Mechanistic Considerations on the Hydrodechlorination Process of Polychloroarenes

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Abstract

Defunctionalization of organochlorines through reductive dechlorination (also known as hydrodechlorination—replacement of chlorine atoms by hydrogen—is one of the main methodologies used in the detoxification of these harmful compounds. Most of the published papers on this particular matter focused on specific reagents, reaction conditions, and mainly result efficiency. Some of the authors were also concerned with reaction pathways (e.g., the order in which chlorine atoms were removed from a polychlorinated aromatic substrate—polychlorinated biphenyls, PCBs; polychlorinated dibenzo-p-dioxins, PCDDs; or polychlorinated dibenzofurans, PCDFs). However, the papers that dealt with the investigation of reaction mechanism were rather scarce. This chapter presents the advances made by researchers in understanding, from a mechanistic point of view, the hydrodechlorination process, along with our own assumptions. In doing so, it would be easier to predict the behavior of such compounds in a specific environment, showing more clearly the scope and limitations of each process, depending on the reaction conditions and reagents.

Keywords: hydrodechlorination, reaction mechanism, metal/hydrogen donor

1. Introduction

Most chlorinated and especially polychlorinated arenes (such as polychloro-dibenzo-p-dioxins 1, polychloro-dibenzofurans 2, or polychlorobiphenyls 3) are persistent organic pollutants (POPs) that are harmful to both man and the environment [1–5].
As a result, numerous techniques and procedures were implemented for their destruction/ degradation [6–11]. Initially, these procedures focused on the separation/_extraction of polychlorinated compounds and subsequent treatment. Nowadays, researchers value the in situ procedures the most, with the advantage of time and the economic aspects [7, 12–14]. Indeed, such compounds are stable molecules, which are resistant to hydrolysis, oxidation, and temperature changes, thus being difficult to degrade and showing long half-life times in the environment [15]. For example, dioxins could have atmospheric half-lives of 10–20 years, while, in soils, they can reach staggering values of up to 150 years.

This means that it might be an impossible task to deliver a dioxin-free Earth for future generations, but it lies on the present generation of scientists and engineers to try to do so. In that spirit, early attempts appealed to mankind’s most powerful discovery of destructive technology—fire [16]. In the early 1990s, most of the processes were thermal. But as it was soon discovered, these procedures were in fact a source for a de novo polychlorinated compound synthesis, the process by which dioxins are re-formed being investigated in the recent years [17–19]. Therefore, greater attention was focused on more chemical-based processes [6, 10, 20-23], along with microbial ones [24].

In particular, attention was focused on those procedures that were based on the combination of a metal and a hydrogen donor, processes that allowed the hydrodechlorination of the polychlorinated aromatic substrate to less toxic hydrocarbons [6–9, 14, 21–23]. Since these are among the most studied procedures in the past few years, we turned our attention to the particular reaction mechanism of the hydrodechlorination reaction. Indeed, understanding the reaction mechanism of a particular process is important in view of understanding the role played by each reagent but also in view of the predictive modeling of similar processes or the same process applied to various other substrates [25].

2. Proposed hydrodechlorination mechanisms—Literature survey

From an historical perspective, the formation of polychlorinated arenes (PCDDs, PCDFs, and PCBs) were first investigated [23, 26–34] and soon the catalytic role of various metals was understood [35–41]. If metals can do, they can also undo: indeed, they can effectively intervene in numerous defunctionalization processes, including hydrodechlorination [22, 42]. Since the process implies a reductive approach, researchers naturally oriented themselves toward reduction catalysts, such as Ru, Rh, Pd, or Pt. One remark must be made for the pioneering efforts of Ukisu and coworkers [43–46], who used a hydrogen donor (isopropanol),
NaOH, and Pd/C or Ru/C. Ukisu also provided the first insights on the possible reaction mechanism of the hydrodechlorination process, apprehending the intervention of atomic (or nascent) hydrogen:

\[
\begin{align*}
\text{CH}_3\text{CH(OH)CH}_3 & \rightarrow \text{CH}_3\text{C(O)CH}_3 + 2 \text{H}^- \\
\text{Ar}^-\text{Cl} + 2 \text{H}^- & \rightarrow \text{Ar}^-\text{H} + \text{HCl} \\
\text{HCl} + \text{NaOH} & \rightarrow \text{NaCl} + \text{H}_2\text{O}
\end{align*}
\]

Later on, Ukisu also tried to explain the intervention of the catalyst. Based on much earlier studies, Ukisu stated that the dehydrogenation of 2-propanol to acetone on rhodium complexes implied the elimination of a hydride ion \[47\]—Ukisu assumed that the α-hydrogen of isopropanol transfers to PCDD/F in the form of hydride, on the catalyst’s surface \[45, 46\], the reaction resembling to an aromatic nucleophilic substitution (Figure 1):

The trail of reduction catalysts is still a heavily investigated one. Ayame’s team started from the premise that, in the catalytic hydrodechlorination of monochlorobenzene, the hydride ion formed on the Pd surface spills over the alumina carrier surface and attacks the electron-deficient carbon of a monochlorobenzene adsorbed on Lewis acid sites of the alumina to produce a benzene molecule and a chloride ion. The chloride ion, which coordinated to a Lewis acid site, would be converted to hydrogen chloride in the reaction with H+ spilled over from the Pd surface \[48\]. However, most scientists were at that point more interested in the various pathways with regard to the reactivity of the differently positioned chlorine atoms \[49–54\]. Based on density functional theory calculations, rules of thumb for assessing the reductive dechlorination pathways of PCDDs were proposed \[55\]. These included “(1) the chlorine atoms in the longitudinal (1,4,6,9) positions are removed in preference to the chlorine atoms on lateral (2,3,7,8) positions; (2) the chlorine atom that has more neighboring chlorine atoms at ortho-, meta- and para-positions is to be eliminated; (3) reductive dechlorination prefers to take place on the benzene ring having more chlorine substitutions; and (4) a chlorine atom on the side of the longitudinal symmetry axis containing more chlorine atoms is preferentially eliminated” \[55\].

Anyway, one important aspect resulted from these studies, and that is, that adsorption phenomenon on the catalyst’s surface certainly play a role in the process \[49, 56, 57\]. Nevertheless, there was no consensus on the hydride transfer mechanism. If such transfer seems plausible when an alcohol is used as hydrogen donor \[43–46, 54\], and even if the formation of hydride

![Figure 1. Ukisu’s hydrodechlorination mechanism proposal [45, 46].](http://dx.doi.org/10.5772/intechopen.79083)
is postulated when molecular hydrogen is involved (through a heterolytic dissociation of H₂) [48], for Hirota and coworkers, the reaction mechanism involves a single-electron transfer (SET) step [58]. This team used triethylamine (instead of NaOH) for HCl trapping, its role being also an activator of the Pd/C-catalyzed hydrodechlorination process. Upon addition to the hydrodechlorination reaction mixture of small amounts of tetracyanoethylene or 7,7,8,8-tetractanoquinodimethane, which are well-known electron scavengers, the reaction was suppressed, suggesting thus a single-electron transfer (SET) mechanism (Figure 2).

The SET mechanism was reprised in several other papers in which the reaction conditions were more suitable for such a process: either photochemical [59, 60] or electrochemical [61]. The radicalic mechanism was also the center of hydrodechlorination processes, involving more active metals such as Na or K [62, 63], the main argument being the recorded formation of compounds such as quarterphenyls (as results of Fittig-Wurtz-type coupling). Another testimony for the single-electron transfer mechanism came from the study of a dual depolluting process for industrial wastewaters simultaneously polluted with chlorinated compounds and nitrites/nitrates. The authors observed a competition for electrons between reductive dechlorination and denitrification—NO₃⁻ is reduced to NH₄⁺ retarding the dechlorination due to the competition for electrons [64].

Nevertheless, the use of metals in the palette of hydrodechlorination processes took a new turn with used metals such as iron, zinc, magnesium, or calcium [65, 66]. Again, for these techniques, the electron transfer from the metal, with subsequent formation of nascent hydrogen through reaction with a proton donor prevailed, the process being summarized as:

\[
\text{Metal}^{0} + RX + H^{+} \rightarrow \text{Metal}^{+} + RH + X^{-}
\]

Among the metals tested, iron occupies a place of choice, used either alone [66–68] or in combination with other metals, especially Pd or Pt [57, 66, 69–74]. Three mechanisms were proposed to explain the observed dechlorination process [66]: one that involves direct electron transfer from Fe to the adsorbed alkyl halide (Fe⁰ + RX + H⁺ → Fe²⁺ + RH + X⁻) and other two that involve corrosion of Fe in water under anaerobic conditions (Fe⁰ + 2H₂O⁺ → Fe²⁺ + H₂ + 2OH⁻). The idea of using a bimetallic system, Pd along with Fe, made the process much more effective (Figure 3):
An interesting twist to the method is represented by the replacement of Fe with Mg in Fe/Pd [75–78], which is based on the following reasons: Mg has a relatively high oxidation potential (2.37 V; Fe has just 0.44 V), providing thus a greater thermodynamic force, and, while Fe tends to rather rapidly corrode, Mg can form a protective magnesium oxide shell (Figure 4).

Figure 3. Proposed surface reaction of PCBs with Fe/Pd nanoparticles [74].

Figure 4. Proposed mechanism for the dechlorination of PCBs over Mg/Pd [76].
A comparison of the hydrodechlorination effectiveness of Pd-deposited metals (Mg, Al, Mn, Zn, Fe, Sn, and Cu) was made by Yang et al. [79], who found that, in acidic aqueous solution, Mg/Pd present the highest reactivity, while at the other end are Sn and Cu that showed little to none dechlorination capability.

An important breakthrough in understanding the reaction mechanism of palladized magnesium-mediated hydrodechlorination was made by the Geiger team [80–83]. By working in pure methanol, the source of H₂ is the reaction between Mg and the alcohol (Mg⁰ + 2CH₃OH → Mg(CH₃O)₂ + H₂). The reaction exhibits pseudo-first-order kinetics, and the order of dechlorination rates of chlorine atoms in 100% methanol is ortho->para->meta-positions, which differ from that in water/methanol (9:1 v/v) or 100% water (para->meta->ortho-).

But, more importantly, the possible reaction mechanisms were discussed. This team proposed either an S₉N₁ mechanism or an S₉N₂ type of mechanism, in which a nucleophilic substitution, involving a radical intermediate, occurs. One major difference from classical S₉N₁ mechanism though is that the initiation step is the homolytic rupture of the C-Cl bond by either atomic hydrogen or hydride ion, with subsequent formation of aryl radical and HCl. In the more classical S₉N₂ mechanism, an aryl radical anion is formed due to hydride formed on bulk Pd. Basically, the three proposed mechanisms differ by the nature of the hydrogen involved: simple radicalic H (or atomic/nascent H), atomic H with an enhanced negative charge (a radical-anion H with a fractional negative charge – Hδ⁻), or a hydride ion (H⁻) (Figure 5).

Figure 5. Proposed mechanism for the dechlorination of PCBs by Mg/Pd in methanol by scheme A/B atomic hydrogen or “hydride-like” radicals, and scheme C hydride (H⁻ denotes both hydrogen and “hydride-like” species) [82].
An interesting assumption for the hydride mechanism is that the latter act as a nucleophile, which can transfer an electron to the aromatic chlorinated substrate, which will cause the elimination of a chlorine atom, leaving an aryl radical. This aromatic radical can quickly react with another H\(^-\). The charged biphenyl species can then transfer an electron to another PCB substrate, so that process can continue to propagate.

Among the reasons given for the possibility that all three mechanisms could occur are the fact that both atomic hydrogen and hydride species can be formed on Pd from molecular hydrogen and the lack of dimerization products (quarterphenyls) or additional chlorinated by-products. These mechanisms require initial adsorption of the PCBs onto the surface of the bimetallic system, then reaction at the interface of the palladium and graphite, limiting thus considerably the mobility of the aryl radical. This limited mobility and the abundance of atomic hydrogen, hydride-like radicals, and hydrides on the surface of the catalyst almost certainly allow for the reaction of the aryl radical and second nucleophilic hydrogen rather than two separate aryl radicals coming into contact [82].

For similar reasons, Ca was used instead of Mg [84–91]: not only does Ca have an even higher thermodynamic driving force when compared to Fe or Mg (0.44 V—Fe, 2.37—Mg, 2.87—Ca) but also CaCO\(_3\) coating both protect metallic Ca surface and is easily removed, allowing this procedure to be applied both ex situ and in situ (Figure 6).

Two potential mechanisms were proposed over the years: one purely radicalic, that involves nascent hydrogen, and one radicalic but which implies a pseudo-nucleophilic substitution mechanism in which the addition of electrons from calcium (Ca \(\rightarrow\) Ca\(^{2+}\) + 2\(\text{e}^-\)) transforms the aromatic ring into a radical-anion that rapidly expels chlorine atoms. The hydrogen atom on the hydroxyl group of the alcohol is then added to the radical anion yielding a hydrodechlorinated substrate and an alkoxide (Figure 7).

Upon working with deuterated methanol (CH\(_3\)OD), the authors observed both the formation of deuterodechlorination products and aryl dimers, suggesting the intermediacy of the radicalic aryl species [84].

Recent results based on zeta potential determinations and hydrodechlorination reactor’s internal pressure monitorization suggested that the radicalic process could be favored. Indeed, no pressure rise is a hint that molecular H\(_2\) is not formed in the reaction Ca\(^3+\) + 2CH\(_3\)OH \(\rightarrow\) Ca(CH\(_3\)O\(_2\)) + H\(_2\).

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Figure 6. Possible dechlorination pathway [88].
but instead nascent hydrogen is generated: Ca$^0 + 2$CH$_3$OH $\rightarrow$ Ca(CH$_3$O)$_2$ + 2[H]. Thus, the authors assumed that during the hydrodechlorination process of chloroanisole, the only proton source is the alcoholic (protic) hydrogen, the mechanism being most probably radicalic (the recorded formation of biphenyls as coupling products is an indication for this). Even at lower H$_2$ pressures, the hydrodechlorination of chloroanisole to anisole was achieved in at least 95% or even higher yields. The reaction efficiency implies that the transfer of atomic hydrogen (formed in calcium reaction with methanol) to catalyst surface (such as Pd/C) proceeded directly, without the formation of molecular hydrogen in solution. The surface of the catalyst showed differential conditions electrostatically, depending on the concentration of calcium as electron source (Figure 8).

Along with metallic Ca, other Ca compounds were tested in a hydrodechlorination process: Ca(OH)$_2$ [92], CaO [93–95] or CaSiO$_3$ [95]. Although most of these studies favored a radicalic mechanism, Gao and coworkers [95] discussed alternative pathways that involved either an electron transfer (with subsequent formation of a radical-anion that expels the chlorine anion and form the aryl radical) or a direct hydrogen transfer (in an S$_{N}$1-type mechanism). Based on calculations of the adiabatic electron affinities of PCDFs, the chloride ion dissociation yielding aryl radicals is considered the major pathway of chlorine abstraction [96]. Moreover, when traces of Cu are present, Ullman-type coupling products can be formed.

Figure 7. Hydrodechlorination mechanism following a pseudo-nucleophilic aromatic substitution [87].

Figure 8. Proposed reaction pathway and deuterium route from H$_3$C-OD to deuterodechlorination product [84].
Similar mechanistic observations were made by different teams that used metals other than Fe, Mg, or Ca. For example, for a zero-valent Zn hydrodechlorination of tetrachlorophenol, the intermediate in the reaction mechanism is again the aryl radical formed by expelling the chlorine anion from the initial radical-anion [97]. The latter is considered to be formed by the aromatic ring quenching of an electron from zero-valent Zn \((1/2\text{Zn}^0 \rightarrow 1/2\text{Zn}^{2+} + 1\text{e}^-)\) (Figure 9).

Analogous conclusions were drawn for bimetallic systems such as Fe/Ni [98], Mg/Zn [99], or Ni/Mo [100].

Another approach was taken by Lim and coworkers when comparing the performances of Pd/Fe nanoparticles with other bimetallic systems such as Pt/Fe, Ni/Fe, Cu/Fe, and Co/Fe nanoparticles during the hydrodechlorination of trichlorophenol [72], since the process was studied in an aqueous environment. Starting from the premise that chlorinated organic compound treatment in water were reduced according to three different mechanisms—(1) direct reduction on fresh zero-valent iron (ZVI) surface, (2) reduction by ferrous iron, and (3) reduction by \(\text{H}_2\) through catalysis [101]—the authors assumed that the bimetal/water system, having a stronger reductive ability, allowed more easily the formation of an activated reducing species, atomic hydrogen (\(\text{H}^*\)) (Figure 10).

![Figure 9. Hydrodechlorination of tetrachlorophenol with zero-valent Zn [97].](image)

![Figure 10. Schematic of proposed catalytic hydrodechlorination mechanism of chlorophenols over nanoscale Pd/Fe (a) production of atomic hydrogen and (b) surface-mediated hydrodechlorination of chlorophenols on Pd surface [72].](image)
The production of $H^*$ may follow two routes: catalyzed decomposition of $H_2$ gas to $H^*$ and electron abstraction by $H^+$. For this particular process, the authors considered more plausible electrophilic addition, followed by subsequent elimination of HCl through a dehydrodechlorination process.

But when considering that the degradation process occurs in water or even in supercritical water, true aromatic nucleophilic substitution of the chlorine atoms (and their replacement by $-OH$ moieties) could be considered [102, 103]. In just supercritical water and under oxidative conditions, the hydroxylated PCB only accounted for less than 10% of the reaction mass, while for alkaline, non-oxidative conditions the formation of hydroxylated PCBs could nearly close the mass balance in the early stage of PCB degradation [102]. The authors concluded that the formation of comparable amounts of PCDFs (requiring two oxygen substitution steps under preservation of both aromatic systems) in the experiments under oxidative and non-oxidative, alkaline conditions indicated that under both treatments, an oxygen substitution under preservation of the aromatic rings is the major initial step. On the other hand, hydroxylated PCBs are less susceptible to nucleophilic substitution compared to PCBs due to the electron-donating effect of the $-OH$ group. Therefore, under the alkaline, non-oxidative conditions, the initial degradation products (hydroxylated PCBs) are less reactive toward further degradation compared to the starting compounds (PCBs). But when the treatment occurs in the presence of $Co_3O_4$, the reaction pathway, involving the formation of chlorophenolate and dichlorophenolate, is similar to the Mars Van Krevelen mechanism [104]. Nucleophilic substitution of the chlorine atom occurs through attack of the lattice oxygen atoms ($O_2^-$) and a Co-Cl bond is formed, yielding chlorophenolate and dichlorophenolate as partial oxidation products. Similar reaction routes have been reported for the formation of phenolates during the degradation of HCB over $Al_2O_3$ [105] and the degradation of chlorobenzene over iron and titanium oxide catalysts [106] (Figure 11).

An even more suggestive hint of a nucleophilic substitution of chlorine atoms was represented for the catalytic degradation of PCBs with Ni complexes [107]. A simplified model of the successive reactions was presented, clearly suggesting in steps 3 and 4 a nucleophilic attack of a hydride ion upon the aromatic chlorinated substrate:

\[
\text{Ivr4321} \]

1. Ligand displacement:

\[
NiL_4 \rightarrow NiL_3 + L
\]

Figure 11. Oxidative attack mechanism for 1,2,4-trichlorobenzene degradation over cabbage-like $Co_3O_4$ [103].
2. Oxidative addition:
\[ \text{C}_{12}\text{Cl}_{10} + \text{NiL}_3 \rightarrow \text{C}_{12}\text{Cl}_9\text{NiL}_2\text{Cl} + \text{L} \]

3. Reductive elimination:
\[ \text{C}_{12}\text{Cl}_9\text{NiL}_2\text{Cl} + \text{H}^- + \text{L} \rightarrow \text{C}_{12}\text{Cl}_9\text{H} + \text{Cl}^- + \text{NiL}_3 \]

4. Partial dechlorination:
\[ \text{C}_{12}\text{Cl}_{10} + \text{nH}^- \rightarrow \text{C}_{12}\text{Cl}_{10-n}\text{H}_n + \text{nCl}^- \]

5. Complete dechlorination
\[ \text{C}_{12}\text{Cl}_{10} + 10\text{H}^- \rightarrow \text{C}_{12}\text{H}_{10} + 10\text{Cl}^- \]

A study of polychlorinated biphenyls’ reactivity in nucleophilic versus electrophilic substitutions demonstrated that SN reactions are of the hard acid-hard base type [108], having a lesser probability to occur.

Meanwhile, several other procedures seem to favor the radicalic hypothesis: for example, PCBs are more rapidly hydrodechlorinated when in the presence of a mixture of persulfate and quinines, a system known to generate free radicals [109]. Ultrasonication of a polychlorinated biphenyls also seem to lead to a radicalic mechanism, since the first step is presented as a homolytic cleavage of the C-Cl bond [110].

Special attention must also be given to a new entry in panoply of degradation procedures: the mechanochemical approach in the hydrodechlorination/destruction of polychlorinated arenes [11]. The mechanochemical reactions imply activation of the chemical bonds through deformation under mechanical stress, leading to their rupture and subsequent reformation [111]. Even if most mechanochemical processes applied to polychlorinated aromatic compounds implied radical intermediates, it was not uncommon to consider the formation of ionic species. For example, Birke et al. suggested one reductive dechlorination process with alkali metals in the presence of hydrogen donors—the formation in the first step of a radical anion [112] (Figure 12):

Generally, the activation of the substrate takes place on the solid reagent, one of the most used being CaO [113–117]. After the cleavage of CaO crystals and the exposure of new surfaces, the

\[
\text{Ar}^\text{-Cl} + \text{M}^+ \rightarrow \text{Ar}^\text{-Cl} + \text{M}^+ \\
\text{Ar}^\text{-H} + \text{R}^\text{-H} \rightarrow \text{Ar}^\text{-H} + \text{R}^\text{-H} \\
\text{R}^\text{-M}(\text{R}^\text{-M}^+) \rightarrow \text{R}^\text{-M}(\text{R}^\text{-M}^+)
\]

**Figure 12.** Reductive dechlorination of chlorinated aromatics (arylchlorides, Ar-Cl) by alkali metals in solution in the presence of hydrogen donors (R-H) like ethers or alcohols [112].
oxide ions are induced by mechanical activation to transfer an electron to pollutant’s carbon atoms, thus generating an anion radical [11] (Figure 13).

The process does not even need the presence of a H donor, ultimate products being either oxidation one (e.g. CO₂) or of a graphitic nature – through carbonization processes [117] (Figure 14).

The addition to the reaction mixture of a good radical generator, such as SiO₂, accelerates the carbonization process [115, 118, 119]. The presence of zero-valent metals in the ball-mill device may induce the formation of organometallic compounds of a Grignard type [120, 121].

3. Concluding remarks

Understanding the mechanism of a hydrodechlorination process is important only if the degradation products are organic compounds of lesser toxicity. If the destruction is complete, yielding CO₂ and various carbonaceous structures, the mechanism is less important.

Upon the main two hydrodechlorination paths (radicalic versus ionic), it can be observed that both may be encountered, but there seem to be more evidence for the first, although in many cases the first step is the formation of radical anion through single-electron transfer. The type of activation (chemical, photochemical, thermal, cavitation, or mechanochemical)
is instrumental in the type of reaction mechanism. Reaction conditions as well as reagents are also decisive in the type of mechanism the process will adopt. But through a better understanding of these aspects, a grasp on the reaction mechanism could be taken, and thus it could be possible to not only anticipate the advantages but also the limitations of a particular process. For example, when treating polluted soils with a mixture of Al and CaO, according to this type of mechanism, the presence of a hydrogen donor, namely soil moisture, is necessary [122]. Thus, it could be predicted that a soil too dry would be impracticable for treatment. On the other hand, many metallic systems can be effective even in the presence of large quantities of water [123], and even in aqueous media [124]. At the same time, the importance of the chemisorptions of hydrogen ions or nascent hydrogen on metallic surfaces has been understood, and the process can somehow be improved by the addition of stabilizers such as polyvinylpyrrolidone [125] or even biochar [126].

Thus, it will become easier to predict the successful outcome of a certain treatment process for a certain contaminated matrix (fly ash, soil, groundwater or wastewater) by considering the metallic system chosen, the moisture content (or the addition of any other potential hydrogen donor, in the form of an organic solvent—mainly alcohols), and the presence of a sorption substrate for the different forms of hydrogen transfer involved (even if it is only fly ash).

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**References**

[1] Carpenter DO. Polychlorinated biphenyls (PCBs): Routes of exposure and effects on human health. Reviews on Environmental Health. 2006;21(1):1-24

[2] Ni HG, Zeng H, Tao S, Zeng EY. Environmental and human exposure to persistent halogenated compounds derived from e-waste in China. Environmental Toxicology and Chemistry. 2010;29(6):1237-1247

[3] White SS, Birnbaum LS. An overview of the effects of dioxins and dioxin-like compounds on vertebrates, as documented in human and ecological epidemiology. Journal of Environmental Science and Health, Part C. 2009;27(4):197-211
[4] Annamalai J, Namisivayam V. Endocrine disrupting chemicals in the atmosphere: Their effects on humans and wildlife. Environment International. 2015;76:78-97

[5] Hens B, Hens L. Persistent threats by persistent pollutants: Chemical nature, concerns and future policy regarding PCBs—What are we heading for? Toxics. 2018;6:1-21

[6] Kulkarni PS, Crespo JG, Afonso CAM. Dioxins sources and current remediation technologies—A review. Environment International. 2008;34:139-153

[7] Gomes HI, Dias-Ferreira C, Ribeiro AB. Overview of in situ and ex situ remediation technologies for PCB-contaminated soils and sediments and obstacles for full-scale application. Science of the Total Environment. 2013;445-446:237-260

[8] Huang B, Lei C, Wei C, Zeng G. Chlorinated volatile organic compounds (Cl-VOCs) in environment – Sources, potential human health impacts, and current remediation technologies. Environment International. 2014;71:118-138

[9] Dai C, Zhou Y, Peng H, Huang S, Qin P, Zhang J, Yang Y, Luo L, Zhang X. Current progress in remediation of chlorinated volatile organic compounds: A review. Journal of Industrial and Engineering Chemistry. 2018;62:106-119

[10] Fan G, Wang Y, Fang G, Zhu X, Zhou D. Review of chemical and electrokinetic remediation of PCBs contaminated soils and sediments. Environmental Science: Processes and Impacts. 2016;18(9):1140-1156

[11] 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

[12] Frascari D, Zanaroli G, Danko AS. In situ aerobic co-metabolism of chlorinated solvents: A review. Journal of Hazardous Materials. 2015;283:382-399

[13] Yang J, Meng L, Guo L. In situ remediation of chlorinated solvent-contaminated groundwater using ZVI/organic carbon amendment in China: Field pilot test and full-scale application. Environmental Science and Pollution Research. 2018;25(6):5051-5062

[14] Zhang M, Zhao D. In situ dechlorination in soil and groundwater using stabilized zero-valent iron nanoparticles: Some field experience on effectiveness and limitations in “Novel Solutions to Water Pollution”, ACS Symposium Series, Vol. 1123, Chapter 6, pp. 79-96; 2013

[15] Sinkkonen S, Paasivirta J. Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling. Chemosphere. 2000;40:943-949

[16] Poillon F. Dioxin Treatment Technologies. Congress of the United States, Office of Technology Assessment. Washington DC, USA: DIANE Publishing; 1991

[17] Zhang M, Buekens A. De novo synthesis of dioxins: A review. International Journal of Environment and Pollution. 2016;60(1):63-110
[18] Zhou H, Meng A, Long Y, Li Q, Zhang Y. A review of dioxin-related substances during municipal solid waste incineration. Waste Management. 2015;36:106-118

[19] Vallejo M, Fresnedo San Roman M, Ortiz I, Irabien A. Overview of the PCDD/Fs degradation potential and formation risk in the application of advanced oxidation processes (AOPs) to wastewater treatment. Chemosphere. 2015;118:44-56

[20] Tong M, Yuan S. Physiochemical technologies for HCB remediation and disposal: A review. Journal of Hazardous Materials. 2012;229-230:1-14

[21] Guemiza K, Coudert L, Metahni S, Mercier G, Besner S, Blais JF. Treatment technologies used for the removal of As, Cr, Cu, PCP and/or PCDD/F from contaminated soil: A review. Journal of Hazardous Materials. 2017;333:194-214

[22] Modak A, Maiti D. Metal catalyzed defunctionalization reactions. Organic and Biomolecular Chemistry. 2016;14:21-35

[23] Altarawneh M, Dlugogorski BZ, Kennedy EM, Mackie JC. Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). Progress in Energy and Combustion Science. 2009;35:245-274

[24] Bhatt P, Kumar MS, Mudliar S, Chakrabarti T. Biodegradation of chlorinated compounds—a review. Critical Reviews in Environmental Science and Technology. 2007;37(2):165-198

[25] Bess EN, Bischoff AJ, Sigman MS. Designer substrate library for quantitative, predictive modeling of reaction performance. Proceedings of the National Academy of Science. 2014;111(41):14698-14703

[26] Addink R, Olie K. Mechanisms of formation and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans in heterogeneous systems. Environmental Science and Technology. 1995;29:1425-1435

[27] Schoonenboom MH, Zoetemeijer HE, Olie K. Dechlorination of octachlorodibenzo-p-dioxin and octachlorodibenzofuran on an alumina support. Applied Catalysis B-Environmental. 1995;6:11-20

[28] Huang H, Buekens A. On the mechanisms of dioxin formation in combustion processes. Chemosphere. 1995;31(9):4099-4117

[29] Addink R, Govers HAJ, Olie K. Isomer distribution of polychlorinated dibenzo-p-dioxins/dibenzofurans formed during de novo synthesis on incinerator fly ash. Environmental Science and Technology. 1998;32(13):1888-1893

[30] Altwicker ER, Milligan MS. Formation of dioxins: Competing rates between chemically similar precursors and de novo reactions. Chemosphere. 1993;27(1-3):301-307

[31] Altwicker ER. Relative rates of formation of polychlorinated dioxins and furans from precursor and de novo reactions. Chemosphere. 1996;33(10):1897-1904
[32] Milligan MS, Altwicker ER. Mechanistic aspects of the de novo synthesis of polychlorinated dibenzo-p-dioxins and furans in fly ash from experiments using isotopically labeled reagents. Environmental Science and Technology. 1995;29(5):1353-1358

[33] Ritter ER, Bozzelli JW. Pathways to chlorinated dibenzodioxins and dibenzofurans from partial oxidation of chlorinated aromatics by OH radical: Thermodynamics and kinetic insights. Combustion Science and Technology. 1994;101:153-169

[34] Tuppurainen K, Halonen I, Ruokojärvi P, Tarhanen J, Ruuskanen J. Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: A review. Chemosphere. 1998;36(7):1493-1511

[35] Halonen I, Tuppurainen K, Ruuskanen J. Formation of aromatic chlorinated compounds catalyzed by copper and iron. Chemosphere. 1997;34(12):2649-2662

[36] Hinton WS, Lane AM. Characterisation of municipal solid waste incinerator fly ash promoting the formation of polychlorinated dioxins. Chemosphere. 1991;22(5-6):473-483

[37] Manninen H, Perkiö A, Vartiainen T, Ruuskanen J. Formation of PCDD/PCDF: Effect of fuel and fly ash composition on the formation of PCDD/PCDF in the co-combustion of refuse-derived and packaging-derived fuels. Environmental Science and Pollution Research. 1996;3(3):129-134

[38] Gullett B, Bruce K, Beach L, Drago A. Mechanistic steps in the production of PCDD and PCDF during waste combustion. Chemosphere. 1992;25(7-10):1387-1392

[39] Hinton WS, Lane AM. Synthesis of polychlorinated dioxins over MSW incinerator fly ash to identify catalytic species. Chemosphere. 1991;23(7):831-840

[40] Gullett B, Bruce K, Beach L. The effect of metal catalysts on the formation of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran precursors. Chemosphere. 1990;20(10-12):1945-1952

[41] Addink R, Schoonenboom MH. Metals as catalysts during the formation and decomposition of chlorinated dioxins and furans in incineration processes. Journal of the Air and Waste Management Association;48(1997):101-105

[42] Keane MA. Supported transition metal catalysts for hydrodechlorination reactions. ChemCatChem. 2011;3(5):800-821

[43] Ukisu Y, Iimura S, Uchida R. Catalytic dechlorination of polychlorinated biphenyls with carbon-supported noble metal catalysts under mild conditions. Chemosphere. 1996;33(8):1523-1530

[44] Ukisu Y, Kameoka S, Miyadera T. Catalytic dechlorination of aromatic chlorides with noble-metal catalysts under mild conditions: Approach to practical use. Applied Catalysis B: Environmental. 2000;27:97-104

[45] Ukisu Y, Miyadera T. Hydrogen-transfer hydrodechlorination of polychlorinated dibenzo-p-dioxins and dibenzofurans catalyzed by supported palladium catalysts. Applied Catalysis B: Environmental. 2003;40:141-149
[46] Ukisu Y, Miyadera T. Dechlorination of dioxins with supported palladium catalysts in 2-propanol solution. Applied Catalysis A: General. 2004;271:165-170

[47] Charman HB. Hydride transfer reactions catalysed by metal complexes, Journal of the Chemical Society B: Physical Organic. 1967;0:629-632

[48] Hashimoto Y, Uemichi Y, Ayame A. Low-temperature hydrodechlorination mechanism of chlorobenzenes over platinum-supported and palladium-supported alumina catalysts. Applied Catalysis A: General. 2005;287:89-97

[49] Choi H, Al Abed SR, Agarwal S. Catalytic role of palladium and relative reactivity of substituted chlorines during adsorption and treatment of PCBs on reactive activated carbon. Environmental Science and Technology. 2009;43:7510-7515

[50] Fueno H, Tanaka K, Sugawa S. Theoretical study of the dechlorination reaction pathways of octachlorodibenzo-p-dioxin. Chemosphere. 2002;48:771-778

[51] Nomiyama K, Tanizaki T, Ishibashi H, Arizono K, Shinohara R. Production mechanism of hydroxylated PCBs by oxidative degradation of selected PCBs using TiO$_2$ in water and estrogenic activity of their intermediates. Environmental Science and Technology. 2005;39:8762-8769

[52] Miao XS, Chu SG, Xu XB. Degradation pathways of PCBs upon UV irradiation in hexane. Chemosphere. 1999;39(10):1639-1650

[53] Chen JR, Kim D, Park JS, Gil KI, Yen TF. Reductive dechlorination of polychlorinated biphenyls (PCBs) by ultrasound-assisted chemical process (UACP). Environmental Earth Sciences. 2013;69:1025-1032

[54] Zhang F, Chen J, Zhang H, Ni Y, Liang X. The study on the dechlorination of OCDD with Pd/C catalyst in ethanol–water solution under mild conditions. Chemosphere. 2007;68:1716-1722

[55] Lu GN, Dang Z, Fennell DE, Huang W, Li Z, Liu CQ. Rules of thumb for assessing reductive dechlorination pathways of PCDDs in specific systems. Journal of Hazardous Materials. 2010;177:1145-1149

[56] Choi H, Al Abed SR. PCB congener sorption to carbonaceous sediment components: Macroscopic comparison and characterization of sorption kinetics and mechanism. Journal of Hazardous Materials. 2009;165:860-866

[57] Choi H, Agarwal S, Al Abed SR. Adsorption and simultaneous dechlorination of PCBs on GAC/Fe/Pd: Mechanistic aspects and reactive capping barrier concept. Environmental Science and Technology. 2009;43:488-493

[58] Sajiki H, Kume A, Hattori K, Hirota K. Mild and general procedure for Pd/C-catalyzed hydrodechlorination of aromatic chlorides. Tetrahedron Letters. 2002;43:7247-7250

[59] Izadifard M, Achari G, Langford CH. The pathway of dechlorination of PCB congener by a photochemical chain process in 2-propanol: The role of medium and quenching. Chemosphere. 2008;73:1328-1334
[60] Izadifard M, Langford CH, Achari G. Photocatalytic dechlorination of PCB 138 using leuco-methylene blue and visible light; reaction conditions and mechanisms. Journal of Hazardous Materials. 2010;181:393-398

[61] Matsunaga A, Yasuhara A. Dechlorination of PCBs by electrochemical reduction with aromatic radical anion as mediator. Chemosphere. 2005;58:897-904

[62] Noma Y, Mitsuhara Y, Matsuyama K, Sakai SI. Pathways and products of the degradation of PCBs by the sodium dispersion method. Chemosphere. 2007;68:871-879

[63] Miyoshi K, Nishio T, Yasuhara A, Morita M. Dechlorination of hexachlorobiphenyl by using potassium-sodium alloy. Chemosphere. 2000;41:819-824

[64] Cao L, Sun W, Zhang Y, Feng S, Dong J, Zhang Y, Rittmann BE. Competition for electrons between reductive dechlorination and denitrification. Frontiers of Environmental Science and Engineering. 2017;11(6):14

[65] Suresh S. Reductive remediation of pollutants using metals. The Open Waste Management Journal. 2009;2:6-16

[66] Wu BZ, Chen HY, Wang SJ, Wai CM, Liao W, Chiu KH. Reductive dechlorination for remediation of polychlorinated biphenyls. Chemosphere. 2012;88:757-768

[67] Shih YH, Hsu CY, Su YF. Reduction of hexachlorobenzene by nanoscale zero-valent iron: Kinetics, pH effect, and degradation mechanism. Separation and Purification Technology. 2011;76:268-274

[68] Varanasi P, Fullana A, Sidhu S. Remediation of PCB contaminated soils using iron nanoparticles. Chemosphere. 2007;66:1031-1038

[69] Kim JH, Tratnyek PG, Chang YS. Rapid dechlorination of polychlorinated dibenzop-p-dioxins by bimetallic and nanosized zerovalent iron. Environmental Science and Technology. 2008;42:4106-4112

[70] Fang Y, Al-Abed SR. Dechlorination kinetics of monochlorobiphenyls by Fe/Pd: Effects of solvent, temperature, and PCB concentration. Applied Catalysis B: Environmental. 2008;78:371-380

[71] Colombo A, Dragonetti C, Magni M, Roberto D. Degradation of toxic halogenated organic compounds by iron-containing mono-, bi- and tri-metallic particles in water. Inorganica Chimica Acta. 2015;431:48-60

[72] Zhou T, Li Y, Lim TT. Catalytic hydrodechlorination of chlorophenols by Pd/Fe nanoparticles: Comparisons with other bimetallic systems, kinetics and mechanism. Separation and Purification Technology. 2010;76:206-214

[73] O’Carroll D, Sleep B, Krol M, Boparai H, Kocur C. Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. Advances in Water Resources. 2013;51:104-122

[74] Venkatachalam K, Arzuaga X, Chopra N, Gavalas VG, Xu J, Bhattacharyya D, Hennig B, Bachas LG. Reductive dechlorination of 3,30,4,40-tetrachlorobiphenyl (PCB77) using...
palladium or palladium/iron nanoparticles and assessment of the reduction in toxic potency in vascular endothelial cells. Journal of Hazardous Materials. 2008;159:483-491

[75] Agarwal S, Al Abed SR, Dionysiou DD, Graybill E. Reactivity of substituted chlorines and ensuing dechlorination pathways of select PCB congeners with Pd/Mg bimetallics. Environmental Science and Technology. 2009;43:915-921

[76] Agarwal S, Al Abed SR, Dionysiou DD. Enhanced corrosion-based Pd/Mg bimetallic systems for dechlorination of PCBs. Environmental Science and Technology. 2007;41:3772-3727

[77] Agarwal S, Al Abed SR, Dionysiou DD. Impact of organic solvents and common anions on 2-chlorobiphenyl dechlorination kinetics with Pd/Mg. Applied Catalysis B: Environmental. 2009;92:17-22

[78] Agarwal S, Al Abed SR, Dionysiou DD. A feasibility study on Pd/Mg application in historically contaminated sediments and PCB spiked substrates. Journal of Hazardous Materials. 2009;172:1156-1162

[79] Yang B, Deng S, Yu G, Zhang H, Wu J, Zhuo Q. Bimetallic Pd/Al particles for highly efficient hydrodechlorination of 2-chlorobiphenyl in acidic aqueous solution. Journal of Hazardous Materials. 2011;189:76-83

[80] Coutts JG, Devor RW, Aitken B, Hampton MD, Quinn JW, Clausen CA, Geiger CL. The use of mechanical alloying for the preparation of palladized magnesium bimetallic particles for the remediation of PCBs. Journal of Hazardous Materials. 2011;192:1380-1387

[81] DeVor R, Carvalho-Knighton K, Aitken B, Maloney P, Holland E, Talalaj L, Fidler R, Elsheimer S, Clausen CA, Geiger CL. Dechlorination comparison of mono-substituted PCBs with Mg/Pd in different solvent systems. Chemosphere. 2008;73:896-900

[82] DeVor R, Carvalho-Knighton K, Aitken B, Maloney P, Holland E, Talalaj L, Elsheimer S, Clausen CA, Geiger CL. Mechanism of the degradation of individual PCB congeners using mechanically alloyed Mg/Pd in methanol. Chemosphere. 2009;76:761-766

[83] Maloney P, DeVor R, Novaes-Card S, Saitta E, Quinn J, Clausen CA, Geiger CL. Dechlorination of polychlorinated biphenyls using magnesium and acidified alcohols. Journal of Hazardous Materials. 2011;187:235-240

[84] Mitoma Y, Katayama Y, Simion AM, Harada H, Kakeda M, Egashira N, Simion C. Considerations on on the mechanism of Ca/ethanol/Pd/C assisted hydrodechlorination of chlorinated aromatic substrates. Chemosphere. 2016;164:92-97

[85] Mitoma Y, Simion AM, Mallampati SR, Miyata H, Kakeda M, Simion C. Hydrodechlorination of PCDD/PCDF/PCB contaminants by simple grinding of contaminated soils with a nano-size calcium reagent. Environmental Progress and Sustainable Energy. 2016;35(1):34-40

[86] Simion AM, Miyata H, Kakeda M, Egashira N, Mitoma Y, Simion C. Direct and complete cleansing of transformer oil contaminated by PCBs. Separation and Purification Technology. 2013;103:267-272
[87] Simion AM, Kakeda M, Egashira N, Mitoma Y, Simion C. A direct method for the decontamination of a fly ash amended wet soil, artificially polluted with dioxins. Central European Journal of Chemistry. 2012;10(5):1547-1555

[88] Mitoma Y, Kakeda M, Simion AM, Egashira N, Simion C. Metallic Ca–Rh/C-Methanol, a high-performing system for the hydrodechlorination/ring reduction of mono- and poly chlorinated aromatic substrates. Environmental Science and Technology. 2009;43(15):5952-5958

[89] Mitoma Y, Egashira N, Simion C. Highly effective degradation of polychlorinated biphenyls in soil mediated by a Ca/Rh bicatalytic system. Chemosphere. 2009;74:968-973

[90] Mitoma Y, Tasaka N, Takase M, Masuda T, Tashiro H, Egashira N. Calcium-promoted catalytic degradation of PCDDs, PCDFs, and coplanar PCBs under a mild wet process. Environmental Science and Technology. 2006;40:1849-1854

[91] Mitoma Y, Uda T, Egashira N, Simion C, Tashiro H, Tashiro M, Fan XB. Approach to highly efficient dechlorination of PCDDs, PCDFs, and coplanar PCBs using metallic calcium in ethanol under atmospheric pressure at room temperature. Environmental Science and Technology. 2004;38(4):1216-1220

[92] Ghaffar A, Tabata M. Dechlorination/detoxification of aromatic chlorides using fly ash under mild conditions. Waste Management. 2009;29:3004-3008

[93] Gao X, Wang W, Liu X. Dechlorination reaction of hexachlorobenzene with calcium oxide at 300-400°C. Journal of Hazardous Materials. 2009;169:279-284

[94] Su G, Huang L, Shi R, Liu Y, Lu H, Zhao Y, Yang F, Gao L, Zheng M. Thermal dechlorination of PCB-209 over Ca species-doped Fe2O3. Chemosphere. 2016;144:81-90

[95] Gao X, Wang W, Liu X. Low-temperature dechlorination of hexachlorobenzene on solid supports and the pathway hypothesis. Chemosphere. 2008;71:1093-1099

[96] Arulmozhiraja S, Morita M. Electron affinities and reductive dechlorination of toxic polychlorinated dibenzofurans: A density functional theory study. Journal of Physical Chemistry A. 2004;108:3499-3508

[97] Kim Y-H, Carraway ER. Dechlorination of chlorinated phenols by zero valent zinc. Environmental Technology. 2003;24(12):1455-1463

[98] Huang B, Qian W, Yu C, Wang T, Zeng G, Lei C. Effective catalytic hydrodechlorination of o-, p- and m-chloronitrobenzene over Ni/Fe nanoparticles: Effects of experimental parameter and molecule structure on the reduction kinetics and mechanisms. Chemical Engineering Journal. 2016;306:607-618

[99] Begum A, Gautam SK. Dechlorination of endocrine disrupting chemicals using Mg0/ZnCl2 bimetallic system. Water Research. 2011;45:2383-2391

[100] Murena F, Schiooppa E. Kinetic analysis of catalytic hydrodechlorination process of polychlorinated biphenyls (PCBs). Applied Catalysis B: Environmental. 2000;27:257-267

[101] Lim TT, Zhu BW. Practical applications of bimetallic nano-iron particles for reductive dehalogenation of haloorganics: Prospects and challenges. In: Carvalho-Knighton KM,
Geiger CL, editors. Environmental Applications of Nanoscale and Microscale Reactive Metal Particles. USA: American Chemical Society; 2009. pp. 245-261. (Chapter 14)

[102] Lin S, Su G, Zheng M, Jia M, Qi C, Li W. The degradation of 1,2,4-trichlorobenzene using synthesized \( \text{Co}_3\text{O}_4 \) and the hypothesized mechanism. Journal of Hazardous Materials. 2011;192:1697-1704

[103] Weber R, Yoshida S, Miwa K. PCB destruction in subcritical and supercritical waters evaluation of PCDF formation and initial steps of degradation mechanisms. Environmental Science and Technology. 2002;36:1839-1844

[104] Doornkamp C, Ponec V. The universal character of the Mars and Van Krevelen mechanism. Journal of Molecular Catalysis A: Chemical. 2000;162(1-2):19-32

[105] Zhang L, Zheng M, Liu W, Zhang B, Su G. A method for decomposition of hexachlorobenzene by \( \gamma \)-alumina. Journal of Hazardous Materials. 2008;150:831-834

[106] Khaleel A, Al-Nayli A. Supported and mixed oxide catalysts based on iron and titanium for the oxidative decomposition of chlorobenzene. Applied Catalysis B: Environmental. 2008;80:176-184

[107] King CM, King RB, Bhattacharyya NK, Newton MG. Organonickel chemistry in the catalytic hydrodechlorination of polychlorobiphenyls (PCBs): Ligand steric effects and molecular structure of reaction intermediates. Journal of Organometallic Chemistry. 2000;600:63-70

[108] Gorbunova TI, Subbotina JO, Saloutin VI, Chupakhin ON. Reactivity of polychlorinated biphenyls in nucleophilic and electrophilic substitutions. Journal of Hazardous Materials. 2014;278:491-499

[109] Fang G, Gao J, Dionysiou DD, Liu C, Zhou D. Activation of persulfate by quinones: Free radical reactions and implication for the degradation of PCBs. Environmental Science and Technology. 2013;47:4605-4611

[110] Zhang G, Hua I. Cavitation chemistry of polychlorinated biphenyls: Decomposition mechanisms and rates. Environmental Science and Technology. 2000;34:1529-1534

[111] Dubinskaya AM. Transformations of organic compounds under the actionof mechanical stress. Russian Chemical Reviews. 1999;68:637-652

[112] Birke V, Mattik J, Runne D. Mechanochemical reductive dehalogenation of hazardous polyhalogenated contaminants. Journal of Materials Science. 2004;39:5111-5116

[113] 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;74:2303-2309

[114] Tanaka Y, Zhang Q, Saito F. Mechanochemical dechlorination of trichlorobenzene on oxide surfaces. Journal of Physical Chemistry B. 2003;107:11091-11097

[115] Zhang Q, Saito F, Ikoma T, Tero-Kubota S, Hatakeda K. Effects of quartz addition on the mechanochemical dechlorination of chlorobiphenyl by using CaO. Environmental Science and Technology. 2001;35:4933-4935

Mechanistic Considerations on the Hydrodechlorination Process of Polychloroarenes
http://dx.doi.org/10.5772/intechopen.79083
[116] Tanaka Y, Zhang Q, Saito F, Ikoma T, Tero-Kubota S. Dependence of mechanochemically induced decomposition of mono-chlorobiphenyl on the occurrence of radicals. Chemosphere. 2005;60:939-943

[117] Lu S, Huang J, Peng Z, Li X, Yan J. Ball milling 2,4,6-trichlorophenol with calcium oxide: Dechlorination experiment and mechanism considerations. Chemical Engineering Journal. 2012;195-196:62-68

[118] Zhang W, Wang H, Hiang J, Yu M, Wang F, Zhou L, Yu G. Acceleration and mechanistic studies of the mechanochemical dechlorination of HCB with iron powder and quartz sand. Chemical Engineering Journal. 2014;239:185-191

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

[120] Birke V, Schütt C, Ruck WKL. Small particle size magnesium in one-pot Grignard-Zerewitinoff-like reactions under mechanochemical conditions: On the kinetics of reductive dechlorination of persistent organic pollutants (POPs). In: Geiger CL, Carvalho-Knighton KM, editors. Environmental Applications of Nanoscale and Microscale Reactive Metal Particles. Washington DC: American Chemical Society; 2010. pp. 39-54

[121] Birke V, Schütt C, Burmeier H, Ruck WKL. Defined mechanochemical reductive dechlorination of 1,3,5-trichlorobenzene at room temperature in a ball mill. Fresenius Environmental Bulletin. 2011;20:2794-2805

[122] Jiang Y, Shang Y, Yu S, Liu J. Dechlorination of hexachlorobenzene in contaminated soils using a nanometallic Al/CaO dispersion mixture: Optimization through response surface methodology. International Journal of Environmental Research and Public Health. 2018;15:872

[123] Ghaffar A, Tabata M. Enhanced dechlorination of chlorobenzene compounds on fly ash: Effects of metals, solvents, and temperature. Green Chemistry Letters and Reviews. 2010;3(3):179-190

[124] Xia C, Xu J, W W, Liang X. Pd/C-catalyzed hydrodehalogenation of aromatic halides in aqueous solutions at room temperature under normal pressure. Catalysis Communications. 2004;5(8):383-386

[125] Fang L, Xu C, Zhang W, Huang LZ. The important role of polyvinylpyrrolidone and Cu on enhancing dechlorination of 2,4-dichlorophenol by Cu/Fe nanoparticles: Performance and mechanism study. Applied Surface Science. 2018;435:55-64

[126] Zhu M, Zhang L, Zheng L, Zhuo Y, Xu J, He Y. Typical soil redox processes in pentachlorophenol polluted soil following biochar addition. Frontiers in Microbiology. 2018;9:579