

# Reduction of Halogenated Organic Compounds in Water: Comparison of Available Reduction Systems based on Cu, Pd and ZVI

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## Abstract

Catalysts on the basis of copper (Cu) and the reducing agent borohydride (BH<sub>4</sub><sup>-</sup>) have been successfully used for reduction of chlorinated aliphatics with low substitution degree which are usually resistant to zero-valent iron (ZVI) and hydrodehalogenation catalysts, such as Pd. Reactivity screening towards a broad spectrum of halogenated organic compounds (HOCs) helped to reveal the possible application areas of the Cu/BH<sub>4</sub><sup>-</sup> system in water treatment compared to Pd and ZVI. The HOC reactivity was found to depend on: i) the nature of the C-X bond to be cleaved, ii) the functional groups adjacent to the C-X bond and linked to it, iii) the bond dissociation energy (BDE). The use of the deactivation-stable Cu/BH<sub>4</sub><sup>-</sup> can be recommended as alternative reduction method to ZVI and Pd catalysts for on-site treatment of aliphatic HOCs.

**Keywords:** nanoparticles, copper, borohydride, reduction technologies, halogenated organic compounds (HOCs)

## 1. Introduction

Treatment of halogenated organic compounds (HOCs) in aqueous media using zero valent iron (ZVI) is an established method in environmental technology. However, ZVI is unreactive towards HOCs with a low number of halogen substituents (such as 1,2-dichloroethane) and substances with halogens bound to aromatic structures. Amendment of ZVI with noble metal catalysts such as Pd offers high reactivity and also enables cleavage of aromatic carbon-halogen (C-X) bonds. However, Pd is expensive and easily deactivated by reduced sulphur compounds (RSC). Copper in combination with borohydride (Cu/BH<sub>4</sub><sup>-</sup>) is a promising catalyst to bridge this gap which the abilities of ZVI and Pd leave [Huang *et al.*, 2012]. Compared to Pd, Cu is less expensive and shows remarkable stability in the presence of common water solutes. The present work investigates the reactivity of different HOC classes towards Cu/BH<sub>4</sub><sup>-</sup> and gives recommendations for optimal application windows of the reduction methods.

## 2. Experimental

### 2.1. Batch HOCs reduction tests

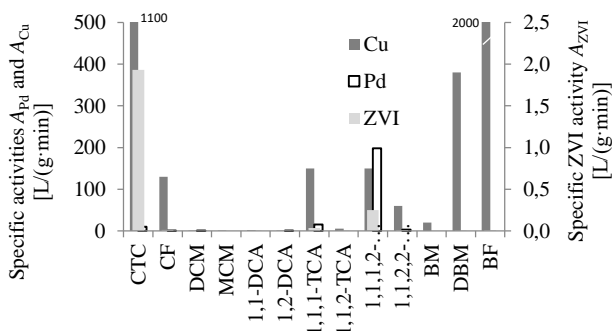
Analytical grade HOCs, reagents and chemicals were purchased from Merck (Germany) or Sigma-Aldrich (Germany) and used as received. 120 mL batch reactors were filled with 60 to 90 mL of an aqueous CuSO<sub>4</sub> solution (0.5-100 mg/L, pH 10) containing poly(acrylic acid) (PAA) with  $c_{PAA}/c_{Cu} = 0.1$ . The reactor was placed in an ultrasonic bath and kept under nitrogen atmosphere before addition of NaBH<sub>4</sub> (300 mg/L) to form well-dispersed Cu nanoparticles. The addition of a methanolic stock solution of the HOC under study into the batch reactor initiated the reaction. Due to extended headspace volume, an appropriate inner standard was used (e.g. methane). Reactors were constantly shaken horizontally at 130 rpm. Headspace sampling using a 25 µL gas tight syringe and analysis by GCMS (QP2010, Shimadzu) was performed for measuring of reaction kinetics and product formation.

## 3. Results and Discussions

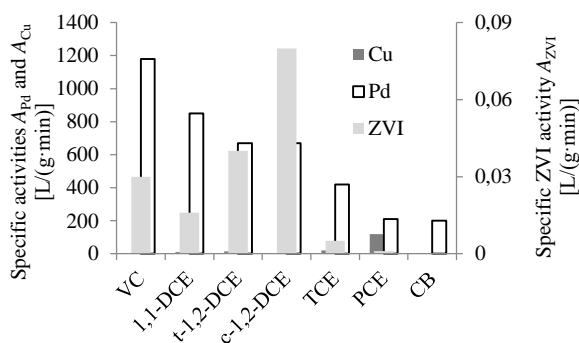
Comparison of HOCs reactivity between Cu, ZVI and Pd was made using the specific metal activity calculated according to eq. (1):

$$A_M = \frac{V_{\text{water}}}{m_M \cdot \tau_{1/2}} = \frac{1}{c_M \cdot \tau_{1/2}} \quad (1)$$

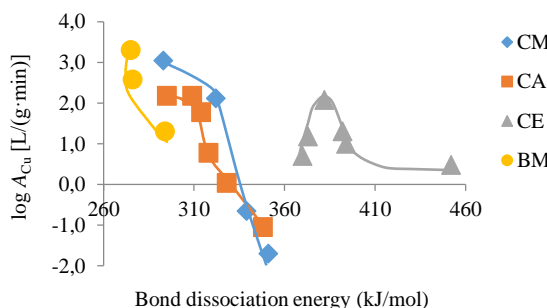
Where  $A_M$  is the specific metal activity [L/(g·min)],  $V_{\text{water}}$  is water volume (L),  $m_M$  is the metal mass (g),  $\tau_{1/2}$  is the HOC half-life (min) obtained from reduction kinetics while  $c_M$  is the metal concentration (g/L). The specific activity for reduction of HOCs using the reagent ZVI and the catalyst Pd were calculated from literature [Song and Carraway 2005, 2008; Mackenzie *et al.*, 2006]. Where possible, surface-normalized activity data were compared. Reactivity values for different HOC classes using Cu, ZVI and Pd are presented in Figure 1 Figure 2 Figure 3.



**Figure 1.** Specific metal activities for reduction of saturated aliphatic HOCs on Cu, Pd and ZVI. Carbon tetrachloride (CTC), chloroform (CF), dichloromethane (DCM), chloromethane (MCM), bromomethane (BM), dibromomethane (DBM) and bromoform (BF)



**Figure 2.** Reactivity of HOCs containing  $\pi$ -bound halogens towards Cu, Pd and ZVI. Chlorobenzene (CB), vinyl chloride (VC)



**Figure 3:** HOCs reactivity against bond dissociation energy (BDE) using Cu nanoparticles and sodium borohydride. Chloromethanes (CM), chloroethanes (CA), chloroethenes (CE), bromomethanes (BM)

## References

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As shown in Figure 1 and Figure 2, the order of specific metal activities for saturated and olefinic HOCs is  $\text{Cu} \gg \text{Pd} \gg \text{ZVI}$  and  $\text{Pd} > \text{Cu} \gg \text{ZVI}$ , respectively. Figure 3 shows that the reactivity of HOCs in the  $\text{Cu}/\text{BH}_4^-$  system depends on i) the nature of the carbon-halogen (C-X) bond being cleaved, ii) weakest C-X BDE, and iii) the presence of  $\pi$ -electrons next to the C-X bond. The weaker C-Br bond makes brominated HOCs more reactive than their chlorinated counterparts. High BDE decreases reactivity for less halogenated HOCs. HOCs with higher number of geminal halogens show high reactivity due to i) decreased BDE with increasing halogenation and ii) better steric attachment at active sites. BDE values represent homolytic cleavage of the weakest C-X bond ( $\text{RX} \rightarrow \text{R}\cdot + \text{X}\cdot$ ). In addition to BDE, single electron transfer (SET) processes are also important in determining reactivity of saturated aliphatic HOCs. High reactivity of olefinic HOCs and cleavage of aromatic C-Cl bonds by Pd is due to the transfer of activated H-atoms in the rate determining step [Mackenzie *et al.*, 2006]. Although SET or H-atom processes control the reactivity, the interplay of other factors such as sorption and mass transfer cannot be ruled out. Opposite reactivity order for olefinic HOCs using Cu ( $\text{PCE} > \text{TCE} > \text{DCEs} > \text{VC}$ ) and Pd ( $\text{VC} > \text{DCEs} > \text{TCE} > \text{PCE}$ ) is observed. The difference in reactivity is due to change in reaction mechanism. For Pd transfer of H-atoms is rate limiting while SET play a role for  $\text{Cu}/\text{BH}_4^-$  system. For ZVI, reactivity for olefinic HOCs follows the order  $\text{VC} > \text{TCE} > \text{PCE}$ . Cleavage of aromatic C-Cl bonds is only possible with Pd.

## 4. Conclusions and Outlook

This work provides a comparison on reactivity data for reduction of various brominated and chlorinated HOCs in water using Cu catalysts in the presence of the reducing agent  $\text{BH}_4^-$ . Saturated aliphatic HOCs show high reactivity using Cu catalysts compared to Pd catalysts and ZVI as reagent. Based on its low cost and high HOCs reactivity,  $\text{Cu}/\text{BH}_4^-$  is viable for on-site treatment of water contaminated with aliphatic HOCs while ZVI is suitable as reagent for *in situ* applications. Pd might be considered for aromatic C-Cl bonds reduction when appropriately protected from deactivation.

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