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## Chapter

# Metallic Copper as Dehalogenation Catalyst in the Treatment of Water and Wastewaters

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## Abstract

Most halogenated organic compounds (HOCs) are toxic and carcinogenic, hence unwanted in the environment. Several technologies exist for the treatment of both legacy and newly contaminated zones. In many contaminated subsurface environments, nano zero-valent iron (nZVI) as a reagent is the tool of choice, while palladium (Pd) as a catalyst faces technical challenges. A system comprising metallic copper and borohydride as a reducing agent (referred herein as copper-borohydride system, CBHS) provides an alternative to nZVI and Pd. This chapter presents a deeper understanding of the CBHS for the treatment of HOCs by highlighting the state of knowledge related to the i) type and classes of compounds that are treatable, ii) possible reaction pathways for their transformation, iii) specific metal activities for transformation of selected classes of HOCs, iv) influence of common water constituents on catalyst stability, and v) future perspectives regarding its application in water treatment applications. Furthermore, an up-to-date discussion is presented regarding the available techniques for the synthesis of copper nanoparticles. Based on the evaluation criteria including product selectivity patterns, amount and the fate of intermediates, and metal cost and stabilities in water, the most suitable application areas for Cu, Pd, and nZVI are presented as recommendations.

**Keywords:** halogenated organic compounds (HOCs), metallic copper catalysts, palladium catalysts, reduction technologies, nano zero-valent iron, water treatment

## 1. Introduction

Environmental contamination of soil, surface water, and groundwater with halogenated organic compounds (HOCs) continues to pose a serious threat to both human and ecological health. HOCs are indispensable in many consumer products and industrial processes, e.g. as solvents, refrigerants, and feedstocks in the manufacture of pharmaceuticals, veterinary drugs, paints, adhesives, and lacquers [1]. HOCs commonly enter the environment by improper use. That includes accidental discharge from the chemical industries, surface runoff, and improper disposal and usage. The low-molecular-weight HOCs including haloacetic acids and halomethanes are also prominent members of disinfection byproducts which are produced when natural

waters containing organic matter are treated with chlorine and chlorine-based disinfectants [2]. Chlorinated compounds become more and more insoluble in water with growing carbon chain length of 10–13 and higher chlorine content which also makes them susceptible to long-range atmospheric transport [3]. In aquatic environments, such substances undergo bioaccumulation and biomagnification in aquatic organisms, e.g. fish, crabs, oysters, etc.; thus, they enter the food chain [3–5]. In addition, human exposure to HOCs occurs via dermal absorption, inhalation, and drinking contaminated water and consumption of contaminated food [1]. Most HOCs are also toxic and possible carcinogens even at very low concentrations [6–8]. Due to their associated public health risks, the production and use of HOCs is under strict control. Many of them are placed under the Stockholm Convention on Persistent Organic Pollutants and are also placed on toxic release inventory in the European Union, Japan, Canada, and the United States [1, 3–5]. When released into the environment, most HOCs are resistant to biodegradation; hence, they are persistent. The removal of HOCs from contaminated environments is therefore of utmost importance. Several technological processes based on biological, physical, and chemical methods have been evaluated for various contaminant types. So far, there is no single technology that can be applied for the detoxification of all contamination problems. Important factors which need to be considered before selecting a treatment technology include the chemical nature of the HOCs, the nature of contaminated media, the extent of contamination, overall treatment time, cost of the treatment system, degree of detoxification, and fate of the treated media.

Biological processes in most cases are characterized by low conversion degrees of the contaminant and slow reaction rates but low maintenance. Hence, long treatment times are necessary for bringing the contaminants concentrations to levels of low toxicity. Also, microbial processes such as methanogenesis are sometimes inhibited by the presence of high concentrations of some target contaminants, e.g. chloroform (CF) [9, 10]. Air-stripping and adsorption processes for removal of HOCs from water only transfer the contaminants from one phase into another, where further treatment of the resultant effluents is necessary [11]. For adsorption processes, regeneration of the adsorber (e.g. activated carbon) or its frequent replacement is not only expensive but also time-consuming. Incineration which is sometimes applied to more complex and toxic industrial effluents is energy-intensive and costly. The major environmental problem associated with incineration of HOCs include the release of incomplete combustion products, fly ash generation, and particularly the generation of toxic byproducts, especially polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs) [12, 13].

Chemical destruction techniques based on photooxidation, Fenton's reagent, and advanced oxidation processes (AOPs) when applied to HOCs are characterized by low reaction selectivity and a higher probability of generating toxic and recalcitrant byproducts. Hence, the provision of excess redox equivalents is necessary when full mineralization is desired [14, 15]. Reduction processes are more suited for the treatment of HOCs than oxidation processes. Reduction involves the selective removal of the halogen (X) atoms by H-atoms ( $R-X + \text{reducing agent} \rightarrow R-H + H-X$ ). Generally, the replacement of X atoms from higher halogenated contaminants results in significant detoxifications. However, there are exceptions. A prominent example is vinyl chloride (VC), which is more toxic than the higher chlorinated chloroethene homologs, e.g. perchloroethylene (PCE) [16]. The coupling of reduction processes with biological processes can sometimes be used to achieve significant detoxification [17, 18].

For about three decades (since 1994) [19], technologies employing microscale zero-valent iron (mZVI) or nano zero-valent iron (nZVI) as reagents to reduce HOCs were

the methods of choice for *in situ* groundwater treatment of HOCs [20, 21]. Due to the higher HOCs reaction rates and better particle mobility, nZVI is widely used for direct injection into the aquifer. In the presence of water, nZVI as a reagent is consumed, thereby releasing electrons (and consecutively also hydrogen) that are essential for the cleavage of the R–X bond ( $R-X + Fe^0 + H_2O \rightarrow R-H + Fe^{2+} + X^- + OH^-$ ). Reducing agents based on metallic iron are comparably cheap, environmentally compatible, and offers long-term treatment solutions for contaminated aquifers under anaerobic conditions. nZVI can be applied to treat mainly the halogenated alkanes and alkenes. It shows very low activity for the reduction of saturated aliphatic compounds with lower chlorination degrees such as dichloromethane (DCM) and 1,2-dichloroethane (1,2-DCA) [22, 23]. Also, iron's limitations are its inability to reduce C–Cl bonds attached to aromatic structures, especially those with lower chlorination degrees [24, 25], its tendency to deactivate under aerobic conditions, its loss of activity at pH > 10, and its consumption with time by anaerobic corrosion in water ( $Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$ ). The consumption of nZVI in water due to corrosion is pH-sensitive. When pH < 7 is applied, nZVI is consumed quickly producing hydrogen as the major product. At pH > 10, the coating of nZVI core with iron oxides/hydroxides occurs inhibiting further reaction. Hence for the reduction of HOCs in water by nZVI, the pH need to be maintained in the range 7–10 using suitable buffers [26].

Reduction processes catalyzed by H-activating metals, especially rhodium (Rh), platinum (Pt), and Pd, are applicable to treat a broader spectrum of compounds which include the reduction of C–X bonds attached to aromatic structures. Among the noble metals, Pd is the most potent hydrodehalogenation (HDH) catalyst. However, Pd is sensitive to deactivation due to poisoning and even self-poisoning by released hydrogen halide (HX). Nevertheless, the effect of HX can be prevented by its withdrawal from the surface through uptake by the water bulk phase or by the addition of a base, e.g. NaOH [27–30]. Whereas nZVI does not require the addition of an additional reductant, Pd must be used together with H-donors (reducing agents) such as H<sub>2</sub>, borohydride (BH<sub>4</sub><sup>-</sup>), Fe<sup>0</sup> as H<sub>2</sub> producer, formic acid, hydrazine, or alike [31, 32]. The HDH reaction occurs at Pd surfaces and is mediated by activated H-species (H\*) or adsorbed surface hydrogen (Pd–H<sub>ads</sub>) [33–35]. The cleavage of R–X bonds by Pd catalyst and in the presence of hydrogen as the reductant can be described as ( $R-X + H_2 + Pd^0 \rightarrow R-H + HX + Pd^0$ ). The specific metal activity ( $A_m$ ), which will be discussed later in this chapter, can be used to formally compare the treatment efficiencies of reagents and catalysts.  $A_m$  is a second-order parameter that tells us the amount of metal required to treat a given amount of contaminated water per time (required number of half-lives until desired treatment goal is reached). For similar compounds and under comparable reaction conditions, the specific Pd activity ( $A_{Pd}$ ) seems to depend on the nature of H-donors [32]. Nevertheless, for all HOCs classes,  $A_{Pd}$  is found to be between two and five orders of magnitude higher than the specific nZVI activity ( $A_{nZVI}$ ) [36, 37]. Pd as a catalyst is reusable several times and is required only in very small amounts. Therefore, in comparison with nZVI, only a small amount of Pd metal is necessary to treat large volumes of contaminated water in very short times. Another advantage of Pd compared to nZVI is that it can be applied over a broad range of pH (2–9) and to nearly all HOCs classes including the reduction of chlorinated aromatics [38, 39]. In comparison with nZVI, the application of Pd for the reduction of HOCs in water is not limited by pH. Nevertheless, dissolution of Pd metal under highly acidic conditions can occur [40].

Despite the huge potential of Pd in HDH reactions, its use in water treatment applications under field conditions is limited due to major drawbacks. Pd is more

expensive and rarer than nZVI and is readily deactivated by manifold processes which inhibit or even destroy the catalyst function. The Pd catalyst loses its activity in the presence of macromolecular and ionic poisons such as heavy metals, organic matter (e.g. natural organic matter (NOM), humic acids (HA), and fulvic acids) [40–44]. The most significant substances with a detrimental effect on Pd are reduced sulfur compounds (RSCs), e.g.  $\text{SO}_3^{2-}$  and  $\text{S}^{2-}$  [45]. Under anaerobic conditions,  $\text{S}^{2-}$  can also be produced in aqueous environments by sulfate-reducing bacteria, especially in the presence of hydrogen. Regeneration of deactivated Pd catalysts using oxidants, e.g. hypochlorite is tedious, expensive, and time-consuming, results in loss of metal due to leaching and may not restore original (baseline) catalyst activity [40, 41, 44]. Also,  $A_{\text{Pd}}$  values are extremely low for saturated aliphatic compounds with lower chlorination degrees such as dichloromethane (DCM) and 1,2-dichloroethane (1,2-DCA) [22, 23, 38, 39]. DCM, 1,2-DCA, and similar compounds are contaminants of interest to water treatment professionals, since they are toxic and possible carcinogens. Saturated aliphatic compounds with lower chlorination degrees such as chloromethane (CM), DCM, and chloroethane (CA) are also produced as stable byproducts during the dechlorination of the corresponding higher chlorinated homologs. For example, the dechlorination of CF and carbon tetrachloride (CTC) by nZVI and Pd produces CM and DCM as recalcitrant byproducts [22, 38, 46, 47]. Similarly, CA is usually a dead-end byproduct during the dechlorination of 1,1,1-trichloroethane (1,1,1-TCA) by nZVI and Pd [23, 38].

Cu is the eighth most abundant element of the earth's crust, and its unique properties such as good ductility, malleability, high thermal and electrical conductivity, and high corrosion resistance make it suitable for a broad range of applications. Common applications for metallic Cu catalysts include oxidative degradation of HOCs [48],  $\text{NO}_x$  reduction [49],  $\text{CO}_2$  reduction [50], electrocatalytic reduction of chlorinated alkanes [51–53], and aryl coupling reactions [54, 55]. Despite this widespread application, the utilization of metallic Cu as reduction catalysts for the treatment of HOCs in water is limited. Under ambient conditions (1 atm and  $25^\circ\text{C}$ ) and in water, metallic Cu is less reactive toward the activation of  $\text{H}_2$  into  $\text{H}^*$ . Hence, it must be used together with a more reactive reductant such as  $\text{BH}_4^-$  ( $E^\circ = -1.24$  V vs. standard hydrogen electrode (SHE)) [56]. In this chapter, CHBS represents  $\text{Cu} + \text{BH}_4^-$ . The HDH reaction by the copper-borohydride system (CBHS) may be mediated by several reactive species. The cleavage of R–X bonds could be mediated by surface adsorbed H-species or hydrides [57–59]. Like in hydrosilylation reactions, the insertion of Cu species may as well be implicated [60, 61]. In this chapter, we review important literature to provide a deeper understanding of the CBHS for the reductive treatment of HOCs in water. Consideration will focus on product selectivity patterns, specific Cu activities ( $A_{\text{Cu}}$ ), and catalyst stability in water. For a broad spectrum of HOCs, the HDH ability of the CBHS is compared with the common reduction tools based on nZVI and Pd. The comparison is intended to provide a guide to water treatment professionals during the decision-making process in selecting an appropriate tool that is best suited to a particular class of HOCs under certain reaction conditions. In order to do the comparison, several essential criteria are defined in this chapter.

## 2. Evaluation criteria for reagents and catalysts

The evaluation of the efficiency of a treatment system involves several parameters which are discussed in this section. Conversion ( $X_{\text{HOC}}$ ) which shows the fraction of a given contaminant transformed at any given time can be calculated using Eq. (1):

$$X_{\text{HOC}} = \left( 1 - \frac{n_{\text{HOC},t}}{n_{\text{HOC},0}} \right) \times 100\% \quad (1)$$

where  $n_{\text{HOC},t}$  represents the moles of educt at any given time (mol) and  $n_{\text{HOC},0}$  refers to the initial moles of educt fed into the batch reactor at  $t = 0$  (mol). The product yield ( $Y_{i,\text{product}}$ ) which shows the amount of product formed with respect to the initial moles of educt fed into the reactor is calculated based on Eq. (2):

$$Y_{i,\text{product}} = \frac{n_{i,\text{product}}}{n_{\text{HOC},0}} \times 100\% \quad (2)$$

where  $n_{i,\text{product}}$  represents the moles of product  $i$  obtained at a given time (mol). In order to determine the actual amount of product formed with respect to the actual amount of educt transformed at any given time, product selectivity ( $S_{i,\text{product}}$ ) can be calculated based on Eq. (3):

$$S_{i,\text{product}} = \frac{n_{i,\text{product}}}{n_{\text{converted HOC}}} \times 100\% \quad (3)$$

where  $n_{\text{converted,HOC}}$  represents the moles of educt converted at the given time (mol). In order to determine the reaction rates for the transformation of HOCs using nZVI, Pd, and Cu, the pseudo-first-order kinetics as shown in Eq. (4) can be applied:

$$\frac{dc_i}{dt} = -k_{\text{obs}} \cdot c_i \quad (4)$$

where  $c_i$  represents the concentration of HOCs (mg/L), while  $k_{\text{obs}}$  is the pseudo-first-order rate constant (1/min). For slow-reacting compounds, such as CA, that are characterized by lower conversion degrees,  $k_{\text{obs}}$  can conveniently be calculated from products formation as shown in Eq. (5):

$$\ln \left( 1 - \frac{c_{i,\text{product}}}{c_{\text{product,max}}} \right) = -k_{\text{obs}} \cdot t \quad (5)$$

where  $c_{i,\text{product}}$  and  $c_{\text{product,max}}$  represent the concentration of product at the given time (mg/L) and the maximum concentration of product (mg/L), respectively, while  $t$  refers to the reaction time (min). The value of  $k_{\text{obs}}$  calculated based on Eq. (4) and Eq. (5) and for metal particles with similar particle sizes can be used to compare the HDH ability of a remediation tool only for HOCs transformation reactions carried out under similar reaction conditions (same metal concentrations and reaction pH). Since in most cases reaction conditions are hardly the same, the surface area-normalized rate constant ( $k_{\text{SA}}$  in [L/(m<sup>2</sup>·min)]) that is calculated based on Eq. (6) can be used:

$$k_{\text{SA}} = \frac{k_{\text{obs}}}{c_m \cdot a_s} \quad (6)$$

where  $c_m$  is the concentration of the metal (g/L) and  $a_s$  is the metal-specific surface area (m<sup>2</sup>/g). The value of  $a_s$  is commonly obtained from N<sub>2</sub> adsorption/desorption (Brunauer–Emmett–Teller (BET)) measurements. The use of  $k_{\text{SA}}$  assumes that the entire exposed surface area of the metal participates in the reaction. Based on this understanding, nanosized particles which have larger available surface areas are

preferred for HDH reactions compared to their micro-sized particles. However, it is noteworthy to point out that for heterogeneous systems, only a fraction of the available surface area takes part in the HDH reaction. Specifically, only the available surface atoms as determined by dispersion data (from CO chemisorption measurements) are involved. In the absence of metal dispersion data, the specific metal activity ( $A_m$ ) which is calculated as shown in Eq. (7) can be used:

$$A_m = \frac{V_w}{m \cdot \tau_{1/2}} = \frac{1}{c_m \cdot \tau_{1/2}} = \frac{\ln(c_{t1}/c_{t2})}{\ln 2 \cdot c_m (t_2 - t_1)} = \frac{k_{obs}}{\ln 2 \cdot c_m} \text{ [L/(g} \cdot \text{min)]} \quad (7)$$

where  $V_w$  is the volume of the water contaminated with HOCs (L),  $m$  refers to the metal mass (g), and  $\tau_{1/2}$  refers to the HOCs half-life (min) obtained from the pseudo-first-order kinetics profile. The variables  $c_{t1}$  and  $c_{t2}$  refer to the concentrations of contaminants at any two sampling times  $t_1$  and  $t_2$ , respectively.  $A_m$  can be used for different metals which have nearly the same particle sizes to provide a solid comparison where dispersion data is not available. In terms of technical and economical points of view,  $A_m$  shows the amount of metal required to treat a given volume of contaminated water in several half-lives. By using  $A_m$  as a basis for comparing the dehalogenation abilities of nZVI, Pd, and Cu, it is important to point out that we are comparing three “reduction systems” and not the metals, because different reductants are applied ( $\text{BH}_4^-$ ,  $\text{H}_2$ , and  $\text{Fe}^0$ ).

### 3. Synthesis strategies for copper nanoparticles (Cu NPs)

The synthesis of Cu nanoparticles (Cu NPs) can be done by using physical, bio-based, and chemical methods. Top-down or physical methods are used to reduce bulk material into nanosized dimensions by mechanical milling, grinding, cutting, etching, laser ablation, vacuum vapor deposition, and pulsed wire discharge [62, 63]. Top-down methods are less preferred; since it is difficult to obtain Cu NPs with uniform sizes, they are energy-intensive and require specialized equipment and technical knowledge.

Bio-based methods for the synthesis of Cu NPs employ the use of plant extracts and microorganisms. Cu NPs can be produced by heating a mixture of plant extracts and copper salts. The reducing and stabilizing agents present in plant extracts include phenols, flavonoids, proteins, tannins, and terpenoids. Common microorganisms used include bacteria, fungi, and green algae [64, 65]. Bio-based methods are preferred because they are considered cost-effective and environmentally friendly. For the rapid and large-scale synthesis of Cu NPs, chemical reduction techniques are preferred over biological methods.

Bottom-up approaches involve the synthesis of Cu NPs from a copper salt or copper oxide. Common bottom-up methods applied include chemical reduction, sonochemical reduction, micro-emulsion techniques, electrochemical reduction, hydrothermal or sol-gel synthesis, polyol, and microwave irradiation [62, 63]. Chemical reduction techniques for the synthesis of Cu NPs are the most common, since they are simple and usually have the tendency to produce smaller and uniform nanoparticles. Furthermore, in chemical reduction methods, nanoparticles of desired sizes and morphology can be obtained by manipulation of reaction conditions, e.g. time, pH, solvent, and suspension stabilizer. The reduction of a copper salt can be done using reductants such as  $\text{BH}_4^-$  and hydrazine combined with stabilizers

including ascorbic acid, starch, poly(ethylene glycol), poly(vinylpyrrolidone) (PVP), cetyltrimethylammonium bromide, poly(acrylic acid) (PAA), and carboxymethyl cellulose (CMC). When stabilizers are used, the reaction mixture needs to be refluxed at 60–100°C for about 30–120 min.

The most widely used method for the synthesis of Cu NPs in water and under ambient conditions involves the reduction of a copper precursor with sodium borohydride (NaBH<sub>4</sub>). This method is preferred, since it is simple to implement and produces nanoparticles with uniform sizes, narrow size distribution range, and uniform surface morphology [66, 67]. Under ambient conditions and in water, BH<sub>4</sub><sup>-</sup> is unstable and the decomposition rate is pH-sensitive [58, 68, 69]. Therefore, to control BH<sub>4</sub><sup>-</sup> decomposition, reaction pH ≥ 10 is ideal for the growth and development of Cu NPs. The recommended molar ratio for Cu<sup>2+</sup> : NaBH<sub>4</sub> is 1 : 8. A lower molar ratio between Cu<sup>2+</sup> and NaBH<sub>4</sub> is characterized by a slower reaction and nonuniform particle sizes. To prevent agglomeration of the freshly prepared nanoparticles, the stabilizers (PVP, PAA, CMC, etc.) are usually introduced already during the synthesis process.

#### 4. Reduction of HOCs in water: Comparison of Cu, Pd, and nZVI

The CBHS for reduction of HOCs in water has received less attention than with Pd + H<sub>2</sub> and nZVI. Previous work applied the CBHS for dechlorination of DCM [66], 1,2-DCA [67], and selected monochloroaromatics [70]. Recently, a deeper understanding of the system was applied to a broad spectrum of HOCs, highlighting product selectivity patterns, reaction rates of the individual compounds, and the efficiency of the system in comparison with Pd and nZVI [36, 37]. The HDH ability of the CBHS for the treatment of saturated aliphatic HOCs is markedly superior to nZVI and Pd. This section provides an extensive overview of the HDH abilities of the three systems. Evaluation criteria include reduction (dehalogenation) rates of individual HOCs, product selectivity patterns, amount and fate of chlorinated intermediates, metal cost, and metal stability in water. It is noteworthy to point out this is not a comparison of the individual metals but rather a comparison of their reduction abilities (Cu + BH<sub>4</sub><sup>-</sup>, Pd + H<sub>2</sub>, and nZVI). Using both experimental and literature data, Shee (2021) calculated the specific metal activities for the reduction of individual HOCs in water using Cu, Pd, and nZVI as shown in **Table 1**. The data in **Table 1** were calculated using nanoparticles of comparable dimensions ( $d_{50,Cu} = 50$  nm,  $d_{50,Pd} = 60$  nm, and  $d_{50,nZVI} = 75$  nm) [36].

From the data in **Table 1**, for most compounds, the ease of dehalogenation is based on the weakest C–X bond strengths.

Since C–Br (285 kJ/mol) are weaker than C–Cl bonds (337 kJ/mol), brominated compounds show higher  $A_m$  values than their chlorinated counterparts. As can be seen in **Table 1**, for Cu, the dehalogenation rates (presented as  $A_{Cu}$ ) for halogenated methanes and ethanes depend on i) the strength of the weakest C–X bond and ii) the number of geminal X atoms. The  $A_{Cu}$  values are generally inversely proportional to the strength of the calculated C–X bonds. For example,  $A_{Cu,CTC}$  is five orders of magnitude higher than  $A_{Cu,DCM}$ . For the chlorinated ethanes, their reactivity depends not only on the number of Cl atoms but also on the number of geminal Cl atoms. An increase in the number of geminal Cl atoms leads to i) a decrease in C–Cl bond strengths and ii) an increase in the initial attachment of Cl atoms to the catalyst surface. This trend in reactivity for chlorinated methanes and ethanes was also observed for reactions carried out in the gas phase using solid metallic Cu [71] and Pd



Halogenated organic compound classes	BDE (kJ/mol)	Specific metal activities $A_m$ [L/(g·min)]			
		m = Cu	m = Pd	m = nZVI	
Chlorinated methanes and ethanes with higher chlorination degree	CTC	293	1100 ± 100	200 ± 20	0.30 ± 0.05
	CF	322	130 ± 10	5 ± 1	0.003 ± 0.001
	1,1,1-TCA	309	170 ± 20	n.a.	0.102 ± 0.006
	1,1,2-trichloroethane	318	6 ± 1	1.3 ± 0.2	0.0016 ± 0.0002
	1,1,1,2-tetrachloroethane	295	900 ± 200	380 ± 20	0.36 ± 0.03
	1,1,2,2-tetrachloroethane	314	60 ± 5	n.a.	0.021 ± 0.003
	Hexachloethane	304	2500 ± 500	n.a.	0.52 ± 0.04
Chlorinated methanes and ethanes with lower chlorination degree	DCM	339	0.22 ± 0.02	n.a.	n.a.
	CM	351	0.0020 ± 0.0002	n.a.	n.a.
	CA	352	0.010 ± 0.005	n.a.	n.a.
	1,1-dichloroethane	328	5 ± 1	3 ± 1	0.000014 ± 0.000003
	1,2-DCA	345	0.10 ± 0.04	0.0010 ± 0.0005	< 0.000003
	1,2-dichloropropane	319	0.40 ± 0.08	0.006 ± 0.001	n.a.
	1,2,3-trichlopropane	n.a.	0.30 ± 0.01	0.007 ± 0.002	n.a.
1,2-dichlorobutane	n.a.	0.50 ± 0.03	0.004 ± 0.002	n.a.	
Brominated compounds	Bromotrichloromethane,	231	1300 ± 100	n.a.	n.a.
	Bromoform	275	2000 ± 300	300 ± 50	0.060 ± 0.005
	Dibromomethane	276	390 ± 20	40 ± 10	0.03 ± 0.01
	Bromomethane	294	20 ± 3	n.a.	n.a.
	Vinyl bromide	338	67 ± 10	2500 ± 500	0.0028 ± 0.0002

Halogenated organic compound classes		BDE (kJ/mol)	Specific metal activities $A_m$ [L/(g·min)]		
			m = Cu	m = Pd	m = nZVI
Chlorinated ethenes	VC	452	4 ± 2	1600 ± 200	n.a.
	1,1-dichloroethene (1,1-DCE)	394 <sup>d</sup>	10 ± 1	590 ± 50	n.a.
	<i>trans</i> -DCE ( <i>t</i> -DCE)	373	17 ± 5	1200 ± 100	n.a.
	<i>cis</i> -DCE ( <i>c</i> -DCE)	370	5 ± 2	840 ± 60	n.a.
	Trichloroethene (TCE)	392	17 ± 1	220 ± 50	0.00024 ± 0.00004
	PCE	382	3 ± 1	110 ± 10	0.00040 ± 0.00022
Halogenated aromatic compounds	Chlorobenzene (CB)	399	0.00004 ± 0.00001	500 ± 150	n.a.
	Bromobenzene (BB)	337	80 ± 10	900 ± 100	n.a.

**Table 1.** Calculated specific metal activities for the dehalogenation of single HOCs in water using Cu-, Pd-, and nZVI-based systems and the corresponding weakest C–X bond dissociation energies.

[72, 73]. The correlation between reactivity and the weakest C–X bond strength shows that the HDH reactions at Cu and Pd surfaces for saturated aliphatic HOCs follow similar reaction mechanisms. Hence, the cleavage of the C–X bond is rate-determining and involves homolytic cleavage of the weakest C–X bond ( $R-X \rightarrow R\cdot + X\cdot$ ). It is also important to point out that the adsorption strengths of X atoms at the catalyst surface are essential for bond cleavage. During aqueous phase hydrodechlorination (HDC) of CTC and CF by Cu and Pd, radical coupling byproducts such as ethane and ethene [37, 46] were detected in trace amounts. Homolytic cleavage of CF and CTC to form dichloromethyl and trichloromethyl radicals, respectively, is therefore rate-determining. Radical coupling reactions are only minor. The radical intermediates undergo further reactions to form various products, e.g. methane ( $CH_4$ ), CM, and DCM [22, 37].

In environmental catalysis, the proportion of the fully dechlorinated product with respect to the chlorinated intermediates, i.e. selectivity, is essential in evaluating the efficiency of a treatment system. By using compounds with the general formula  $CCl_3-R$  where  $R = H, F, Cl, Br,$  and  $CH_3$ , the CBHS was applied to evaluate product selectivity patterns [37]. By using CF (where  $R = H$ ) as a model compound, it was found that for both Cu and Pd, the selectivity to DCM was 10–15 mol-%. Further assessment of the ratio of specific metal activities for dechlorination of CF and DCM using Cu and Pd,  $A_{Cu,CF}/A_{Cu,DCM} = 591$  and  $A_{Pd,CF}/A_{Pd,DCM} = 531$ , respectively, show that both systems have a problem with DCM formation. In the same study, it was reported that for nZVI, CM and DCM selectivities were 30–40 mol-% and 35–45 mol-%, respectively, and  $A_{nZVI} = 0.003 \pm 0.001$  L/(g·min). Further assessment of the CBHS showed that variation in reaction conditions, e.g. catalyst amount, type, and concentration of reductants and catalysts support, had no significant effect on DCM selectivity. A multi-catalytic approach was essential in changing DCM selectivity. DCM selectivity was decreased by more than 80% by combining the CBHS with either silver (Ag) or vitamin B<sub>12</sub>. Whereas CM and DCM remain more-or-less as dead-end byproducts when Pd and nZVI are used for the dechlorination of CF and CTC, the CBHS readily dechlorinates these compounds in subsequent steps [37]. This ability of CBHS to dechlorinate DCM and similar compounds (see **Table 1**) makes it more appropriate for the treatment of saturated aliphatic HOCs. Therefore, metallic Cu can be considered the “agent of choice” for the treatment of these classes of compounds in highly contaminated wastewaters.

Similar to the halogenated methanes and ethanes, brominated ethenes are more easily transformed than their chlorinated counterparts (see **Table 1**). This could be attributed at least to the strength of the C–Br and C–Cl bonds. However, the HDC mechanism for chlorinated ethenes is not as straightforward as that of the chlorinated methanes and ethanes. Both Mackenzie et al. (2006) and Shee (2021) have demonstrated that the HDC rates for chlorinated ethenes are independent of the C–Cl bond strengths. For chlorinated ethenes, two reaction steps are involved: i) cleavage of the C–Cl bond and ii) hydrogenation of the double bond. Mackenzie et al. (2006) have shown that the rate-determining step for HDC of chlorinated ethenes by Pd is a concerted step involving the addition of  $H^*$  to the double bond and simultaneous cleavage of the C–X bond. The hydrogenation of the double bond occurs later after the cleavage of the C–X bond. For compounds containing pi-systems, the essential step is C=C di- $\delta$  bond formation at the catalyst surface (active centers) [39, 74, 75]. However, it is important to point out that in addition to C=C di- $\delta$  bonding, the Cl atoms also interact with the catalyst surface. Hence, dissociative adsorption of the C–Cl bonds followed by hydrogenation of C=C bonds are characteristic reaction steps for

chlorinated ethenes. Based on this description, Pd as a potent hydrogenation catalyst smoothly dechlorinates chlorinated ethenes. For all halogenated ethenes (see **Table 1**),  $A_{Pd}$  increases with increasing C–Cl bond strengths. Hence, the order of reactivity for Pd is VC > DCE isomers > TCE > PCE. In general,  $A_{Pd}$  values for all compounds (see **Table 1**) are two to three orders of magnitude than  $A_{Cu}$  values. For the CBHS, there is no clear distinction in the reactivity of the chlorinated ethenes. The  $A_{Cu}$  values differ only by one order of magnitude which is less significant. Therefore, in the HDC of chlorinated ethenes by the CBHS, we suggest that the lower  $A_{Cu}$  values could be due to i) minimal interaction of the C=C bond with the metallic Cu surface for di- $\delta$  bonding, and ii) the actual reductants could be adsorbed hydride species (Cu–H) instead of  $H^*$  that are predominant in Pd. Although the  $A_{nZVI}$  values for reduction of halogenated ethenes are five to eight orders of magnitude lower than  $A_{Cu}$  and  $A_{Pd}$ , it can be considered the “agent of choice” for *in situ* treatment of the highly chlorinated homologs, PCE and TCE. Fe is abundant in nature; it is cheaper than both Pd and Cu; it is environmentally compatible and does not require the addition of a reductant. Furthermore, the formation of an oxidic layer that protects the metallic nZVI core offers a long-term treatment solution for contaminated plumes and groundwater. Since the transformation of TCE and PCE results to accumulation of VC and the DCE isomers with time, coupling nZVI with microbial processes can achieve significant detoxification. However, for the treatment of chlorinated ethenes derived from industrial processes where rapid detoxification is desired, Cu catalysts are in such cases more appropriate than nZVI.

Other than halogenated alkanes and alkenes, halogenated aromatic compounds (HACs) are also a significant class of environmental contaminants. These compounds are more hydrophobic than the corresponding aliphatic HOCs. In the presence of organic matter, HACs are strongly immobilized in soil compartments and sediments [76, 77]. Hence before treatment, the HACs need to be desorbed using solvents and surfactants. *Ex situ* treatment technologies such as soil washing and pump and treat need to consider that the extraction solvent constitutes a cocktail of HACs, solutes, heavy metals, and organic matter. Most of the matrix components are catalysts inhibitors, and therefore pretreatment steps such as coagulation, flocculation, and filtration need to be considered. For the CBHS, Shee (2021) has demonstrated that Cu is rather resistant to deactivation by most water matrix constituents including  $S^{2-}$  and  $SO_3^{2-}$ . In contrast, Pd is known to undergo either partial or permanent deactivation in the presence of several solutes from soil washing processes. RSCs are the most dangerous poisons whose presence even in trace levels leads to permanent catalyst deactivation [40, 42, 44, 45, 78]. In order to prolong Pd activity, several protection steps have been investigated with little success. These include i) pretreatment steps such as coagulation, flocculation, sedimentation, and filtration steps to precipitate heavy metals and organic macromolecules, ii) addition of oxidants to convert RSCs into non-deactivating substances, e.g.  $SO_4^{2-}$  [78], iii) regeneration of the fouled catalysts by the addition of oxidants such as  $KMnO_4$ ,  $H_2O_2$ , and hypochlorite, and iv) minimizing contact between the poisons and catalysts by introducing a protective layer of adsorbent, e.g. zeolites, silica material, and poly(dimethylsiloxane) (PDMS) [40, 79–81].

In addition to water matrix composition, the reaction rates of the individual HACs are important in selecting the appropriate reduction system. Numerous literature studies show that unmodified nZVI is able to dechlorinate chlorobenzene (CB) and dichlorodiphenyltrichloroethane (DDT) [82–84]. However, these studies are subject to debate. nZVI is an electron-transmitting reagent, and the transfer of an electron leading to cleavage of the weakest C–X bond is rate-controlling. For HACs, the

cleavage of the C–X bond involves at least two important steps [85] which are described in Eq. (8) and Eq. (9).

- i. Formation of a radical anion as a true intermediate after the first electron transfer step:



- ii. Formation of an aryl radical and halide anion:



If the first step is essential and therefore rate-controlling, then the electron affinity of the substrate is an important consideration. Thus, CB ( $E_A = -0.14$  eV) is less reactive than hexachlorobenzene (HCB) with  $E_A = +0.94$  eV). Since the electron transfer process (Eq. (8)) occurs with much difficulty, unmodified nZVI is not suitable for the reduction of aromatic C–Cl bonds attached to aromatic structures [24, 25]. Both Cu and Pd are able to reduce C–Br and C–Cl bonds attached to aromatic structures, and the reaction rates are substance- and system-specific. Under similar reaction conditions and for nanoparticles with comparable sizes, Shee (2021) determined that the  $A_{\text{Cu}}$  for dehalogenation of CB and BB were ( $A_{\text{Cu,CB}} = (4 \pm 1) \times 10^{-5}$  L/(g·min)) and ( $A_{\text{Cu,BB}} = (8 \pm 1) \times 10^1$  L/(g·min)), respectively. In the same study, Pd activities were the highest where  $A_{\text{Pd,CB}} = (5 \pm 1.5) \times 10^2$  L/(g·min) and  $A_{\text{Pd,BB}} = (9 \pm 1) \times 10^2$  L/(g·min). Therefore, Cu which is cheaper and stable in water can be applied as the “agent of choice” for the treatment of brominated aromatic compounds. The niche application of protected Pd catalyst is seen only in *ex situ* treatment of chlorinated aromatics such as in soil washing and pump and treat technologies.

## 5. Future perspectives and application areas of the CBHS

The CBHS has shown potential for use in water treatment technologies for a broad range of compounds. However, the technology is still in its initial stages, and there are still some aspects that need further investigation. First, the possible reductants either hydrides or  $\text{H}^*$  need to be clarified in order to explain the difference in reactivity between halogenated alkanes and alkenes.

Since  $\text{BH}_4^-$  is used as a reductant, clarification on the exact number of H-atoms (hence electrons) transferred to the contaminant is essential. This clarification is needed for the evaluation of reductant costs. Based on reduction equivalents and unit prices of the reductants, it was estimated that  $\text{NaBH}_4$  costs more than  $\text{H}_2$  by at least a factor of 12 [36].

The comparison of the HDH ability of Cu and Pd has been investigated using two different reductants and in the aqueous phase where a layer of the solvent is introduced around the metal particles. Although nanosized particles were applied and the batch reactors were continuously shaken, mass transfer limitations especially for fast-reacting substances need consideration. For better comparison, we suggest experiments carried out under similar elevated temperature conditions, and that  $\text{H}_2$  is used as a reductant. The HDH reactions are then conducted in the gaseous phase at hot solid metal catalysts (Cu and Pd).

Another challenge is connected with effluents at pH values between 9 and 10 when  $\text{BH}_4^-$  is applied as a reductant, as well as the formation of the undesired borates and boric acid [36]. Removal of boric acid and borates may be necessary before the effluent is discharged.

Trace amounts of Cu are essential for the functioning of various biological processes in humans, plants, and animals. Nevertheless, higher Cu doses are toxic [86]. Therefore, the leaching of Cu into the environment must be controlled. Simple iron beds are effective police filters. Embedding Cu onto cation-exchange resins was also seen to minimize Cu leaching after repeated reaction cycles [36, 87]. Amberlite IRP 69 as support for Cu does not only offer partial protection of the catalysts against  $\text{S}^{2-}$  but also enables regeneration of the deactivated catalyst simply by washing with water [36]. Apart from cation-exchange resins, other adsorbents such as zeolites may be investigated. The speciation of Cu within these adsorbents and the role of the support on catalyst performance are possible topics for further research. Since contact between the embedded Cu and  $\text{BH}_4^-$  may not be possible, it is also necessary to identify the nature of reducing species that facilitate the HDH reaction.

## 6. Conclusions

This chapter shows that CBHS although has received less attention should be considered as an alternative tool to nZVI and Pd in water treatment applications. The high potential of the CBHS is seen in the *in situ* regeneration of HOCs-loaded adsorbents in small-scale treatment plants. For detoxification of contaminated soils, preliminary processes including soil washing, filtration, adsorption, and desorption should be implemented in the initial stages to transfer immobilized HOCs into an aqueous media. The CBHS can then be added into the HOCs concentrated aqueous media for detoxification.

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## Conflict of interest

The authors declare no conflict of interest.

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