A critical review. *Journal of Hazardous Materials*. 2016;**313**:85-102
- [15] Zhang K, Huang J, Wang H, Liu K, Yu G, Deng S, et al. Mechanochemical degradation of hexabromocyclododecane and approaches for the remediation of its contaminated soil. *Chemosphere*. 2014;**116**:40-45
- [16] Zhang W, Huang J, Yu G, Deng S, Zhu W. Mechanochemical destruction of dechlorane plus with calcium oxide. *Chemosphere*. 2010;**81**(3):345-350
- [17] Zhang W, Wang H, Jun H, Yu M, Wang F, Zhou L, et al. Acceleration and mechanistic studies of the mechanochemical dechlorination of HCB with iron powder and quartz sand. *Chemical Engineering Journal*. 2014;**239**:185-191
- [18] Tanaka Y, Zhang Q, Saito F. Mechanochemical dechlorination of

chlorinated compounds. *Journal of Materials Science*. 2004;**39**(16/17): 5497-5501

[19] Nomura Y, Fujiwara K, Terada A, Nakai S, Hosomi M. Mechanochemical degradation of γ -hexachlorocyclohexane by a planetary ball mill in the presence of CaO. *Chemosphere*. 2012;**86**(3):228-234

[20] Vakili M, Qin R, Cagnetta G, Huang J, Wang B, Yu G. Improved fractal kinetic model to predict mechanochemical destruction rate of organic pollutants. *Chemosphere*. 2021; **284**:131307

[21] Cagnetta G, Huang J, Wang B, Deng S, Yu G. A comprehensive kinetic model for mechanochemical destruction of persistent organic pollutants. *Chemical Engineering Journal*. 2016; **291**:30-38

[22] Dubinskaya AM. Transformations of organic compounds under the action of mechanical stress. *Russian Chemical Reviews*. 1999;**68**(8):637-652

[23] Pizzigallo MDR, Napola A, Spagnuolo M, Ruggiero P. Mechanochemical removal of organo-chlorinated compounds by inorganic components of soil. *Chemosphere*. 2004;**55**(11):1485-1492

[24] Ikoma T, Zhang Q, Saito F, Akiyama K, Tero-Kubota S, Kato T. Radicals in the mechanochemical dechlorination of hazardous organochlorine compounds using CaO nanoparticles. *Bulletin of the Chemical Society of Japan*. 2001;**74**(12):2303-2309

[25] Cagnetta G, Huang J, Lu M, Wang B, Wang Y, Deng S, et al. Defect engineered oxides for enhanced mechanochemical destruction of halogenated organic pollutants. *Chemosphere*. 2017;**184**:879-883

[26] Kaupp G. Mechanochemistry: The varied applications of mechanical

bond-breaking. *CrystEngComm*. 2009; **11**(3):388-403

[27] Hu A, Cagnetta G, Huang J, Yu G. Mechanochemical enhancement of the natural attenuation capacity of soils using two organophosphate biocides as models. *Journal of Hazardous Materials*. 2018;**360**:71-81

[28] Liu X, Zhang X, Zhang K, Qi C. Sodium persulfate-assisted mechanochemical degradation of tetrabromobisphenol A: Efficacy, products and pathway. *Chemosphere*. 2016;**150**:551-558

[29] Wang N, Lv H, Zhou Y, Zhu L, Hu Y, Majima T, et al. Complete defluorination and mineralization of perfluorooctanoic acid by a mechanochemical method using alumina and persulfate. *Environmental Science & Technology*. 2019;**53**(14): 8302-8313

[30] Cagnetta G, Zhang Q, Huang J, Lu M, Wang B, Wang Y, et al. Mechanochemical destruction of perfluorinated pollutants and mechanosynthesis of lanthanum oxyfluoride: A waste-to-materials process. *Chemical Engineering Journal*. 2017;**316**:1078-1090

[31] Deng S, Feng N, Kang S, Zhu J, Yu B, Chen J, et al. Mechanochemical formation of chlorinated phenoxy radicals and their roles in the remediation of hexachlorobenzene contaminated soil. *Journal of Hazardous Materials*. 2018;**352**:172-181

[32] Leitch JA, Browne DL. Mechanoredox chemistry as an emerging strategy in synthesis. *Chemistry – A European Journal*. 2021; **27**(38):9721-9726

[33] Birke V, Mattik J, Runne D. Mechanochemical reductive dehalogenation of hazardous polyhalogenated contaminants. *Journal*

- of Materials Science. 2004;**39**(16/17): 5111-5116
- [34] Zhang K, Cao Z, Huang J, Deng S, Wang B, Yu G. Mechanochemical destruction of Chinese PFOS alternative F-53B. *Chemical Engineering Journal*. 2016;**286**:387-393
- [35] Yan X, Liu X, Qi C, Lin C, Li P, Wang H. Disposal of hexabromocyclododecane (HBCD) by grinding assisted with sodium persulfate. *RSC Advances*. 2017;**7**(38): 23313-23318
- [36] Zhang K, Huang J, Wang H, Yu G, Wang B, Deng S, et al. Mechanochemical destruction of decabromodiphenyl ether into visible light photocatalyst BiOBr. *RSC Advances*. 2014;**4**(28): 14719-14724
- [37] Cagnetta G, Liu H, Zhang K, Huang J, Wang B, Deng S, et al. Mechanochemical conversion of brominated POPs into useful oxybromides: A greener approach. *Scientific Reports*. 2016;**6**(1):28394
- [38] Nasser A, Mingelgrin U. Mechanochemistry: A review of surface reactions and environmental applications. *Applied Clay Science*. 2012;**67-68**:141-150
- [39] Cagnetta G, Huang J, Yu G. A mini-review on mechanochemical treatment of contaminated soil: From laboratory to large-scale. *Critical Reviews in Environmental Science and Technology*. 2018;**48**(7-9):723-771
- [40] Ancona V, Di Leo P, Pizzigallo MDR. Sequestration of catechol and pentachlorophenol by mechanochemically treated kaolinite. *Clays and Clay Minerals*. 2016;**64**(5): 513-522
- [41] Wang H, Hwang J, Huang J, Xu Y, Yu G, Li W, et al. Mechanochemical remediation of PCB contaminated soil. *Chemosphere*. 2017;**168**:333-340
- [42] Zhang X, Liu X, Zhao J, Sun W, Li X, Li J, et al. NaOH-activated persulfate-assisted mechanochemical mechanism and removal of lindane from contaminated soil. *Journal of Environmental Chemical Engineering*. 2021;**9**(4):105391
- [43] Zhao Z, Ni M, Li X, Buekens A, Yan J. Combined mechanochemical and thermal treatment of PCBs contaminated soil. *RSC Advances*. 2017;**7**(34):21180-21186
- [44] Cagnetta G, Intini G, Liberti L, Boldyrev VV, Lomovski OI. The biomec process for mechanochemically assisted biodegradation of PCBs in marine sediments. *Journal of Soils and Sediments*. 2015;**15**(1):240-248
- [45] Cagnetta G, Hassan MM, Huang J, Yu G, Weber R. Dioxins reformation and destruction in secondary copper smelting fly ash under ball milling. *Scientific Reports*. 2016;**6**(1):22925
- [46] Chen Z, Mao Q, Lu S, Buekens A, Xu S, Wang X, et al. Dioxins degradation and reformation during mechanochemical treatment. *Chemosphere*. 2017;**180**:130-140
- [47] Peng Y, Buekens A, Tang M, Lu S. Mechanochemical treatment of fly ash and de novo testing of milled fly ash. *Environmental Science and Pollution Research*. 2018;**25**(19):19092-19100
- [48] Lu M, Lv T, Li Y, Peng Z, Cagnetta G, Sheng S, et al. Formation of brominated and chlorinated dioxins and its prevention during a pilot test of mechanochemical treatment of PCB and PBDE contaminated soil. *Environmental Science and Pollution Research*. 2017;**24**(24):20072-20081
- [49] Cagnetta G, Zhang K, Zhang Q, Huang J, Yu G. Mechanochemical pre-

treatment for viable recycling of plastic waste containing haloorganics. *Waste Management*. 2018;**75**:181-186

[50] Qin B, Lin M, Chen X, Xu Z, Fu Y, Hu J, et al. A novel approach for determining the accurate debromination time in the ball-milling process of nonmetallic particles from waste printed circuit boards by computation. *Journal of Hazardous Materials*. 2021; **410**:124611