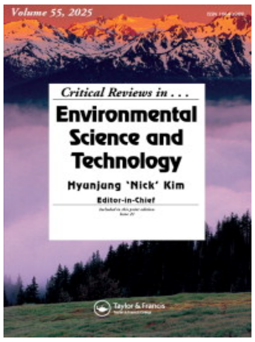

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Chloroaromatics remediation: Insights into the chemical reduction and hydrodechlorination of chlorobenzenes

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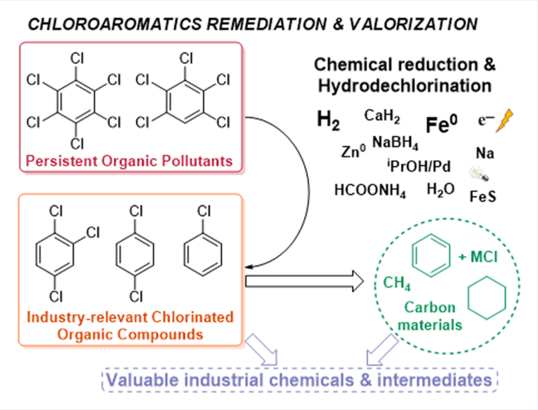
ABSTRACT



Chloroaromatic compounds—including not only chlorobenzenes, but alsochloroanilines, chlorophenols and others—are chemicals widely used for decades as industrial solvents, synthetic intermediates, and pesticides. However, many of these compounds are classified as persistent organic pollutants due to their biaccumulative nature, additionally having toxic and neurotoxic effects to humans and animals. Significant stocks of obsolete chloroaromatics, along with numerous heavily contaminated sites worldwide—including air, surface water, groundwater, and soil—underscore the urgent need for efficient remediation strategies. Chemical reduction has emerged as a well-stablished and effective approach for the transformation and/or valorization of chloroaromatics, particularly chlorobenzenes, into less toxic and higher-value compounds, such as cyclohexane and benzene. This approach may also yield other specific products such as methane, polyaromatics, and carbon-based nanomaterials.

In this review, we provide the first comprehensive and also critical assessment of all hydrodechlorination and chemical reduction methods applied to the transformation, remediation, and valorization of chlorobenzenes. All the available literature has been analyzed in terms of practical feasibility, limitations, cost-effectiveness, and scalability. Reduction strategies are categorized by the type of reducing agent, distinguishing between stoichiometric and catalytic methods. The performance of various reductants—including metals, metal sulfides, hydrogen gas, hydrides, and water—in combination with a long series of organic and inorganic hydrogen donors (*e.g.* hydrocarbons, alcohols, formates, silanes, hydrazine) is thoroughly evaluated. Finally, insights into the electrochemical and photochemical reduction of chlorobenzenes in both polluted water and soil are also provided.

LIST OF ABBREVIATIONS: **CB**: Monochlorobenzene; **CBs**: Chlorinated Benzenes or Chlorobenzenes (with no specific number of Cl atoms); **CMD**: Copper-Mediated Destruction; **COC**: Chlorinated Organic Compound; **DCB**: Dichlorobenzene; **DMCR**: Dehalogenation by Mecanochemical Reaction; **DRE**: Destruction and Removal Efficiency; **GPCR**: Gas-Phase Chemical Reduction; **HCB**: Hexachlorobenzene; **HCH**: Hexachlorocyclohexane; **ISCR**: *In Situ* Chemical Reduction; **NPs**: Nanoparticles; **PCBs**: Polychlorinated Biphenyls; **PeCB**: Pentachlorobenzene; **POP**: Persistent Organic Pollutant; **TCB**: Trichlorobenzene; **TeCB**: Tetrachlorobenzene; **ZVI**: Zero-Valent Iron

KEYWORDS Chlorobenzenes remediation; hydrodechlorination; hydrogenolysis; zero-valent iron; electroreduction

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Introduction

Origin

Chlorinated benzenes or chlorobenzenes (CBs) constitute a versatile family of chlorinated organic compounds (COCs) very used in the chemical industry since the nineteenth century (Figure 1). The synthesis of monochlorobenzene was described in 1851 by the reaction of phenol with phosphorus pentachloride. A few years later (1868), the synthesis still in use was described, consisting of the chlorination of benzene in the presence of a Lewis acid such as iron(III) chloride (Beck & Löser, 2011). Chlorobenzenes with more chlorine atoms are obtained from the chlorination of CB, as well as through the Sandmeyer reaction on (chloro)anilines. More recently, the dehydrochlorination of hexachlorocyclohexanes (HCHs) became a relevant procedure for the preparation of trichlorobenzenes. This latter pathway is of particular interest today, due to the need for remediation of 4.8–7.4 million tons of HCH waste, as a consequence of the worldwide production of the former pesticide lindane (Leal-Duaso et al., 2025).

As can be seen from Figure 1, chlorobenzenes can appear substituted by different functions, representing a diverse industrial production of chloroaromatics such as chloroalkylbenzenes, chlorophenols, chloroanilines, chlorothiophenols, and chlorobenzoic acid derivatives.

Monochlorobenzene (CB), along with the three dichlorinated isomers (1,2-DCB, 1,3-DCB, and 1,4-DCB), and 1,2,4-trichlorobenzene (1,2,4-TCB) are colorless liquids that display boiling points in the range of 132 to 213 °C. The rest of the trichlorinated isomers (1,2,3-TCB and 1,3,5-TCB), tetrachlorobenzenes (1,2,3,4-TeCB, 1,2,3,5-TeCB, and 1,2,4,5-TeCB), pentachlorobenzene (PeCB), and hexachlorobenzene (HCB) are crystalline solids with melting points from 63 °C—for 1,3,5-TCB—to 228 °C—for HCB—. In general, all of these compounds are poorly soluble in water, but miscible with organic solvents depending on the chlorine substitution degree (Beck & Löser, 2011).

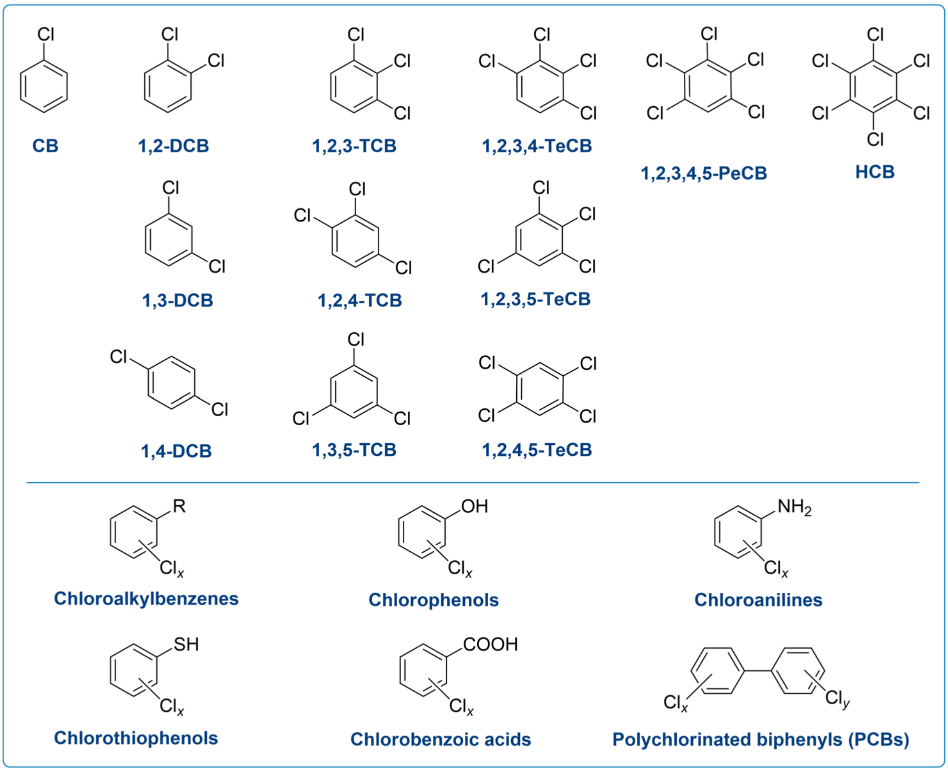

Figure 1. Structures and abbreviations for CBs isomers and related substituted chloroaromatics.

Uses of chlorobenzenes

Chlorobenzenes have relevant applications as solvents and raw materials for electronics, pharmaceuticals, dyeing, pesticides, and textile/leather manufacturing (Feng et al., 2023). For example, monochlorobenzene is a high-boiling solvent for the processing of oils, resins, and polymers in the chemical industry, and an intermediate for the synthesis of nitrophenols, nitroanisole, chloroanilines, and phenylenediamines. These chloroarenes enable the production of dyes, polymers, herbicides and drugs. In the past, CB was used in the large-scale manufacturing of phenol, by treatment with sodium hydroxide (Dow process), and of chlorinated pesticides, such as the well-known DDT.

Regarding dichlorobenzenes, 1,2-DCB allows the synthesis of 1,2-dichloro-4-nitrobenzene. Also, it is a well-established solvent for carbon-based materials in cleaning processes and in fullerenes research. 1,3-DCB, the less common isomer, is transformed into polymers, while 1,4-DCB is a precursor of 1,4-dichloronitrobenzene for pigments synthesis. It was very applied as a disinfectant and deodorant pesticide in form of mothballs, instead of naphthalene, because of its less flammability. Furthermore, both 1,3-DCB and 1,4-DCB are used for the preparation of polyphenylenes. These polymers are key materials in fields such as electronics, optics, electrophoresis, and controlled release of pharmaceutical molecules (Beck & Löser, 2011).

All trichlorobenzenes are currently produced. In particular, 1,2,4-TCB is applied as a large-scale solvent for oils, greases, resins, and polymers such as polyethylene and polypropylene, as well as a platform molecule toward dyes and pharmaceuticals. 1,2,3-TCB is a common herbicide and a coolant in electrical installations and glass tempering, while 1,3,5-TCB is a precursor for polymers, battery electrodes, and photoluminiscent molecules (Beck & Löser, 2011).

All three TeCBs were precursors for pesticides as trichlorophenols, and more recently, for liquid crystals and fluorescent dyes. The only pentachlorinated isomer is a persistent organic pollutant (POP), now banned from its former applications as a pesticide, fungicide, and fire retardant. Finally, the use of HCB was banned by the Stockholm Convention. In the past, it was used extensively as a fungicide in seed formulations (Bailey, 2001).

Environmental impact of chlorobenzenes

The growing environmental concern on POPs, including chlorinated pesticides such as DDTs and lindane (HCHs), polychlorobenzenes, polychlorophenols, and polychlorinated biphenyls (PCBs), claims for the substitution of these chemicals from industrial applications, as well as the remediation of their contamination (Leal-Duaso et al., 2025; Rodrigues et al., 2020). In particular, chlorobenzenes are bioaccumulative compounds, with varying degrees of toxicity and neurotoxicity (Arshad et al., 2024). Risks to human health and the environment, especially for aquatic ecosystems, from exposure to chlorobenzenes were early reported (Meek & Giddings, 1991). Furthermore, and despite the aforeseen interest of chlorobenzenes as chemical intermediates and solvents, their moderate flammability also triggers risk during combustion, due to the production of hazardous gases, including chlorine (Cl_2), hydrogen chloride (HCl), and polychlorinated dibenzo-*p*-dioxins and dibenzofurans.

As introduced, a number of chloroarenes was listed as POPs in the Stockholm Convention (2001). Among them, the production and use of PeCB, HCB, polychlorobenzenes, and chlorinated aromatic pesticides as DDT were banned since 2004—or the 2009 extension—. In the EU context, TCBs, HCB, polychlorophenols, and chlorotoluenes were placed on the EU "Red List" of dangerous compounds (Meharg et al., 2000). More recently, the REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals), became since 2007 an effective tool for the substitution of these chemicals from their industrial applications, controlling the environmental risks posed by them.

Major transnational programs have been recently developed to clean up contaminated soil, water, and sediments, as well as to respond to environmental emergencies and spills caused by hazardous chemicals, with a particular focus on COCs and legacy pesticides. These include the Superfund Program from the US Environmental Protection Agency (EPA), the LINDANET-Interreg program for HCHs and polychlorobenzenes, and the IHPA association for legacy pesticides (Leal-Duaso et al., 2025; McGinley et al., 2023).

In this context, hundreds of publications have analyzed the environmental impact and relevance of halogenated pesticides, PAHs and PCBs (Flid et al., 2020; Leal-Duaso et al., 2025; Xie et al., 2025). However, the number of in-depth studies on chloroaromatics is much smaller, maybe with the exception of chlorophenols (Yadav et al., 2023). It is possible to find examples in many countries of environmental pollution by chlorobenzenes in water, soil, sediments, and air, but few of them have been scientifically documented or evaluated in peer-reviewed journals (Beck & Löser, 2011; Brahushi et al., 2017; Leal-Duaso et al., 2025). The origin of this pollution lies in uncontrolled industrial emissions, discarded stockpiles, failed attempts at chemical remediation, and, above all, in the widespread application of polychlorobenzenes in agriculture and painting for decades (Bailey, 2001; Meek & Giddings, 1991). All these concerns are conveyed in a remarkable increase in the number of scientific publications on chloro- and polychlorobenzenes (Figure 2).

Remediation approaches for chlorobenzenes

Current status and challenges of chlorobenzenes contamination in soil and groundwater were recently reviewed from a bibliometric approach, highlighting the need of unified and efficient remediation tools (Feng et al., 2023). In fact, different physicochemical methodologies have been reported in the literature for the transformation and remediation of aromatic COCs (Brahushi et al., 2017). Due to their chemical stability, chlorobenzenes are not easy to be oxidized, reduced or photodegraded in the natural environment, thus becoming ubiquitous

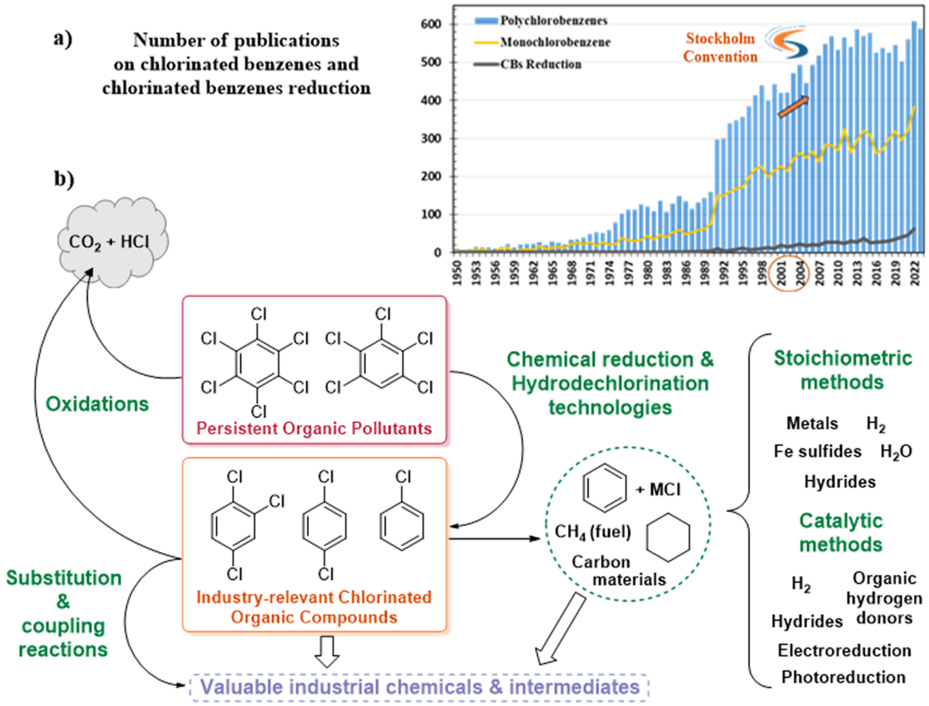

Figure 2. a) Evolution in the number of publications on CBs and CBs reduction (Source WOS). The orange arrow highlights growth in interest since the Stockholm Convention implementation. b) Panorama of chemical transformations of chlorobenzenes: destruction vs. valorization.

pollutants in both water and soil. The detoxification of chloroarenes requires the complete removal, or at least the diminution in the number of chlorine atoms. This can be achieved by means of reduction or hydrodechlorination processes, where products such as benzene or cyclohexane are obtained (Figure 2). In the case of applying oxidizing processes, including catalytic oxidations and combustions, chlorobenzenes are converted into HCl and CO_2, thus destroying the original carbon skeleton. Moreover, chlorobenzenes incineration is strongly discouraged because of the above-mentioned formation of polychlorinated dibenzodioxins (Meek & Giddings, 1991).

Consequently, the chemical reduction of COCs has attracted considerable interest in the literature due to the possibility of simultaneously detoxifying and valorizing these compounds (Rodrigues et al., 2020; Zhang et al., 2025). Chlorobenzene (C_6H_5Cl) is a molecule that presents two functions able to be reduced. First, chlorine atoms can be exchanged for hydrogen atoms by hydrodechlorination processes using metals, metal hydrides or other hydrogen species (Equations 1–3). The main product, benzene (C_6H_6), remains today an essential platform molecule in the production of commodities and chemicals including cumene-phenol, synthetic fibers, and styrene-based polymers (Zuiderveen et al., 2024). Indeed, the global benzene market reached 51.5 million tons in 2022 (24% of the global chemicals market), at an increasing growth rate of over 3% (Miller et al., 2022).

$$C_6H_{(6-n)}Cl_n + 2n\,M + n\,H_2O \rightarrow C_6H_6 + n\,MCl + n\,M(OH) \tag{1}$$

$$C_6H_{(6-n)}Cl_n + n\,MH \rightarrow C_6H_6 + n\,MCl \tag{2}$$

$$C_6H_{(6-n)}Cl_n + n\,H_2 \rightarrow C_6H_6 + n\,HCl \tag{3}$$

Secondly, the CB aromatic ring can be reduced toward cyclohexane (C_6H_{12}). In this case, the higher stability of the aromatic molecule usually requires the use of a catalyst and hydrogen gas (Equation 4). The cyclohexane production is more modest (*ca.* 7.5 million tons in 2025), but still essential in the production of nylon-6, engineered plastics, and packaging.

$$C_6H_{(6-n)}Cl_n + (n+3)H_2 \rightarrow C_6H_{12} + n\,HCl \tag{4}$$

It is relevant to highlight that, even if polychlorobenzenes are partially hydrodechlorinated, the subsequent formation of mono- and dichlorobenzenes, which are not considered as POPs yet, allows converting hazardous COCs into useful industrial intermediates (Beck & Löser, 2011). Other minor reduction products from CBs, such as methane and carbon nanomaterials, have greater economic value in fuel or technology applications.

This review focuses on the reactivity of chlorobenzenes through chemical reduction, with the aim of summarizing and critically evaluating, for the first time, all possible reductive transformations in which they can participate, thus facilitating their remediation and/or valorization either at laboratory scale or in real contaminated sites. Reduction methodologies have been classified herein according to the reducing agent, distinguishing between stoichiometric (Sections 1–8) and catalytic methods (Sections 9–19). Effectiveness, feasibility, and applicability to real situations have been evaluated when possible. Figures 3 and 5 show a summary of the methodologies, stoichiometric and catalytic respectively, for the reduction and hydrodechlorination of chlorobenzenes discussed throughout this review. These methods can be carried out in a reactor (*ex situ*) or applied *in situ* (*In Situ* Chemical Reduction, ISCR) to the remediation of contaminated soil and water. Finally, biodegradation of low-chlorinated benzenes is well documented, but these methodologies are poorly effective for polychlorobenzenes (Brahushi et al., 2017). In these cases, certain tandem

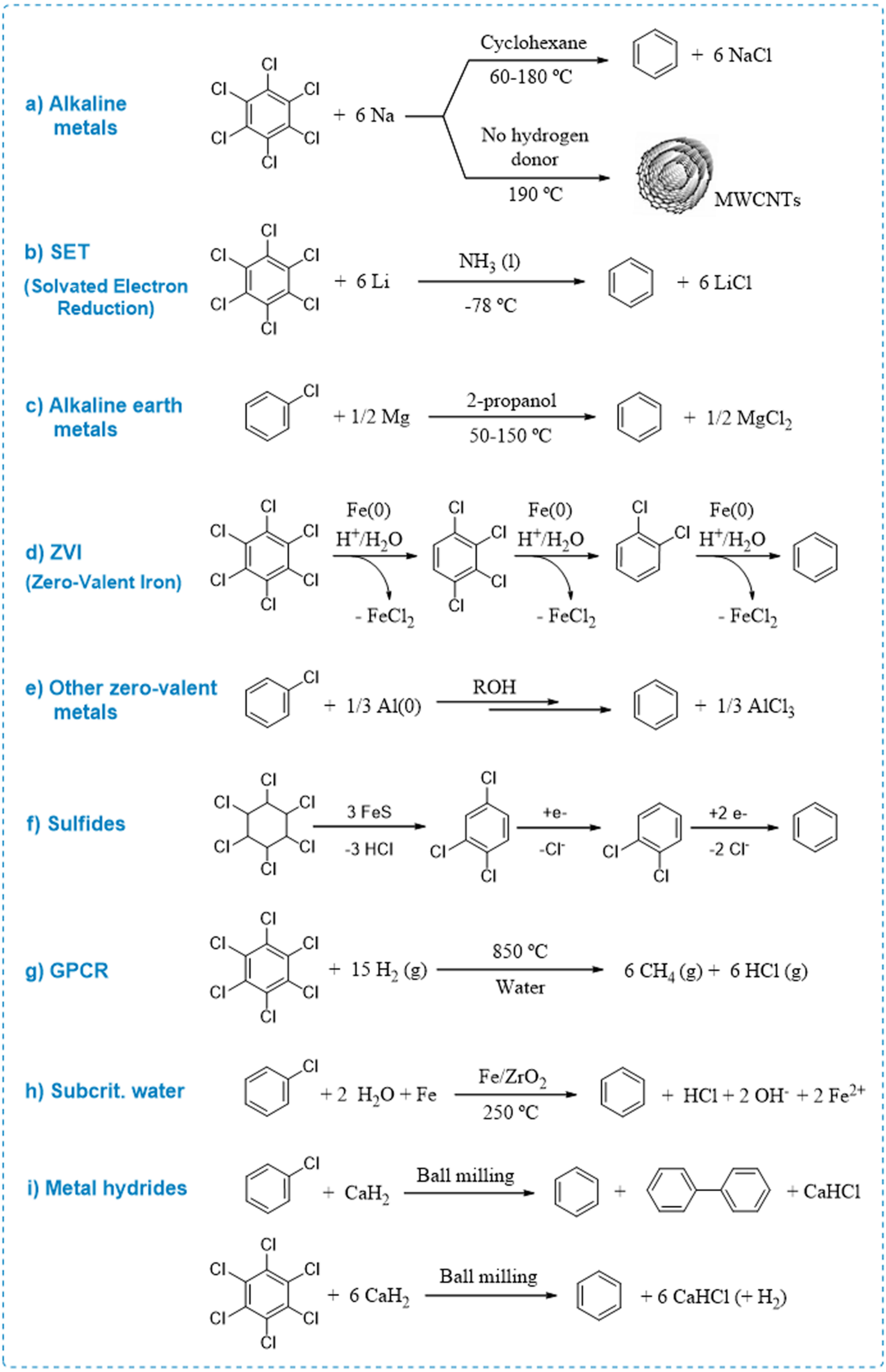

Figure 3. Representative stoichiometric methodologies for chlorobenzenes reduction.

(chemical + biochemical) processes may be an interesting remediation possibility to consider. Chlorobenzenes reduction mechanisms were recently investigated theoretically (Nitu & Crespi, 2023).

Stoichiometric reduction methods

Reduction using alkaline metals

The reduction by alkaline metals, such as metallic sodium and potassium, is a methodology that has been widely applied on an industrial scale in the past. In the presence of chloroarenes, sodium reacts with chlorine atoms to generate non-chlorinated compounds and sodium chloride (Figure 3a, equation 1). Low-chlorinated benzenes, polyphenylenes, hydrogen gas, sodium hydroxide, and water can be formed, which separate readily under these reducing conditions. Prior to reduction, all COCs must be dried because of the violent reactivity of alkalines with water. However, reduction using alkaline metals requires the addition of a hydrogen donor, mainly hydrocarbons like cyclohexane.

Chemical reduction of CB using alkaline metals, mainly Na, has been carried out within minutes at 60–180 °C. After reduction, sodium chloride and benzene can be separated from the organic phase by filtration and centrifugation, respectively, and reused as industrial chemicals. This method was used on a large scale since the 1980s for *ex situ* treatment of over 60,000 tons of HCB and PCBs by companies such as Kinectrics Inc., Sanexen Environmental Services Inc., and Powertech Labs (Bell & Luscombe, 2015). Sodium application also allowed the remediation of soils contaminated with chlorobenzenes and chlorophenols, after soil pretreatment by thermal desorption and exhaustive drying. Instead of using Na, HCB has been completely dechlorinated to benzene in 30 min using a potassium-sodium alloy in cyclohexane solution at a laboratory-scale (Miyoshi et al., 2004). An excess of metallic lithium, in this case in combination with $FeCl_2 \cdot 4H_2O$, provided excellent reduction results at ambient temperature for differently-substituted chlorobenzenes in tetrahydrofuran (Moglie et al., 2006). In particular, 83% to 93% yields of dechlorinated products were obtained from polychlorobenzenes, chlorotoluenes and chlorophenols in 2–5 h. Interestingly, deuterium-labeling experiments proved the role of structural water in the iron(II) salt as the hydrogen source (Moglie et al., 2006). It is relevant to note that, when placing chlorobenzenes in the presence of alkaline metals, the Wurtz-Fittig dimerization can take place as a side-reaction. Anyway, the formed coupling products are also dechlorinated under these conditions.

In conclusion, reduction using alkaline metals is an effective and consolidated method for the transformation of chloroaromatics (destruction removal efficiency, DRE = 99.9999%). The energy requirements are low, with operating costs estimated at 0.9–7 $\$\cdot L^{-1}$, due to the required amounts of sodium (Bell & Luscombe, 2015). The high risk in the management of metallic sodium requires careful safety measures and exhaustive drying of materials to avoid the presence of water and alcohols.

Besides benzene, it should be noted that (monochloro)cyclohexadienes, which are precursors for light aromatic chemicals, can be prepared from chlorobenzene by a selective reduction method (Birch) using metallic lithium (Cao et al., 2008). More surprisingly, a catalyst-free method, claimed to be scalable, for the synthesis of carbon nanomaterials from HCB (Figure 3a) was developed thanks to the absence of hydrogen donor (Ellis et al., 2013). Remarkable yields (80%) of multiwalled carbon nanotubes (MWCNTs) and carbon nanobubbles were obtained by treating HCB with Na at, respectively, 190 °C and 100 °C.

The application of alkaline metals to the reduction of COCs is also found in the Solvated Electron reduction Technology (Leal-Duaso et al., 2025). In this method, a highly reducing solvated-electron solution is formed by dissolution of sodium or lithium in liquid ammonia at −78 °C. Then, CBs are added to this characteristic blue solution, being instantaneously dechlorinated toward benzene (Figure 3b). This commercial technology has been applied to polychlorobenzenes, PCBs, pesticides, chlorofluorocarbons, polychlorinated dibenzodioxins and dibenzofurans, both *ex situ* and into contaminated soils, in the last case at ambient temperature and enriching the soil in nitrogen coming from ammonia (Pittman & He, 2002). Although very fast and effective, this method has much higher costs, estimated at 5.512–6.614 $\$\cdot kg^{-1}$ for COCs including CBs (Bell & Luscombe, 2015).

Reduction using alkaline earth metals

Alkaline earth metals, outstanding magnesium and calcium, are strong reducing agents, but less reactive with COCs than alkaline metals (Nallaparaju et al., 2024). CB has been fully reduced to benzene (Figure 3c) in *ca.* 2 h using magnesium powder in alcohols such as 2-propanol as the hydrogen donor (Bryce-Smith & Wakefield, 1973). The main way to enhance the dechlorinating activity of alkaline earth metals is applying mechanochemical activation (DMCR) through ball milling in the presence of hydrogen donors. In this context, chloroaromatics have been recently transformed into the corresponding Birch products with high chemoselectivity using low-reactive calcium and magnesium at ambient temperature under ball milling in the presence of diamines and ammonium chloride (Nallaparaju et al., 2024). Otherwise, chloroanisoles and polychlorobenzenes have been dechlorinated at 50 °C in 6–48 h using a combination of Grignard reagents (*e.g.* BuMgCl) and iron chloride or $Fe(acac)_3$ (Czaplik et al., 2010; Guo et al., 2004). In these cases, the catalytic amount of iron is the responsible for activating the magnesium species, forming $[Fe(MgCl)_2]$ that coordinates to the aromatic ring and releases $MgCl_2$. Reduction using alkaline earth metals is an alternative method for the dechlorination of COCs, in combination with mechanoactivation or the use of iron, but the effectiveness may be a limiting factor. Instead, its combination with transition metals for the remediation of CBs-contaminated soil may be a more promising approach (following Section).

Reduction using transition metals and aluminum

Metals present reduction potentials toward COCs according to the general trend $Na > Mg > Al > Ni > Zn > Fe$ (Cagnetta et al., 2016). In particular, the use of zero-valent iron (ZVI) as an accesible, non-expensive, and benign reducing agent has revolutionized the ISCR of soil (Rodrigues et al., 2020), groundwater (Leal-Duaso et al., 2025), and wastewater (Plessl et al., 2023). However, the low reactivity of iron(0) requires the use of promoters, along with its application at granular or nanometric form (scraps, nanoparticles, etc.). These materials can be prepared according to diverse methodologies, including reduction of iron precursors, precipitation of iron(III) chloride and top-down methods. In the case of *in situ* remediation of soil, the effectiveness decreases due to the iron agglomeration, the limited contact between solid soil particles, and the soil adsorption capacity. Indeed, the iron core of ZVI nanoparticles can be coated by iron oxide or stabilizers prior to the injection into the soil.

ZVI-reduction has proven to be an effective strategy for any kind of COCs, including CBs and HCB, chlorophenols, PCBs, and chlorinated solvents and pesticides (Alonso et al., 2002; Gunawardana et al., 2011). The dechlorination of chlorobenzenes takes place through successive β-elimination steps assisted by iron(0) species (Figure 3d). Throughout this process, all differently-chlorinated benzenes (Figure 4a) can be detected in different proportions as intermediates from the treatment of HCB with nanoscale iron (Shih et al., 2009). This iron(0) is first oxidized to iron(II), and then to iron(III), thus providing the electrons for the chlorobenzenes reduction (Figure 4b). The use of zero-valent iron allows the remediation of polluted waste, soil and water. For instance, real groundwater contaminated by a mixture of 10 CBs (plus 17 aliphatic organochlorine pollutants, $\Sigma COCs = 93\,mg\,L^{-1}$) arising from the former lindane landfill of Bailín (Aragón) was pumped and remediated on-site using commercial ZVI microparticules (Dominguez et al., 2018). Depending on the chloroaromatic chlorination degree, dechlorination efficiencies of 60% to 80% and different dechlorination rates were determined at full-scale *via* hydrogenolysis. Also, the construction of ZVI-based permeable reactive barriers, as for example in Jaworzno (Poland) and Bailín (Spain), represents a very efficient technology for the ISCR of water courses and groundwater polluted with CBs (Leal-Duaso et al., 2025).

The technological development degree for the use of ZVI is really high, with numerous works available on the design and application of ZVI nanomaterials (Plessl et al., 2023). Moreover, ZVI reduction has a positive impact in soil (enhancement of native biota activity), operating

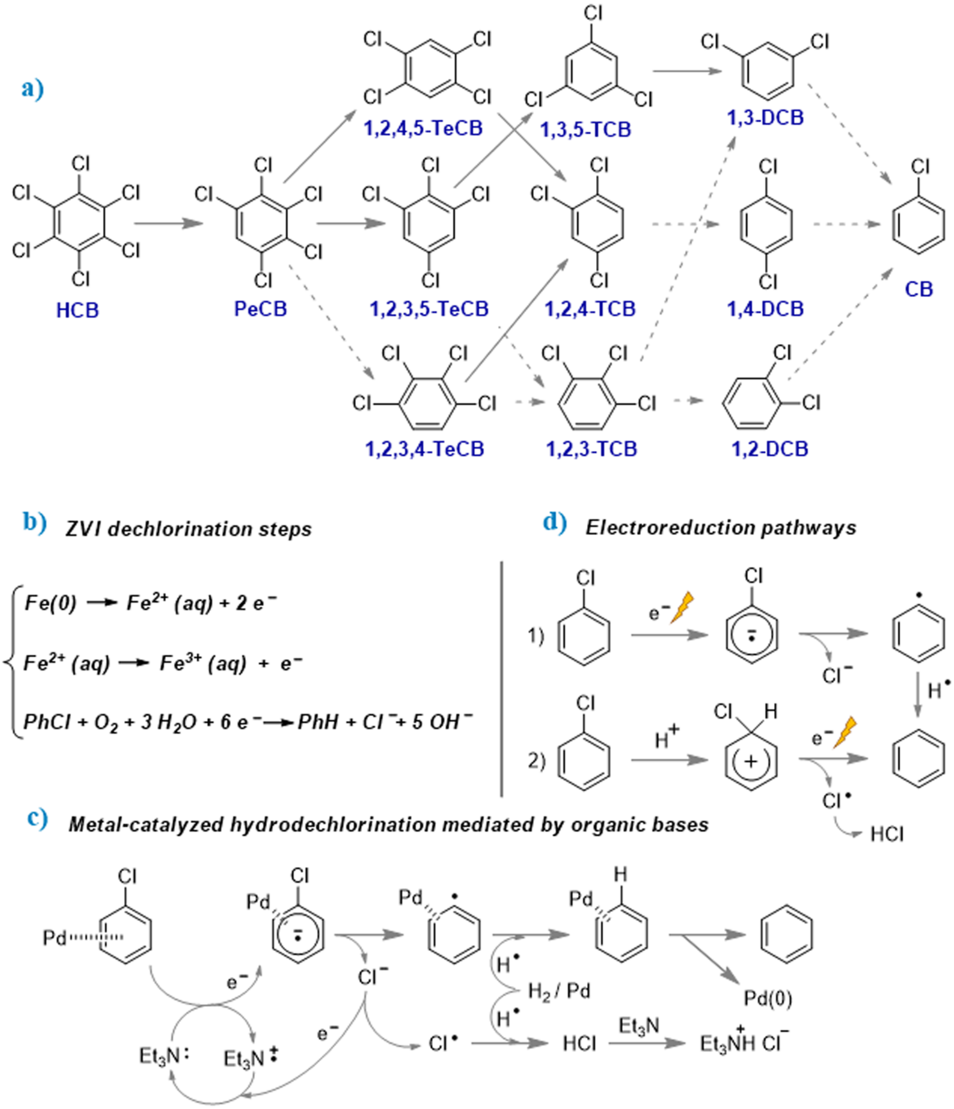

Figure 4. Selected mechanistic aspects of CBs reduction using transition metals (inspired from works of Monguchi et al., 2006; Brahushi et al., 2017; and Mitoma et al., 2018).

costs are notably lower than for other ISCR technologies, and presents strong synergies when combining with other chemical reduction, even oxidation, and bioremediation technologies (Lee & Jou, 2012; Ye et al., 2011). In fact, there are a growing number of papers describing the synergistic reductive dechlorination of chlorobenzenes, chlorophenols, and chlorotoluenes by "nanobioremediation", usually bacterial consortia supplemented with micro- or nanoscaled ZVI. This technology is supposed to have a negligible environmental impact and can be scaled for the full-scale remediation of groundwater polluted with chlorobenzenes, but over long periods (Li et al., 2025).

Besides iron, the application of zero-valent nickel to the elimination of chloroaromatics such as 1,3-DCB was studied (Suresh, 2009), describing an improved coordination of the chloroarene to the Ni(0) surface, together with activation of the hydrogen source on the metal surface. Also, Raney nickel was recently applied, in the absence of additional reductants, to the dechlorination of 4-chlorophenol (Raut et al., 2020). The use of zero-valent zinc for the dechlorination of chlorobenzenes to benzene is described in certain patents in the presence of a Lewis acid and butanol as solvent/hydrogen source (Leal-Duaso et al., 2025). In this case, up to 77% benzene yield was obtained in shorter reaction times than using zero-valent iron. Otherwise, zinc can be used for the *in situ* generation of H_2 from acetic, oxalic, formic, and citric acids, achieving the hydrodechlorination of hazardous polychloroaromatics such as HCB and DDTs, directly in contaminated soils, within 4–8 h (Alonso et al., 2002). Interestingly, a combination of zinc and nickel powders, as electron donors in alkaline medium evidenced the participation of water as the hydrogen donor for CB hydrodechlorination (Alonso et al., 2002). This technology is competitive with ZVI, but the technology level is lower.

The reduction of COCs such as CBs, PCBs, and HCHs has also been accomplished by copper-mediated destruction technology (CMD). In this patented method (Pekarek et al., 2004), the target compound is heated at around 300 °C in the presence of a copper(II) salt, a hydrogen donor, activated carbon, and an additional reducing agent for the reduction of copper(I) and (II) back to zero-valent copper. As an example, silica gel containing 4% HCB was decontaminated in 4 h by CMD technology heating at 260–300 °C in a closed system (absence of oxygen), and using copper(II) oxide, activated carbon, and formic acid. The reaction mechanism runs through the formation of an arylcopper intermediate, responsible for the HCB dechlorination and its homocoupling to form biaryls. Alternatives at ambient temperature use other copper(II) salts such as $CuCl_2 \cdot 2H_2O$ in presence of 4,4-di-*tert*-butylbiphenyl as an electron carrier (Alonso et al., 2004). CMD is a well-developed, cost-effective method for the transformation of COCs with high effectiveness (DRE = 99.999–100% for HCB and pentachlorophenol). The obtained products are valuable chemicals, while hazardous by-products are not formed. The application of nanoscale zero-valent copper was also reported for degradation of chlorobenzene in (waste)water. In this case, the removal efficiency was enhanced from 28% to 72% under microwave irradiation (Lee et al., 2010), and up to 100% after addition of $NaBH_4$ (Raut et al., 2016).

Finally, the use of zero-valent aluminum for the degradation of COCs, including CB (Figure 3e), was proposed due to the higher reducing power of this metal with respect to transition metals. However, the availability of aluminum, in comparison with iron, can limit its use on a large scale. As said before, the interest in using mechanical activation for chemical reduction relies on the enhanced contact between reactants that increases reactivity (Cagnetta et al., 2016). This kind of activation is particularly efficient when using low amounts of aluminum or transition metals together with hydrogen donors such as alcohols, amines, amides, and hydrides. Following this methodology, CB, 1,3-DCB, HCB, pentachlorophenol, PCBs, HCHs, polychlorinated benzodioxins, and pesticides such as aldrin, chlordane, and DDT, have been successfully dechlorinated (Birke et al., 2009; Cagnetta et al., 2016).

Reduction using bimetallic nanomaterials

The combination of zero-valent iron with other metals in design bimetallic nanomaterials allows to increase the effectiveness in the reductive dechlorination applied to soil and water (Rodrigues et al., 2020). Fe–Cu, Fe–Ni, Fe–Pd, and Fe–Pt were reported in the literature with different results under mild conditions (Alonso et al., 2002; Liu et al., 2001). In general, the major interest of using bimetallic species is the incorporation of a second metal with the capacity of generating H_2, which increases the reducing power of the metal itself. The thermodynamic reducing driving force of iron(0) is then combined with the catalytic hydrogenation on metals such as palladium, nickel or silver, being the reaction rate determined by the substituents present in the CB aromatic ring (Liu et al., 2001). For example, Fe–Ag sub-colloidal particles showed outstanding results in the dechlorination of HCB, keeping the reducing capacity from 24 h to 57 d (Alonso et al., 2002). Similar results were described for HCB using Cu–Fe assisted by TritonX surfactant (Zheng et al., 2009).

The application of bimetallic nanomaterials to chlorobenzenes reduction is thus more effective than simple zero-valent iron. However, these methodologies are not feasible for the remediation of acidic soils due to the iron deactivation. Alternatively, Mg(0)–Pd(0) bimetallic materials showed good results in the reductive dechlorination of chloroaromatics, especially in acidic medium (Suresh, 2009). In this case, magnesium is a sacrificial electron donor that facilitates the formation of reductive hydrogen species on the palladium surface. Using this technology, chlorobenzenes, chlorophenols, PCBs, and DDTs were completely dechlorinated, even at pilot-scale.

Reduction using metal sulfides

A very recent alternative for the remediation of soil contaminated by COCs is the application of metal sulfides, usually in form of iron sulfide nanoparticles (FeS NPs) stabilized by (bio) polymers (Leal-Duaso et al. (2025). This ISCR methodology seems to be very efficient, leading to full conversions in some hours, especially in combination with bioremediation. In this sense, a tandem methodology was recently proposed for the efficient reduction of chlorobenzenes (Figure 3f), and especially at high soil pH values. This tandem method is based on the application of FeS NPs to achieve first the dehydrochlorination of persistent α-hexachlorocyclohexane toward 1,2,4-TCB, and then the *in situ* hydrodechlorination of formed trichlorobenzene to benzene (Badea et al., 2021).

Thermal hydrogenolysis

The application of a mixture of hydrogen gas (H_2) and water vapor at high temperature and atmospheric pressure is a thermal method—known as Gas-Phase Chemical Reduction (GPCR)—leading to the total reduction of COCs (Leal-Duaso et al., 2025). During GPCR, thermal hydrodechlorination and cracking of chlorobenzenes to methane and hydrogen chloride occurs in a high-temperature reactor at 600–850 °C (Figure 3g). Then, resulting gases are collected, cooled down and washed with water to separate inorganic species (Flid et al., 2020). Interestingly, generated HCl can be reused as an industrial chemical, and methane, together with small amounts of carbon monoxide and light hydrocarbons, can be *in situ* recycled as fuel to provide the required temperatures. The GPCR method has been applied to the *ex situ* remediation of aqueous and oily residual streams, polluted soils, and stockpiles of high-concentrated CB, HCB, chlorophenols, and PCBs. For example, the treatment of 7 tons of HCB and 2000 tons of PCBs in a full-scale GPCR plant in Kwinana (Australia) with an excellent reported effectiveness (DRE_{CBs} >99.9999%) (Bell & Luscombe, 2015). Therefore, GPCR allows the efficient hydrodechlorination of chloroaromatics with high technological development degree at any scale, and also enables their valorization as the only reductive methodology that converts chloroaromatics into fuels. The operating costs for a 5–10 million dollars GPCR plant were estimated at 2300 $\$\cdot kg_{PCB}{}^{-1}$ (Bell & Luscombe, 2015). Several of these GPCR plants are available in countries as Canada, Australia, and Japan.

Subcritical water reduction

Subcritical water, *i.e.,* water vapor at around 250 °C, can be applied to the reductive dechlorination of chloroarenes. For instance, monochlorobenzene was hydrodechlorinated in subcritical water through an ionic mechanism in the presence of Fe/ZrO_2 (Figure 3h). Water is supposed to act as the hydrogen donor, leading to the formation of hydrogen that reacts with CB, while the formed hydroxyl anions participate in the dechlorination mechanism (Wei et al., 2009). Despite the authors indicate a catalytic role of iron, whether a reductive mechanism occurs, iron would be the last electron donor thus being consumed during the reaction. In any case, this method is effective, fast—reaction times of some minutes—, clean—good environmental profile—economic, and scalable. The CB reduction using subcritical water was also studied in the presence of Ni/ZrO_2 and Cu/ZrO_2 with good results, but iron resulted more active and affordable (Wei et al., 2009).

Reduction using metal hydrides

Besides hydrogen gas, metal hydrides have been used as a safer industrial hydrogen source. Both alkaline (NaH, KH) and alkaline earth (CaH_2) hydrides present high reducing capacity. Unfortunately, when monochlorobenzene is mixed with a solid metal hydride, no reaction is observed (Loiselle et al., 1997). Thus, mechanochemical (a), thermal (b), or catalytic (c) activations are necessary to enhance the C–Cl bond hydrogenolysis in chlorobenzenes (Equation 2). a) Under mechanochemical activation, the treatment of CB with CaH_2 in a ball mill leads to its conversion into benzene (Figure 3i), and sometimes, biphenyl (Alonso et al., 2002). The use of higher rotation speed and ball mass increases reactivity (Loiselle et al., 1997). This method presents an additional interest for the reduction of solid polychlorobenzenes. For instance, HCB was completely transformed into benzene (Figure 3i) using a single stainless-steel ball within 6 h (Loiselle et al., 1997). This reaction is strongly exothermic, but has a high activation energy that can be provided by a hot wire or an electric spark. After the appropriate ball milling time, the temperature reaches a stable plateau, suggesting a self-propagating reaction that forms benzene as the major product. b) Under thermal activation, which means heating at very high temperatures (2277–2627 °C), chlorobenzenes such as HCB are completely degraded by calcium hydride to carbon and $CaCl_2$. This technology, known as self-propagating high-temperature dehalogenation (SPHTD), was developed as an *ex situ* method for the destruction of HCB-containing wastes (Orrù & Cao, 2014). The mixture of contaminated waste and CaH_2 is introduced in a dry reaction chamber equipped with a tungsten coil. An electric spark sets off the self-propagating reaction, and calcium chloride, carbon, and H_2 are formed as only products. This technology is highly efficient for the complete destruction of chlorinated waste. However, the handling of hydrides at the large scale can be problematic due to the explosion risk. c) As will be seen from here onwards, the need of high temperatures and energies for activation of the reductant can be circumvented by means of a catalyst. For the case of metal hydrides, a rapid catalytic hydrogenolysis of CB with sodium hydride of nanometric size was described in the presence of a multimetallic catalyst, $Ni(OAc)_2$-$TiCl_4$-*i*PrONa (Li et al., 1996). Later, Ni–Al nanoclusters prepared from $Ni(OAc)_2$ and $Al(acac)_3$ were applied to the reductive dechlorination of polychlorobenzenes to benzene induced by NaH (Massicot et al., 2000). The catalytic approach presents better sustainability than the aforedescribed activations, but the high specificity of the catalysts may hamper scalability for real contamination situations.

Catalytic reduction methods

Catalytic hydrodechlorination using H_2

Metal-catalyzed hydrodechlorination of chlorobenzenes by means of H_2-mediated hydrogenolysis (Figure 5a) leads to different reduction products with a lower chlorine content (Equation 3). In general, the transition-metal catalyst, together with the reaction conditions, allow to adjust the degree of dechlorination and control the formation of specific valorizable chemicals such as benzene or cyclohexane (Keane, 2011). As a result, the order in which chlorine atoms are removed from polychlorinated arenes leads to different hydrodechlorination pathways. However, the investigation of the reaction mechanism has hardly been addressed, highlighting the work of Mitoma et al. (2018).

The vast amount of works on this reduction approach have been classified regarding catalyst type.

Homogeneous hydrodechlorination

The use of homogeneous catalysts, in the same phase as substrates and solvent, leads to good results in the hydrodechlorination of chlorobenzenes to benzene, while exhibiting tolerance to diverse functional groups (Moon & Lee, 2009; Zhang et al., 2015). These catalysts, frequently

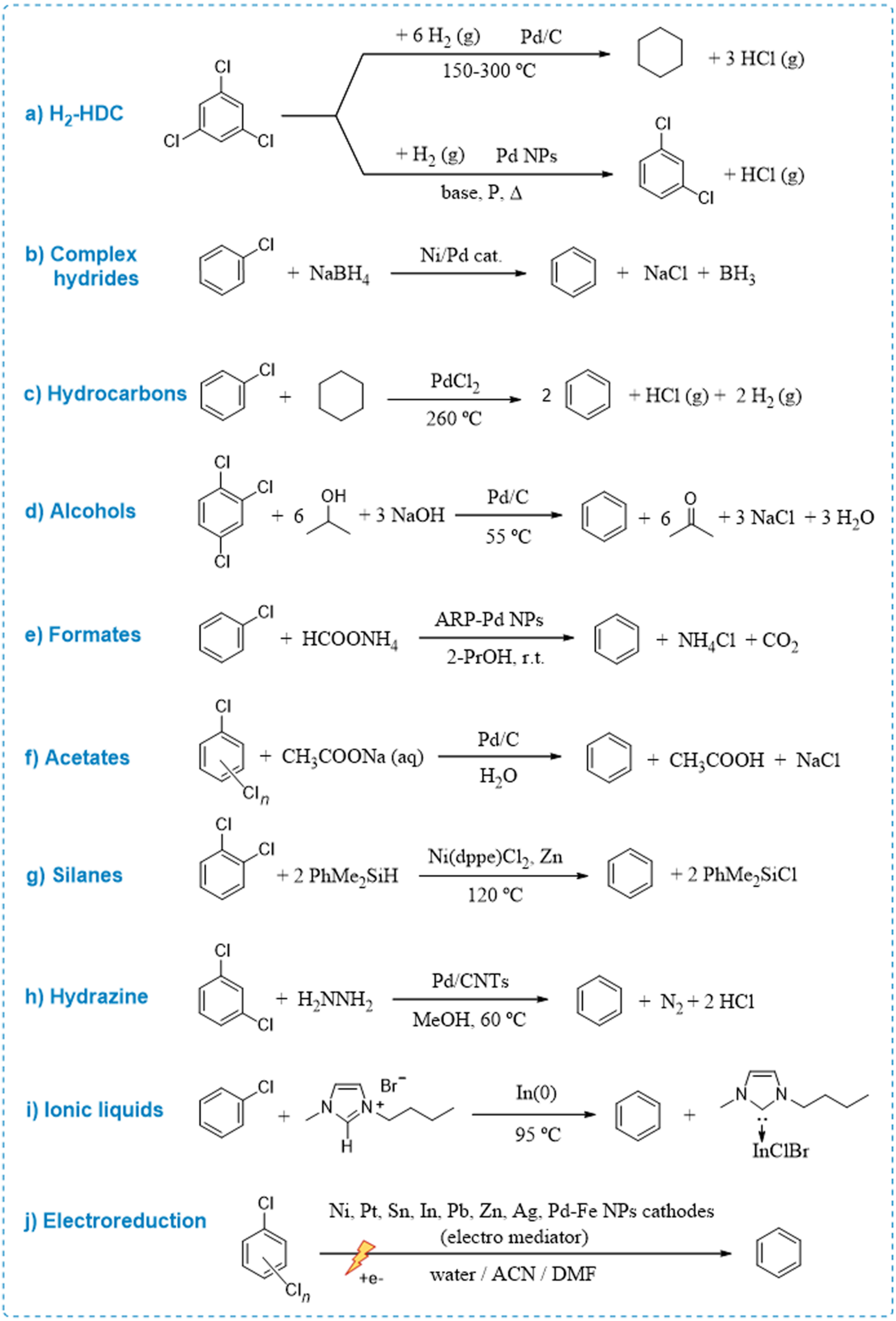

Figure 5. Representative catalytic methodologies for chlorobenzenes reduction.

palladium complexes, easily dissociate the hydrogen molecule, thus promoting the hydrogenolysis of C–Cl bonds. The most used solvents are water and methanol, and mild reaction conditions are described even for polychlorobenzenes (Giannoccaro et al., 2005). The combination of a rhodium complex with palladium catalysts, led to excellent results in the exhaustive dechlorination of different chloroaromatics toward cyclohexane or cyclohexyl-derivatives within 24 h by a tandem process of hydrodechlorination and hydrogenation of the aromatic ring (Ghattas et al., 2003). Besides palladium, a *N*-heterocyclic carbene nickel(0)/imidazolium chloride catalytic system showed outstanding results in the dechlorination of CB to benzene at 65 °C in 1 h (Desmarets et al., 2002). This non-expensive catalyst was active for DCBs (in 3 h), chlorofluorobenzenes, chlorophenols and chloroanilines.

Heterogeneous hydrodechlorination

Heterogeneous catalysts, combining good stability and activity, are readily recovered thanks to the use of solid supports (Yasuda & Shinoda, 2003). This decreases the impact of the transition metal cost, usually palladium, thus increasing the feasibility of the scale-up. Depending on the reaction temperature, this process is known as "gas-phase" (150–300 °C) or "liquid-phase" (>120 °C) hydrodechlorination (Amorim et al., 2011; Aramendía et al., 1999; Keane, 2011).

Complete hydrodechlorination of chlorobenzenes with up to four chlorine atoms can be catalyzed by palladium on carbon (Pd/C), at low temperature, but under moderate-to-high hydrogen pressures (Marques et al., 1993). In this case, the presence of ammonia or sodium or potassium hydroxide, as proton acceptors, helps to the dechlorination of tetra-, tri-, di-, and monochlorobenzene to benzene at acceptable rates under lower pressures (Anusiewicz et al., 2010; Janiak & Błażejowski, 2004; Simagina et al., 2009). Similar results were described for substituted chlorobenzenes, such as 3- and 4-chloroaniline, 1-chloro-3-fluorobenzene, 3-chloroanisole, and 3-chlorotoluene (Janiak & Okal, 2009; Konuma & Kameda, 2002). The effect of the substituent nature in the chloroaromatics dehydrochlorination was studied using Pd/C and correlated to the electronic acceptor and donor capacities of those substituents (Konuma & Kameda, 2002).

Alternatively to the use of sodium hydroxide as a base, triethylamine is capable of activating the CB molecule by donation of one electron that is recovered during the further dechlorination of the resulting CB radical (Monguchi et al., 2006). Then, triethylamine traps the formed HCl, thus regenerating the Pd catalyst (see mechanism depicted in Figure 4c). In the case of using other bases, hydrodechlorination (C–Cl bond activation) is given by the attack of $H^\bullet$ radicals formed by homolytic cleavage of H_2 on the palladium surface (Mitoma et al., 2018). The addition of a second metal, mainly iron or calcium, leads to a Pd/C activity enhancement in polychlorobenzenes (Lokteva et al., 2015). Doped-Pd catalysts can be easily supported over alumina to convert 1,3,5-TCB completely into benzene through multiphase hydrodechlorination (Golubina et al., 2019). Pd/C is also able to hydrodechlorinate polychlorophenols to phenols, and PCBs to biphenyl (Keane, 2011). Indeed, this last example was available in the Osaka plant (Japan) as the "Catalytic Hydro-Dechlorination" method, consisting of the treatment with H_2 on Pd/C, heating at 180–260 °C in paraffin oil as solvent. Another interesting example, using H_2 on Pd/C without base, maximizes the chlorine valorization at laboratory-scale, since bio-based epoxides act as both hydrogen and chlorine acceptors, being *in situ* transformed into versatile 1,2-chlorohydrines (Dorado et al., 2021).

Palladium supported on alumina or silica catalyzes the conversion of CB, 1,2-DCB, and 1,3-DCB to benzene in water saturated by H_2 at ambient temperature and pressure (Jujjuri & Keane, 2010; Schüth & Reinhard, 1998). This alumina-supported catalysts were also applied to the transformation of 1,2,4,5-TeCB into benzene in water/ethanol mixtures (Wee & Cunningham, 2008), as well as to the continuous treatment of chlorobenzenes under microwave activation (Pillai et al., 2004). Selective hydrodechlorination of polychlorobenzenes like HCB to CB is possible using Pd catalysts supported on design aluminosilicates (Alonso et al., 2002), or even to the formation of cyclohexane using Pd immobilized on polymers (Leal-Duaso et al., 2025). On the other hand, the exhaustive hydrodechlorination of 1,2,4-TCB to benzene is also possible using palladium on Mg–Al mixed oxides, which in turn requires higher temperatures and catalytic loadings (Ali et al., 2020).

Palladium nanoparticles (Pd NPs) have shown notable hydrodechlorinating activity and recyclability over solid supports, such as mesoporous metal–organic frameworks (Huang et al., 2012) and resins (Shabbir et al., 2017). An example of a hybrid methodology based on the combination of Pd NPs-catalyzed hydrodechlorination and biodegradation was carried out in a pilot reactor (200 L-scale). After a 10-days test, 63–68% of chlorobenzenes (51.1 $\mu g\ L^{-1}$) were removed applying residence times from 4 to 8 h (Hennebel et al., 2011). The large amount of catalyst (100 $mg\ L^{-1}$ palladium encapsulated in alginate beads) must certainly be optimized before implementing this scaled technology.

Although palladium displays the greatest hydrodechlorinating activity due to its intrinsic number of active sites (Flid et al., 2020), nickel catalysts supported on silica, alumina, ceria, carbon, hydrotalcites or Raney Ni have shown interesting results in the gas-phase hydrogenolysis (200–350 °C) of CB (Cecilia et al., 2013; Ma et al., 2016; Mishakov et al., 2020), DCBs (Keane, 2004), 1,2,4-TCB (Cesteros et al., 2001), 1,2,3-TCB (Keane, 2004), 1,3,5-TCB (Keane, 2004), and HCB (Alonso et al., 2002). Platinum on alumina (Hashimoto & Ayame, 2003) and ruthenium on metal oxides and activated carbon (Srikanth et al., 2011), addressed the chlorobenzenes hydrodechlorination at lower temperatures, but the price of these metals may hamper their use at larger scales. Likewise, a bimetallic Cu–Ni catalyst supported on zirconia was designed to hydrodechlorinate CB under mild conditions, due to the synergistic effect between both metals (Mallick et al., 2011). Finally, Cu–Al and Ni–Al alloys have offered good results under alkaline conditions at ambient temperature and pressure (Weidlich et al., 2020). Alternatively to the formation of benzene, the use of Ni/alumina at high temperature (500 °C) allows to convert CB into nanostructured carbon materials (Mishakov et al., 2020).

The use of nanoparticles generated from rhodium and ruthenium complexes was also reported (Buil et al., 2010). Indeed, magnetically-retrievable Rh(0) NPs were described for the remediation of water polluted with CB (Pélisson et al., 2016). As a more affordable, but still efficient catalyst, Ni NPs supported on mesoporous MCM-41 completed CB conversion in less than 1 h (Wu et al., 2014). Advances in the development of supports and bimetallic combinations for CBs hydrodechlorination, even for *in situ* scenarios, were published in recent years. Oppositely, the inclusion of abundant iron, *e.g.* using Pd–Fe NPs, leads to limited activity increases in CBs hydrodechlorination (Cao et al., 2011).

As shown, metal nanoparticles merge advantages of homogeneous and heterogeneous catalysts. A particular case allows to avoid the use of solid supports, by stabilizing the NPs in low-volatile liquid phases. For example, Pd NPs immobilized in bio-based deep eutectic solvents (Leal-Duaso et al., 2017), provided interesting results in the hydrodechlorination of chlorobenzenes using H_2 and a base under moderate pressures (Leal-Duaso et al., 2021). In particular, CB was fully converted to benzene, and 78% 1,3,5-TCB was converted selectively to 1,3-DCB (Figure 5a). Using a conventional ionic liquid as solvent and NPs stabilizer, good benzene yields were described from CB (89%) and 1,4-DCB (85%) (Calò et al., 2007). Also, Au–Pd NPs stabilized in an imidazolium ionic liquid provided good results in the hydrodechlorination + hydrogenation of 2-chloronitrobenzene toward a (9:91) mixture of aniline and cyclohexylamine at 80 °C within 4 h (Dang-Bao et al., 2017). Alternatively, Pd NPs stabilized by surfactants converted CB into benzene in 24 h under 1 atm H_2. However, these nanoparticles were not efficient in the 1,2,4-TCB hydrodechlorination (La Sorella et al., 2018).

The main deactivation cause for hydrodechlorination catalysts, *i.e.,* accumulation of chlorides that compete with chlorobenzenes for the active sites, has been deeply studied, observing higher catalytic stability for greater particle sizes and for the presence of materials or supports able to capture chloride species (Aramendía et al., 1999, 2001). In this sense, bimetallic palladium catalysts (Pd–Fe, Pd–Pt, Pd–Ni) have been developed to minimize catalytic deactivation (Babu et al., 2009; Liu et al., 2010).

Metal-catalyzed hydrodechlorination is probably the most studied reduction methodology for chlorobenzenes and chlorophenols (Mackenzie et al., 2006), allowing the efficient detoxification of any type of polychloroarene (Mitoma et al., 2018). The availability of new catalysts and supports, decreasing more and more the reaction temperature and time, the high technological development degree and effectiveness (up to 99.9999%) encourage the use of this methodology. Moreover, the main products (benzene or cyclohexane) find direct application in the chemical industry. However, the risks on H_2 management, the price of some aforedescribed catalysts, and the energy consumption to provide moderate pressures can limit in some cases its application on the large scale. Note that the H_2-management risk can be circumvented by *in situ* generation of H_2 from a precursor. For instance, water electrolysis was proposed as an effective tool to provide *in situ* the H_2 for the Pd-catalyzed hydrodechlorination of CB in contaminated groundwater (Xie et al., 2015). This latter example represents the direction toward the applicability of catalytic hydrodechlorination technologies as major remediation tools for real scenarios.

Catalytic reduction using complex hydrides

The use of complex hydrides, such as $NaBH_4$, $LiAlH_4$, and $LiBH_4$, is another possibility for dechlorinating chlorobenzenes, always in combination with transition metal catalysts (nickel, palladium or titanium, Figure 5b). The dechlorination of CB and 1,2-DCB was reported with low yields at 80 °C, using $NaBH_4$ as reductant, a nickel pincer complex as catalyst, and *N,N*-dimethylacetamide as solvent (Wang & Gardinier, 2020). However, using $NaBH_4$ and a titanium dicyclopentadienyl complex in *N,N*-dimethylformamide, the reduction of 1,2,4,5-TeCB to valuable 1,2,4-TCB was achieved at 85 °C (Liu & Schwartz, 1995). The use of $NaBH_4$ with LiCl allowed full 1,2,4-TCB dechlorination in 2 h, but at 300 °C. More sustainably, $NaBH_4$ was combined with Devarda's alloy powder (45% Al, 50% Cu, and 5% Zn) and calcium hydroxide for the tandem dehydrochlorination of the pesticide lindane to TCBs, and further TCBs hydrodechlorination to benzene (Leal-Duaso et al., 2025). This tandem methodology, carried out in aqueous-ethanol medium, led to 94% benzene yield within 70 min.

The relevance of solvent on reactivity and products selectivity was deeply studied in the catalytic dechlorination of chlorobenzenes (Lassová et al., 1999). Among other solvents, tetrahydrofuran, acetonitrile, dimethylsulfoxide, *N,N*-dimethylformamide, diglyme, and *N,N*-dimethylacetamide were tested in the dechlorination of 1,2,3-TCB, 1,2,4-TCB, 1,2,3,4-TeCB, 1,2,3,5-TeCB, and PeCB, catalyzed by a palladium ferrocene complex, and using tetramethylethylenediamine as a base. The best results were found using *N,N*-dimethylacetamide or *N,N*-dimethylformamide, observing that the reaction selectivity strongly depends on the solvent. For instance, PeCB in *N,N*-dimethylacetamide was fully converted into 1,2,4,5-TeCB within 15 min, but into CB after 48 h. The reduction with complex hydrides generally requires long reaction times to exhaustively dechlorinate polychlorobenzenes, and the *ex situ* scale-up has low feasibility due to the cost of both catalysts and hydrides. Nevertheless, PeCB was recently fully dechlorinated in methanol at 30 °C within an unprecedented time of 20 min, through a mechanism involving palladium nanoparticles and diverse active hydrogen species (Lei et al., 2021).

Catalytic reduction using hydrocarbons

Hydrocarbons are a common safe hydrogen source used in refinery and industrial reduction processes. As a consequence, different hydrocarbons have appeared herein as hydrogen donors, together with alkaline and alkaline earth metals as stoichiometric reducing agents. Nonetheless, catalytic reduction of chlorobenzenes has also been addressed using hydrocarbons as the promotor and hydrogen donor, including linear alkanes, cyclohexane and cyclohexene (Figure 5c). For instance, the use of cyclohexane led to the complete conversion of CB and 1,2-DCB selectively to benzene, HCl and H_2 in the presence of catalysts consisting of palladium(II) or cerium(III) chlorides on activated carbon, at 260 and 300 °C, respectively (Yasuda & Shinoda, 2003). These catalyzed processes present high interest for scaled-up situations.

Catalytic reduction using alcohols

The combination of alcohols, typical industrial hydrogen sources, with a base and a heterogeneous palladium or rhodium catalyst is another dechlorination tool for chloroaromatics. For example, CB was fully converted into benzene in less than 1 h at 83 °C, using 2:1 excess of 2-propanol, NaOH, and palladium on alumina (Radoiu et al., 2003). Different bases and catalysts have been tested with good results using 2-propanol. For example, the dechlorination of CB with sodium *tert*-butoxide and $Pd_2(dba)_3$ takes 3 h under thermal activation at 80 °C (Moon & Lee, 2009), or 4 h with potassium *tert*-butoxide and a long-chain NHC-Pd complex at 75 °C (Rühling et al., 2017). An ethanol/water mixture was also applied to the total dechlorination of CB at room temperature in the presence of palladium supported on organic polymers (Zhong et al., 2016).

Regarding polychlorobenzenes, 1,2,4-TCB was reduced to benzene using 2-propanol within 3 h at 55 °C (Figure 5d), while 1,2-DCB and 1,4-DCB were completely converted into benzene in 6–12 h at room temperature (Leal-Duaso et al., 2025). It is important to remark here dozens of works of Ukisu and coworkers on catalytic dehalogenation of substituted chloroaromatics using alcohols as the hydrogen source and solvent. They proved that the addition of small amounts of primary alcohols as methanol to 2-propanol notably enhances the dechlorination reactivity, whilst the presence of aromatic hydrocarbons, such as benzene or toluene, inhibits it (Ukisu, 2008, 2010). Chloronaphthalenes and PCBs were also dechlorinated under similar conditions using alcohols (Gorbunova et al., 2020). In general, the most effective alcohol is 2-propanol, but also methanol, ethanol, 2-aminoethanol, 1-octanol, ethylene glycol, glycerol, and benzylic alcohol, have been studied with acceptable results for chloroaromatics. This method is cost-effective and scalable, due to the low cost of alcohols and bases as NaOH, the low energy requirements, and the stability and recyclability of the supported catalysts.

Catalytic reduction using carboxylic acids derivatives

The use of carboxylic acids derivatives as the hydride source for the reduction of chlorobenzenes in water has been reported in numerous works. Using sodium and potassium formates (HCOONa/K), differently-substituted chlorobenzenes were dechlorinated with palladium catalysts (Arcadi et al., 2004; Suzuka et al., 2015). For example, 4-chlorophenol was converted into phenol at ambient temperature after 3 h stirring in aqueous Pd/C. Polychlorophenols required up to 5 h in the same conditions (Arcadi et al., 2004). The use of a rhodium complex ($RhCl(PPh_3)_3$) as the catalyst led to partial dechlorination of polychlorobenzenes in 2-propanol at 85 °C (Atienza et al., 2001). In particular, 1,2,4-TCB was converted into 1,2-DCB (88%), 1,3-DCB into CB (70%), 1,4-DCB into CB (40%), 1,2-DCB into benzene (90%), and CB into benzene (100%). Formates for CBs reduction can be generated *in situ* as well. Using a mixture of formic acid and Na_2CO_3 in aqueous toluene at 90 °C, 1,2,3,4-TeCB was exhaustively dechlorinated to benzene in only 5 min in the presence of Pd/C (Alonso et al., 2002). Similar results were described using Pd(II) acetate on molecular sieves functionalized with diamino-groups. In this case, the reaction of triethylamine with formic acid led to the formation of triethylammonium formate as the effective hydrogen source for a selective halobenzenes reduction (Štěpnička et al., 2011).

Moving to ammonium formate ($HCOONH_4$), better hydrogen donor than its sodium counterpart (Alonso et al., 2002), different palladium catalysts, outstanding Pd/C and Pd NPs supported on polystyrene-polyethylene glycol resins or MOFs, were studied for the dechlorination of 4-chlorotoluene, CB, 1,3-DCB, 1,3,5-TCB, chloronaphtalene, mono-, di-, and trichlorophenol (Huang et al., 2012; Nakao et al., 2005). In the best cases, chlorobenzenes were dechlorinated in 2-propanol at ambient temperature with excellent yields (85–99%) after 2 h (Figure 5e). As these nanoparticles were supported, the catalyst was recovered and reused 10 times without lost of catalytic activity (Nakao et al., 2005). *N,N*-dimethylformamide was also reported as the hydride source in palladium-catalyzed dechlorination of aryl halides, with good results for iodo- and bromo-derivatives under moderate conditions (150 °C, 18–48 h), but poor results for the conversion of CB to benzene (Zawisza & Muzart, 2007).

Despite its direct applicability to polluted water, even in seawater (Suzuka et al., 2015), and its high compatibility with bioremediation strategies (Gomez et al., 2022), it is relevant to note that, using formates as the hydrogen source, one CO_2 molecule is released for each removed chlorine atom, worsening the carbon footprint of the remediation. Alternatively, sodium acetate (CH_3COONa) was found responsible for the hydrodehalogenation of aryl chlorides catalyzed by Pd/C in aqueous solution (Figure 5f). The described benzene yields were 100% from 1,2,3-TCB (in 6 h), 1,2-DCB (in 3 h), and 1,3-DCB (in 3 h), 87% from 1,4-DCB (in 3 h), and 98% from CB (in 2 h). This methodology using acetates is really effective and easily scalable to any type of polluted water (Xue et al., 2016).

Catalytic reduction using silanes

Polychloroarenes and chlorinated solvents and pesticides, outstanding DDTs, methoxychlor and lindane, have been dechlorinated using tertiary silanes, mainly Et_3SiH, as safe hydrogen donors and chlorine acceptors (Leal-Duaso et al., 2025). For instance, 1,2-DCB was fully converted into benzene within 4 h (Figure 5g), using $PhMe_2SiH$ hydrosilane as a hydrogen source at 120 °C (Sakurai & Kochi, 2002). In order to activate the silane, a metal catalyst is essential, in this case, a nickel(II) complex ($Ni(dppe)Cl_2$) in cooperation with zinc(0) as a co-catalyst (Sakurai & Kochi, 2002). Following these results, the simultaneous dechlorination of DCBs and 1,2,4-TCB and the chlorination of triethylsilane, was studied with a long series of Fe, Ru, Os, Co, Rh, and Ir complexes as catalysts (Alonso et al., 2002). $RuHCl(Ph_3P)_3$ and $RhH_2Cl(^iPr_3P)_2$ provided the best results. This methodology is highly effective in achieving chlorine transfer from CBs to silanes under mild reaction conditions, but is severely limited by the cost of catalysts and silanes. The development of cost-effective catalysts and the use of residual silanes from the silicone industry would increase the feasibility of reduction by silanes.

Catalytic reduction using hydrazine

Hydrazine (N_2H_4) is a versatile reducing agent. In the presence of a COC, hydrazine spontaneously produces hydrogen, capable of reducing chlorinated compounds (Kopinke et al., 2004). Hydrazine was proposed as an alternative hydrogen source in the palladium-catalyzed hydrodechlorination of aryl halides (Kopinke et al., 2004). For instance, using palladium on carbon nanotubes in methanol at 60 °C (Figure 5h), CB was converted into benzene (82%), 1,2-DCB to benzene (72%), 1,3-DCB to benzene (88%), and chlorophenol to phenol (100%), all within 6 h (Xu et al., 2013). Unfortunately, in contact with air (oxygen), hydrazine decomposes exothermically. Hydrazine can be applied in a safer presentation, hydrazine hydrochloride ($N_2H_4{\cdot}HCl$), in combination with Pd/C catalysts and bases, to achieve complete dechlorination of 1,2,3-TCB, 1,2,4-TCB, and 1,3,5-TCB (Rodriguez & Lafuente, 2002), as well as 4-chloroanisole and 4-chlorotoluene, after 24 h at 20 °C (Cellier et al., 2003).

Catalytic reduction using phosphorus compounds

Sodium hypophosphite (NaH_2PO_2) has resulted to be an excellent hydrogen donor in the Pd/C-catalyzed surfactant-assisted aqueous hydrodechlorination of CBs (Oba et al., 2013). As an example, PeCB was dechlorinated at 50 °C within 90 min, leading to 86% benzene yield. In this case, moderate excesses of hypophosphite and sodium carbonate, as well as the presence of Tween20 as nonionic tensioactive, are required to achieve this notable dechlorination level.

Reduction using ionic solvents

Ionic solvents, including ionic liquids (ILs) and deep eutectic solvents (DES), appeared in Section 9 as effective media for nanoparticles stabilization and CB dechlorination (Calò et al., 2007; Leal-Duaso et al., 2021). Surprisingly, some works reveal the role of protic ionic solvents as the hydrogen source in CBs reduction. To illustrate this, the indium-induced dechlorination of CB and 1,4-DCB using 1-butyl-3-methylimidazolium-based ionic liquids such as [BMIm]Br and [BMIm]Cl (in 2:1 IL/CB ratio) was optimized at 95 °C (Figure 5i), leading to 60–100% yields after 14 h (Cañete et al., 2012). The role of the IL as the hydrogen source was demonstrated by deuterium labeling. In other cases, the IL was reported to act just as the reaction medium, while the hydrogen source role was attributed to small amounts of water, for instance when using [BMIm]Br in the presence of $Ni[phen]_2(PF_6)_2$ as catalyst (Sun et al., 2013). Despite the interest on these results with ionic solvents, imidazolium-based ILs are often expensive and ecotoxic (Gracia-Barberán et al., 2022). In this context, the use of bio-based DES as hydrogen donors is a feasible alternative thanks to their easy accesibility and low cost, renewable origin, non-toxicity, and biodegradability.

Electrochemical reduction

The electrochemical reduction is an efficient approach for degrading persistent COCs (Figure 5j) (Flid et al., 2020; Zhang et al., 2025). In recent years, intensive research has been performed in the development of more efficient cathodic materials and electrocatalysts, novel electrolytes, electrochemical mediators, and ionic solvents (Leal-Duaso et al., 2024; Zhang et al., 2025). However, electroreduction of chloroaromatics is far from its electrooxidation counterpart in terms of publications, technological level, and, above all, in the limited availability of scaled examples in real scenarios.

The electrochemical cleavage of the C–Cl bond consumes two electrons and one proton through an irreversible process (Flid et al., 2020). In the case of chlorobenzenes, two mechanisms are possible (Figure 4d), 1) an electron transfer where a CB radical-anion is formed prior to the Cl^- release and the formation of the corresponding CB radical, and 2) a hydrogen transfer where a protonated intermedium is generated prior to the $Cl^\bullet$/HCl elimination.

In aqueous media, desirable to develop ISCR electrochemical procedures for remediation of polluted industrial wastewater and groundwater, the competitive reduction of water often limits the faradaic efficiency in the chlorobenzenes electroreduction. Nevertheless, a porous nickel cathode led to the fully electroreduction of 2-chlorophenol in water using a carbon anode and sodium sulfate as the electrolyte (Cong et al., 2005). Various cathode materials, such as graphite, zinc, titanium, RuO_2/Ti design-cathodes, and stainless steel, were studied with different results for the electrochemical reductive dechlorination of HCB in water (Wang & Lu, 2014). The use of the same material as the anode prevented the HCB electrooxidation, even in the environment. What is more interesting here is that chlorine atoms are rapidly replaced one by one, as depicted in Figure 4a, and it is possible to reach different dechlorination degrees by choosing a different cathode.

The electrodeposition of nanomaterials, usually palladium nanoparticles on carbon supports such as glassy carbon or carbon felts is another interesting effective tool to design cathodes/electrocatalysts for the electroreductive dechlorination of chlorobenzenes with application to aqueous real scenarios. For instance, Pd–Fe NPs/glassy-carbon cathodes showed relevant dechlorination results (Luo et al., 2014). An alternative approach for the remediation of real effluents polluted with chloroaromatics as chlorotoluene is the use of palladized-ion exchange membranes. This technology increases the efficiency with respect to 2D-metallic cathodes, due to the larger active surface area and enhanced accessibility to the active palladium sites (Inoue et al., 2003).

Very recently, a Pd/N-Graphene/Ni foam cathode has been developed for an active, durable, and scalable system for electrocatalytic hydrodechlorination of chlorophenols to phenol (Rugira et al., 2025). This technology depollutes real water with 98.4% of efficiency in 1 h, combining direct reduction by cathode electrons and indirect reduction by *in situ* formed $H^•$ radicals, which represents a significant advance toward the remediation of real sites with chloroaromatics.

In the case of solid polychlorobenzenes electroconversion, the use of organic solvents as concentration and reaction media may be of interest. For example, CB, 1,3-DCB and 1,2,4-TCB dissolved in acetonitrile were fully electroreduced on platinum in the presence of a naphthalene mediator (Jalil et al., 2007). Alternative electron mediators, including biphenyl, phenanthrene, anthracene, pyrene, and dibenzofuran (Guena et al., 2000; Jalil et al., 2010), as well as additional Pt, Cd, Sn, In, Pb, Zn, and Ag cathodes (Hoshi et al., 2004), have been studied for the electroreduction of CB, polychlorobenzenes, and chlorobenzoic acid. It is relevant to note that, in the case of using acetonitrile, not only benzene, but toluene was formed due to the reaction of CB with the solvent (Hoshi et al., 2007). Regarding highly-chlorinated benzenes, HCB was electrolyzed on glassy carbon electrodes in *N,N*-dimethylformamide, leading to complex products mixtures (Matsunaga & Yasuhara, 2005), as well as in acetonitrile in presence of cobalt(I)-salen and cobalt(II)-salen electrocatalysts (Leal-Duaso et al., 2025).

The combination of electroreduction with sonoremediation, electrooxidation or bioremediation are feasible alternatives for the conversion of chlorobenzenes, chlorophenols, and chloronitrobenzenes into innocuous chemicals (Guo et al., 2015). In electrobioremediation, the current additionally stimulates the bacterial uptake of biodegradation genes. Another recent example shows the application of single-atom Ni supported on carbon nanotubes to a tandem process that combines reductive hydrodechlorination of chlorophenols to phenols and electro-Fenton oxidation in polluted water (Pei et al., 2024).

Photochemical reduction

Photoremediation is an emerging tool for the decontamination of water polluted by low concentrations of COCs. However, in liquid water, photodegradation of CBs usually leads to the formation of oxidation products, together with phenolic compounds through radical nucleophilic substitution reactions (Klán et al., 2000). Hence, photochemical reduction of chlorobenzenes has been scarcely reported in the literature. One example of chlorobenzenes photoreduction under ultraviolet irradiation was assisted by ZnS nanocrystallites in organic solvents such as *N,N*-dimethylformamide, and using triethylamine as a sacrificial electron donor (Wada et al., 1998). In this case, the photodegradation rate order was 1,2,3-TCB > 1,4-DCB > 1,2,3,4-TeCB > 1,2,4-TCB ≈ 1,3-DCB ≈ 1,2-DCB ≫ CB. 1,4-DCB was also completely photodechlorinated in the presence of organic semiconductors (Yanaida, 2000). Otherwise, the reductive dechlorination of CB in water/2-propanol mixtures was achieved with moderate yields, under anoxic atmosphere and photocatalyzed by palladium-loaded titanium(IV) oxide particles (Kominami et al., 2013). The combination of surfactant solutions and an additional hydrogen source maximizes the photoreduction of chloroaromatic pollutants. Novel photocatalysts have been developed to dechlorinate polychlorobenzenes *via* catalyzed-reductive dehalogenation. Examples are Rhodamine-6G in combination with lanthanide ions (Meyer et al., 2017) or quantum dots (Zhang et al., 2019). Finally, mentioning that reductive photolysis of CB on ice has been studied, as different products are formed, including biphenyl, chlorobiphenyls, and interesting polyaromatics such as terphenyls and triphenylene (Klán et al., 2000).

Conclusions and perspectives

Reductive chemical transformation of chloroaromatic compounds is a key and well-established tool for the valorization of these toxic and persistent, but still-today strategic chemical intermediates, into higher added-value commodities, and for their remediation in soil and water. Most of reduction products remain fundamental intermediates in the chemical industry with enormous economic impact. However, all reduction and hydrodechlorination methods had not yet been reviewed and holistically compared. Therefore, from this review we encourage the improvement of sustainable reduction methodologies. Also, this review evidences the lack of scale-up studies for many of the reviewed processes, which have shown promising results at a laboratory scale, but for which their performance in real scenarios, environmental impact, techno-economic analysis, as well as realistic LCA analysis, are still unknown.

A comparison of the performance and possibilities for the most relevant reduction methodologies is summarized in Table 1. From a remediation point of view, the classification of the reduction methodologies into stoichiometric and catalytic processes should make easier to distinguish between *in situ* and *ex situ* solutions and identify scalable methods.

1. **In the case of contaminated soils**, stoichiometric technologies using alkaline metals, zero-valent transition metals and bimetallic materials are very interesting *in situ* remediation tools.
    a. Reduction using transition metals is safer and more scalable, from economic and environmental points of view, than using alkaline metals.
    b. The use of zero-valent metals and alloys has less environmental impact when applied to real polluted sites, and is economically viable in the case of using iron (or iron sulfides).
    c. Zero-valent metals, FeS and bimetallic materials can be effectively combined with biological, oxidation and electrokinetic processes to maximize the remediation.
2. **For the case of polluted water and waste**, catalytic and electrochemical methodologies present the highest applicability.
    a. The development of more affordable, stable, and recoverable catalysts, especially in flow-systems, would allow a step forward in the remediation of chloroaromatics by effective H_2-mediated hydrodechlorination methods.

Table 1. Summary of key reduction methodologies for the remediation of chlorobenzenes.

Reductant	Operating conditions[a]	Technological degree & Effectiveness[b]	Scalability & Applicability[b]	Environmental impact[b]
Stoichiometric methods				
Na, K	25–180 °C (H donors), min-scale degradation	E	H	M
Mg	50–150 °C, H donors	M	M	M
Fe (ZVI)	Ambient conditions, hour/day-scale	H/E	E[c]	L
Cu (CMD)	25–300 °C, C, H donors	H/E	M	L
Alloys	25–150 °C, H donors	H/E	H[c]	L
FeS	Ambient conditions	H	H[c]	L
H_2 (GPCR)	850 °C, pressure, water, min-scale degradation	E	H	M
SCW	250 °C, Fe/ZrO_2, subcritical water, min-scale degradation	H	M	L
CaH_2	40–2700 °C (H donors)	H	L	M/H
Catalytic methods				
H_2	25–300 °C, Ni/Pd cat. (base, pressure) in water or alcohol	E	M[c]	L/M
$NaBH_4$	30–300 °C, Ni/Pd/Ti cat., solvent	M	L	M
Hydrocarbon	250–300 °C, Pd cat. (H donors, pressure)	H	M	L/M
Alcohols	25–85 °C, Pd cat., base	H	M/H	L
Formates	25–90 °C, Pd cat., alcohol	H	H[c]	M
Acetates	25 °C, Pd cat., water	H	H[c]	L
Silanes	120–150 °C, Ni/Rh/Ru cat.	M	L	M
N_2H_4	25–60 °C, Pd cat., methanol	L/M	L	M
NaH_2PO_2	50 °C, Pd cat., surfactant	M	M	M
Bio-DES/IL	50–95 °C, Ni/In cat.	M	H[c]	L
Electrored.	Ambient conditions, Ni/Pt/Sn/In/Pb/Ag/Zn/Pd–Fe cathode, in W/ACN/DMF	H	H[c]	L
Photored.	Ambient conditions, diverse photocatalysts (solvent)	M	M[c]	L

[a] All the methods have a hour-scale reaction time unless specified in the table.
[b] E = Excellent; H = High; M = Moderate; L = Low.
[c] Possibility of synergistic combination with bioremediation or other chemical transformations.

  b. Interesting catalytic methods based on the use of renewable hydrogen donors (alcohols, formates, acetates or deep eutectic solvents) should be more deeply studied.
  c. Combination of *in situ* chemical reduction, using abundant metals as iron, with photo- or electroreductive approaches, especially in conjunction with bioremediation, are very promising tools that have not yet been sufficiently explored in real-world scenarios.
  d. More active cathode materials, eutectic electrolytes, and electro- and photocatalysts are nowadays available and should be studied for *in situ* remediation of chloroaromatics.
3. **From a valorization perspective**, chlorobenzenes are transformed into a wide variety of useful chemicals through chemical reduction methodologies. Most works report the formation of benzene, but chemicals such as cyclohexane, cyclohexadienes, and polyaromatics, fuels as methane, and various carbon nanomaterials, can be selectively prepared from chloroaromatics. Chemical reduction maximizes the circular economy in the remediation process of chlorobenzenes, which is no possible in alternative technologies such as oxidation and combustion, also minimizing environmental impact, energy consumption, and CO_2 footprint.
4. **Future development of more accessible and efficient hydrogen sources** should significantly increase interest in catalytic reduction methods, for example by organic hydride vectors or hydrogen active species arising from water electrolysis.

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The authors report there are no competing interests to declare.

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