

Treatment of selected Halogenated Organic Compounds in Water using Colloidal Silver Nanocatalysts under Reducing Borohydride Conditions

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Abstract

Halogenated organic compounds (HOCs) are frequently encountered water contaminants. They are widely used as solvents or feed stocks in the production of paints, adhesives, lacquerers, pharmaceuticals and veterinary drugs, cosmetics, pesticides and herbicides. Most HOCs are recalcitrant, toxic and possible carcinogens. HOCs treatment in water may involve physical, biological and chemical processes. Chemical treatment via oxidation or reduction processes are preferred due to their ability to transform HOCs into environmental benign products. Compared to reduction, oxidation may produce toxic byproducts and thus for complete mineralization, huge amounts of redox equivalents are needed. Reductive dehalogenation is selective and more suited for HOCs treatment. It may employ electrocatalysts, metal catalysts and reagents. Nanoscale zero valent iron (nZVI) as an electron-releasing reagent is environmentally compatible but ineffective for transformation of saturated aliphatic HOCs containing < 2 Cl-atoms. Noble metals such as Pt, Rh and Pd are excellent hydrogenation catalysts for HOCs reduction but are expensive and susceptible to deactivation in water. Metallic Ag (Ag^0) is a promising electrocatalyst for dechlorination of saturated aliphatic HOCs. Ag is relatively cheaper than the noble metals and is sparingly stable in water. Despite this potential, colloidal Ag^0 catalysts have received less attention for HOCs treatment. In this study, optimal conditions were established for synthesis of colloidal Ag^0 catalyst using sodium borohydride (NaBH_4). Calculated Ag^0 activities for reduction of dibromomethane, monobromomethane, perchloroethylene, trichloroethylene and vinylbromide were 86.92 ± 2.61 , 3.45 ± 0.17 , 2.38 ± 0.07 , 1.16 ± 0.05 and 3.21 ± 0.10 , respectively. The reduction of diclofenac and bromocresol blue by $\text{Ag}^0 + \text{NaBH}_4$ was slow and incomplete due to catalyst deactivation. Thus, $\text{Ag}^0 + \text{NaBH}_4$ is more appropriate for reduction of aliphatic and olefinic C–Cl and C–Br bonds.

Key Words: Colloidal silver nanocatalysts, Halogenated organic compounds, Reductive dehalogenation, Sodium borohydride, Water treatment

Introduction

Halogenated organic compounds (HOCs) are among the most frequently detected water and environmental contaminants. They are applied as important solvents and industrial feed stocks during the manufacture of pesticides, pharmaceuticals and veterinary drugs, paints, lacquerers, adhesives, cosmetics and household products (Kodavanti et al., 2023). Some low molecular weight HOCs found in water are referred to as disinfection byproducts (DBPs). DBPs are formed during the disinfection of waters containing natural organic matter by chlorine and chlorine derivatives. Due to their high chemical stability and poor biodegradability, these compounds tend to accumulate in the aquatic ecosystems hence posing significant ecological and human health risks, including endocrine disruption, genotoxic effects, and carcinogenicity (Vandana et al., 2022). HOCs are lipophilic hence undergo bioaccumulation and biomagnification in the food chain. The presence of HOCs has been reported in various water sources in Kenya, including rivers, lakes and municipal wastewater effluents, which shows the urgent need for effective and sustainable water treatment strategies (Chepchirchir et al., 2024).

Currently, adsorption of HOCs from water onto various sorbents are the most common. Adsorption only transfers the contaminant onto a solid phase where further treatment is needed. Regeneration of sorbents by strong acids and alkali results to production of huge amounts of sludge as well as sorbent losses. Compared to adsorption, oxidation of HOCs may lead to detoxification. However, oxidation reactions tend to produce toxic halogenated byproducts which are sometimes more toxic than the parent HOCs. Thus, for complete mineralization of the toxic halogenated byproducts, huge amounts of redox equivalents are consumed. Compared to oxidation, reduction of HOCs is more selective and leads to significant detoxification. Since reduction is selective ($R-X + \text{reducing agent} \rightarrow R-H + X^-$), less redox equivalents are needed to accomplish detoxification. In most cases, reduction at ambient environmental

conditions results in transformation of HOCs into benign products but not to full mineralization. Thus, coupling reductive processes with biological follow up treatment might be necessary. Reduction of HOCs in water by metals under anoxic conditions is a promising method, both at laboratory and field scales. Reduction may be facilitated by electrocatalysts, metallic reagents and metal catalyst. Electrocatalytic reduction of HOCs at metal cathodes may be mediated by electrons or surface adsorbed H-species. However, electrocatalytic reduction of HOCs in water is limited to < -1.2 V cathodic potentials. Further increase in cathodic potentials reduces efficiency due to the undesired water electrolytic reaction.

Metallic reagents such as nanoscale zero valent iron (nZVI) as electron-transmitting reagents are more suitable for *in situ* HOCs treatment. nZVI is environmentally compatible and easily injectable into subsurface systems. Nevertheless, drawbacks to nZVI include extremely low reaction rates for saturated aliphatic HOCs, its consumption over time, high corrosion tendency and generation of iron-oxide sludge in the presence of oxygen. Noble metal catalysts in combination with H_2 or H-donors offer higher HOCs reactivity than nZVI. Although noble metals such as Rh, Pd and Pt offer high activity for HOCs transformation, they are expensive and readily undergo surface fouling deactivation in water. Recently, Cu catalysts in combination with sodium borohydride ($NaBH_4$) have been found to offer an alternative to Pd/ H_2 system. Under identical conditions, Cu+ $NaBH_4$ showed high activity for reduction of saturated aliphatic HOCs than Pd/ H_2 system. Although Ag belongs to the same group as Cu in the periodic table, it has received less attention in reductive dehalogenation reactions. Bulk Ag as a cathode has been applied to dechlorination of chlorinated methanes and ethanes. Shee et al., (2022) observed that compared to Cu, Ag nanocatalysts with $NaBH_4$ showed better selectivity to methane during transformation of chloroform. These results although limited show the potential of Ag as a heterogeneous catalyst in reductive dehalogenation

reactions. Similar to Cu, Ag is less active for activation of H_2 into activated H-species. Thus, a strong reducing agent such as $NaBH_4$ is needed. This study provides a deeper understanding on the application of $Ag+NaBH_4$ by providing information regarding optimal synthesis conditions, classes of C—X bonds that could be cleaved and catalytic activities for a selected HOCs. The performance of $Ag+NaBH_4$ was assessed by selected HOCs classes representing saturated aliphatic, olefinic and aromatic HOCs. This study then compares $Ag+NaBH_4$ with other commonly used reduction systems to recommend application areas.

Materials and Methods

Materials, chemicals and reagents

All reagents used were of analytical grade. $NaBH_4$ was purchased from SRL, silver nitrate ($AgNO_3$) from REFCHEM, diclofenac and bromocresol blue were supplied by BDH Chemicals. Trichloroethylene (TCE), perchloroethylene (PCE), dibromomethane (DBM), monobromomethane (MBM), and vinyl bromide (VB) were sourced from Sigma-Aldrich, Germany.

Synthesis of AgNPs

A 60 mL aqueous solution of $AgNO_3$ (0.001-0.002 M) was prepared in a 120 mL glass vial. The pH of the solution was adjusted to 10 using 0.1 M NaOH followed by addition of alkaline $NaBH_4$ (0.00025-0.004 M) under constant stirring in a fume hood. Stirring was continued for 30 min to allow nucleation and growth of the nanoparticles. The formation of AgNPs was monitored by measuring their surface plasmon resonance (SPR) from 400-800 nm using a UV-VIS spectrophotometer (UV1700). The AgNPs were stored in sealed glass vials under inert conditions for further analysis.

Batch dehalogenation experiments

Batch reactors consisted of 120 mL serum bottles sealed with Teflon butyl rubber septa and aluminum crimp caps. The aqueous phase for volatile and non-volatile HOCs were 60 mL and 100 mL, respectively. The degradation of each parent HOC was carried out under ambient conditions. A fixed

concentration of AgNPs were prepared and a methanol extract of the HOC was spiked to initiate reaction. Headspace analysis was applied for volatile HOCs (MBM, DBM, PCE, TCE and VB) while aqueous phase analysis was used for the non-volatile, DFN and BCB. HOCs degradation studies were monitored by gas chromatography mass spectrometry (GC-MS). A 25 μ L headspace was extracted using a gas-tight syringe at each sampling point then analyzed by GC-MS. For DFN and BCB, 1 mL was extracted and analyzed using UV-VIS spectrophotometry (UV 1700) at fixed λ_{max} . The concentrations of HOCs and their degradation products were quantified using external calibration curves. Under identical conditions, control experiments were conducted by mixing the parent HOC separately with distilled water, $AgNO_3$ and $NaBH_4$. All experiments were performed in triplicate and the results presented as mean $\pm$ SD.

Analytical methods

Analysis of HOC as educts and degradation products were performed by GC-MS (GC2010, Shimadzu) coupled with MS (GCMS-QP2010, Shimadzu). Gas chromatography was fitted with a DB-1ms capillary column (J & W, 60 m x 0.25 mm x 0.25 μ m). The temperature conditions for the oven, interface, injector port, and detector were set at 180, 40, 200 and 250 $^{\circ}$ C, respectively. For headspace sampling of aliquots for GC analysis, a 25 μ L gastight syringe was used, where the split ratio was set to 5. For better GC-MS sensitivity, the total ion count for each HOC substance were applied. The analysis of hydrocarbons was done using a gas chromatography (GC 2010 Plus, Shimadzu) equipped with a flame ionization detector (FID). The GC was fitted with a wide bore capillary column (GS-Q, 30 m x 0.53 mm x 1.00 μ m) whose temperature conditions were set at 200, 40 and 280 $^{\circ}$ C for the injector, oven and detector, respectively. A 25 μ L gastight glass syringe was also used for headspace hydrocarbon sampling for GC analysis and the split ratio was also set at 5. Using calibration curves, the external standard approach was applied to

calculate the concentration of parent HOC as educt and degradation products. Due to change in headspace volume by H_2 production from $NaBH_4$, propane was added in the reactor as an internal standard. Upon $\geq 95\%$ conversion of the parent HOCs and their halogenated intermediates, the amount of Cl^- or Br^- were determined by ion chromatography (IC25, Dionex, IonPac AS15/AG15) equipped with a conductivity detector and self-regenerating suppressor. The amount of Cl^- or Br^- (X_q) was calculated using equation 1:

$$X_q = \frac{X_m}{X_t} \times 100 \quad (1)$$

Where X_q is the percent yield of Cl^- or Br^- , X_m is the amount of Cl^- or Br^- and X_t represent the theoretical maximum amount of Cl^- or Br^- when the parent HOC is completely dehalogenated. The amount of AgNPs and HOCs were adjusted to prevent oversaturation of surface-active centers and allow the reaction to follow pseudo-first-order kinetics as given by equation 2:

$$\frac{dC}{dt} = -k_{obs}C \quad (2)$$

Where c is the concentration of HOC (mg/L) and k_{obs} is the pseudo-first-order rate constant (/min). To compare the reactivities of the HOCs under the given reaction conditions, the catalytic activities for metallic Ag (A_{Ag}) were calculated using equation 3:

$$A_{Ag} = \frac{k_{obs}}{\ln 2 \cdot c_m} \quad (3)$$

Also, the value of A_{Ag} can be calculated using equation 4:

$$A_{Ag} = \frac{1}{c_m \cdot \tau_{1/2}} \quad (4)$$

Where $\tau_{1/2}$ is the HOC half-life of the reaction (min) obtained from the HOC reduction profile.

Results and Discussion

Optimal conditions for synthesis of AgNPs using $NaBH_4$

$NaBH_4$ ($E^\circ = -1.24$ V vs Standard Hydrogen Electrode (Njoya et al., 2024)) is a strong reductant that readily reduces most metal ions to their metallic states e.g., Ag^+ to Ag^0 (Silva & Cesarino, 2022). Under identical reaction conditions it has been found the amount of $NaBH_4$ and precursor ($AgNO_3$) controls the size, particle distribution and surface morphology of the nanoparticles produced (Villaverde et al., 2021). A high initial concentration of $NaBH_4$ result to rapid nanoparticles formation. However, rapid reaction produces large and non-uniform nanoparticles (Šutka et al., 2024). A low concentration of $NaBH_4$ result to incomplete nanoparticles formation (Saini et al., 2022). Thus, establishing optimal reaction conditions is necessary to produce nanoparticles of desired sizes, particle distribution and surface morphology. These properties are crucial in determining catalytic activities. In many heterogeneous catalytic reactions, smaller and uniformly sized nanoparticles are preferred due to their high inherent activities. To establish optimal reaction conditions, concentrations of $NaBH_4$ were varied from 0.00025 to 0.004 M at fixed concentrations of $AgNO_3$ (0.001 M). The appearance of the resultant solutions containing AgNPs are shown in Figure 1 where the colour of the solutions changes from deep yellow at high $NaBH_4$ concentration (0.004 M) to light yellow at low $NaBH_4$ concentration (0.00025 M).



Figure 1. Appearance of the solutions of AgNPs upon reduction of 0.001 M $AgNO_3$ as $NaBH_4$

concentration decreases from 0.004 to 0.00025 M (left to right)

Table 1 shows the $\lambda_{\max}$ and absorbance values of the resultant solutions containing AgNPs at the range of 400-450 nm indicating the presence of AgNPs (Tamilselvan et al., 2022).

AgNO ₃ (M)	NaBH ₄ (M)	$\lambda_{\max}$ (nm)	Absorbance
0.001	0.00025	415.4	0.087
0.001	0.00050	412.2	0.179
0.001	0.00100	407.6	0.374
0.001	0.00200	406.6	0.298
0.001	0.00400	405.4	0.443

It has been found that the size, shape and distribution of AgNPs influences position and intensity of SPR peaks (Zein et al., 2022). SPR peaks within 400-450 nm range suggest the formation of spherical-shaped AgNPs (Jameel et al., 2022). As shown in Table 1, the change in $\lambda_{\max}$ as concentration of NaBH₄ changes is an indication to change in AgNPs sizes. A red shift, defined as a shift of the $\lambda_{\max}$ peak to longer wavelengths, implies formation of larger AgNPs. A blue shift towards shorter $\lambda_{\max}$, indicates formation of smaller spherical AgNPs (Sørensen et al., 2022). A higher absorbance implies increased concentrations of AgNPs or an increased average particle size (Bélteky et al., 2021). When NaBH₄ is 0.00025M the $\lambda_{\max}$ is large (415.4 nm) while the absorbance is low implying slow reduction reaction producing larger nanoparticles. It also implies fewer nucleation sites due to incomplete reduction of Ag⁺ and, hence, a lower concentration of nanoparticles (Szczyglewska et al., 2023). As the concentration of NaBH₄ is increased to 0.001 M, a blue shift in $\lambda_{\max}$ is observed indicating a decrease in the AgNPs sizes and higher concentration of nanoparticles with uniform particle sizes and distribution. This further implies that at a higher concentration of NaBH₄, efficient reduction of Ag⁺ occurs, resulting in more nucleation sites and smaller nanoparticles (Zhou et al., 2022). However, at the highest NaBH₄ concentration of 0.004 M, there is minimal decrease in $\lambda_{\max}$ an indication that saturations occur and further addition of the reductant has minimal effect on the size and concentration of the produced AgNPs. The excess reductant

Table 1. Variation in $\lambda_{\max}$ for AgNPs produced at different NaBH₄ concentrations (pH₀ = 10, C_{AgNO₃} = 0.001M)

could be essential in maintaining the nanoparticles in their reduced state. As shown in Table 1, a molar ratio of 1:1 for AgNO₃ and NaBH₄ produces smaller nanoparticles, $\lambda_{\max}$ = 407.6 nm with a higher absorbance. Further increase in reductant concentration has minimal effect on $\lambda_{\max}$ and thus nanoparticle sizes and distribution. Thus, a molar ratio of 1:1 for AgNO₃ and NaBH₄ is ideal to produces smaller and uniform AgNPs.

Dehalogenation activities of colloidal AgNPs under reducing NaBH₄ conditions for selected HOCs classes

Reductive dehalogenation reactions are usually sensitive to the strength of C—X bond as well the chemical environment adjacent to the C—X bond. For example, Pd/H₂ system shows higher activities during the reduction of C—Cl and C—Br attached to olefinic and aromatic systems. However, Pd activities are very low for saturated aliphatic C—Cl bonds. Similarly, nZVI shows higher activities for highly chlorinated compounds but fails for C—Cl bonds attached to aromatic structures. It is noteworthy to point out that both Pd and nZVI fail to reduce saturated aliphatic compounds containing ≤ 2 Cl atoms. Recently, it was established that Cu activities were higher for saturated aliphatic C—Cl and C—Br bonds. In addition, Cu also readily dechlorinates saturated aliphatic compounds containing ≤ 2 Cl atoms. Nevertheless, Cu activities are low for C—Cl attached to olefinic and aromatic structures. In order to determine the type of C—Cl and C—Br bonds

that could be reduced by AgNPs under reducing NaBH_4 conditions, the following HOCs were evaluated: DBM, MBM, PCE, TCE, VB, DFN and BCB. These compounds were selected as representatives for the different classes of HOCs frequently encountered in water and the environment. DBPs are common water contaminants which need constant monitoring and treatment before natural waters could be used for drinking or recreation. As stated earlier, AgNPs with NaBH_4 readily reduces C–Cl bonds in chlorinated alkyls (Wu et al., 2024). A potential application of AgNPs in

reduction of other classes of DBPs and halogenated alkyls was studied with the knowledge that Br^- is a known catalyst deactivator (Sun et al., 2023). The A_{Ag} for selected HOCs and their transformation products are shown in Table 2.

Table 2. Calculated A_{Ag} for reduction of selected HOCs in water

HOC substance	Weakest Bond Dissociation Energy (BDE) (kJ/mol)	A_{Ag} (L/(g.min))	Cl ⁻ or Br ⁻ yield (%)	Final Products (%)
DBM	276 (King & Mitch, 2022)	86.92±2.61	96±3	CH ₄ (98) C ₂ H ₆ (<1%)
MBM	294 (Bajec et al., 2020)	3.45±0.17	98±2	CH ₄ (98), C ₂ H ₆ (<1)
PCE	382 (Zheng et al., 2024)	2.38±0.07	95±4	C ₂ H ₆ (13) C ₂ H ₄ (85%)
TCE	392 (Brumovský et al., 2022)	1.16±0.05	95±3	C ₂ H ₆ (10%) C ₂ H ₄ (88%)
VB	338 (Pagire et al., 2020)	3.2±0.10	98±2	C ₂ H ₆ (4%) C ₂ H ₄ (94%)

Cl⁻ and Br⁻ yield calculated at > 95% of parent HOC and its dehalogenated intermediates. Final products yield calculated at > 95% of parent HOC and its dehalogenated intermediates

Dehalogenation of DBM and MBM in water was performed and the calculated A_{Ag} for reduction of DBM and MBM are 86.92 ± 2.61 and 3.45 ± 0.17 L/(g.min), respectively. For the two compounds, the ease of dehalogenation depends on the strength of C–Br bond (Table 2). Therefore, DMB is readily reduced than MBM. Since the reaction proceeded to completion, colloidal Ag^0 showed great tolerance to residual Br⁻ released during the reaction. Similar to the reduction of DBM and MBM, the ease of dechlorination for PCE and TCE was dependent on the C–Cl bond strength. As shown in Table 2, the calculated A_{Ag} for dechlorination of PCE and TCE were 2.38 ± 0.07 and 1.16 ± 0.05 L/(g.min), respectively. Therefore, PCE with a weaker BDE is readily dechlorinated than TCE.

However, the A_{Ag} for PCE and TCE are within the same order of magnitude, implying that BDE is not the only factor controlling reaction rates for olefinic compounds at Ag surfaces, other factors may as well be controlling the reduction process. In many heterogeneous catalytic reactions, both adsorption and dehalogenation processes control HOCs reactivity (Weidlich, 2021). Metal nanocatalysts strongly interact with compounds containing π -systems. The olefinic compound adsorption via π – π interactions onto active sites on the metal surface precedes dechlorination reactions. Thus, non-destructive adsorption may not be correlated with weakest BDE (Jarosiewicz et al., 2020). As shown in Table 2, the calculated A_{Ag} activity for reduction of VB in water is 3.21 ± 0.10 L/(g.min). Although the A_{Ag} value for VB is higher than for both PCE and TCE (Table 2), it is within the same order of magnitude. Thus, a clear indication that the reduction of olefinic HOCs follows a similar

mechanism and the strength of C–X bond plays only a minor role.

In order to evaluate the ability of AgNPs with NaBH_4 to reduce aromatic C–Cl and C–Br bonds, DFN and BCB were selected as test substances. DFN is a common water

contaminant while BCB was selected as representative for brominated flame retardants. Dehalogenation of DFN and BCB were carried in this study and the time profiles are presented in Figures 2 and 3 for DFN and BCB, respectively.

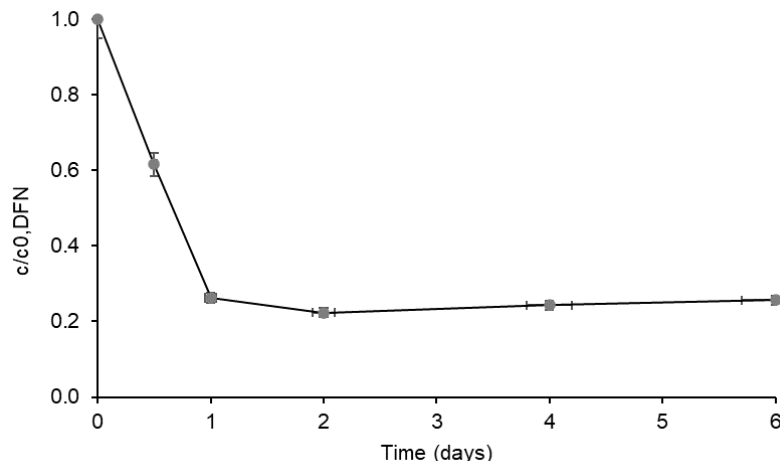


Figure 2. Reaction profile for the dechlorination of DFN using colloidal AgNPs under reducing

NaBH_4 conditions ($c_{\text{AgNPs}} = 2500 \text{ mg/L}$; $c_{0,\text{NaBH}_4} = 3000 \text{ mg/L}$; $c_{0,\text{DFN}} = 10 \text{ mg/L}$; Cl^- yield = $60 \pm 5\%$)

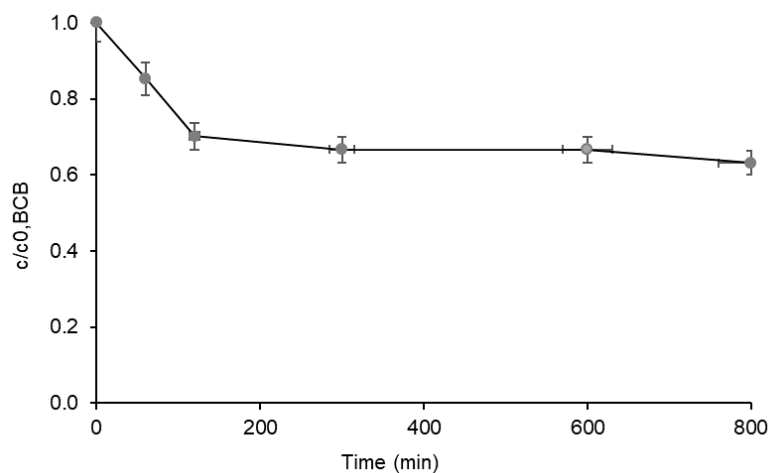


Figure 3. Reaction profile for the dehalogenation of BCB using colloidal AgNPs under reducing NaBH_4 conditions ($c_{\text{AgNPs}} = 2500 \text{ mg/L}$; $c_{0,\text{NaBH}_4} = 3000 \text{ mg/L}$; $c_{0,\text{BCB}} = 10 \text{ mg/L}$; Br^- yield = $20 \pm 5\%$)

From Figures 2 and 3, the reduction of DFN and BCB was incomplete. After 24 h, conversion of DFN was about 74% while that of BCB was only 20-25%. Further addition of NaBH_4 had no effect on the reduction of DFN and BCB, possible due to deactivation of the catalysts. Shee et al., (2022) demonstrated that for fast reacting substances like CHCl_3 ,

AgNPs were tolerant to Cl^- released during the reaction. Since, DFN and BCB have complex aromatic structures compared to the C_1 and C_2 compounds investigated in this study, there adsorption on AgNPs through π – π interactions could block and thus deactivate available surface-active sites. Nevertheless, this is open for further investigation. The deactivation of AgNPs catalysts due to chemical structures of parent HOC molecules and their byproducts although interesting was not part of this study.

Comparison of reduction abilities of AgNPs+NaBH₄ with nZVI, CuNPs+NaBH₄ and Pd+H₂ for selected HOCs in water

In the remediation of water and environmental compartments contaminated with HOCs, the most common reduction systems utilize nZVI as an electron transmitting reagent and Pd catalysts in combination with H₂ (Gong et al., 2022). Recently Cu⁰+NaBH₄ was also investigated

(Shee et al., 2022). The results obtained for the dehalogenation abilities of Ag⁰+NaBH₄ were compared with those of Cu, nZVI and Pd catalysts using DBM, MBM, PCE, TCE and VB as test substances. The results are presented in Table 3.

Table 3. Comparison of catalytic activities of Ag,Cu, nZVI and Pd for selected HOCs under identical conditions

HOC substance	A_m (L/(g.min))			
	m= Ag	m= Cu	m= nZVI	m= Pd
DBM	86.92±2.61	390±20 (Shee et al., 2022)	0.03±0.01 (Shee et al., 2022)	40±10 (Mackenzie, 2022)
MBM	3.45±0.17	20±3 (Shee et al., 2022)	n.a	n.a
PCE	2.38±0.07	3±1 (Shee et al., 2022)	0.00040±0.00022 (Shee et al., 2022)	110±10 (Mackenzie, 2022)
TCE	1.16±0.05	17±1 (Shee et al., 2022)	0.00024±0.00004 (Shee et al., 2022)	220±50 (Mackenzie, 2022)
VB	3.21±0.10	67±10 (Shee et al., 2022)	0.0028±0.0002 (Shee et al., 2022)	2500±500 (Mackenzie, 2022)

n.a = not analyzed

As shown in Table 3, Cu shows better catalytic activities for reduction of saturated aliphatic HOCs than Ag. Since Ag is expensive than Cu and that A_{Cu} is higher than A_{Ag} , Cu⁰+NaBH₄ could be best for reduction of saturated aliphatic HOCs. Although Pd+H₂ shows higher activities for reduction of the olefinic HOCs than all the other systems, it is expensive and readily deactivated by macromolecules e.g., NOM and ionic solutes e.g., SO₃²⁻ and S²⁻. Thus, Pd usage is also limited to water that has been pre-treated to remove deactivators (macromolecules and ionic solutes) which are ubiquitous in water and the environment. These deactivators poison Pd making it inactive. Since nZVI is environmentally compatible, it is best for *in situ* treatment of groundwater contaminated with HOCs. For treatment of industrial wastewaters contaminated with HOCs within a short period of contact time, Cu⁰+NaBH₄ should be considered.

Conclusions

Optimal process conditions for synthesis of colloidal AgNPs catalysts using NaBH₄ are 0.001M AgNO₃ and 0.001M NaBH₄. Calculated A_{Ag} for the reduction of DBM,

MBM, PCE, TCE and VB using colloidal AgNPs catalysts and NaBH₄ at pH0 = 10 were 86.92 ± 2.61, 3.45 ± 0.17, 2.38 ± 0.07, 1.16 ± 0.05 and 3.21 ± 0.10 (L/(g.min)), respectively. DBM and MBM were readily dehalogenated with high A_{Ag} activities dependent on strength of C—Br bond. Dehalogenation of olefinic substances PCE, TCE and VB showed lower A_{Ag} activities than for the brominated methanes. Also, the A_{Ag} activities for PCE, TCE and VB were within the same order of magnitude implying a similar reduction mechanism and the strength of the weakest C—Cl and C—Br bond is not the only factor controlling the dehalogenation reaction. Comparison of Ag activities with those of Cu, Pd and nZVI were done to recommend application areas as follows: Cu⁰+NaBH₄ is to be considered for treatment of saturated aliphatic HOCs in water and olefinic HOCs present in industrial waters and wastewater. nZVI as an environmentally compatible electron-transmitting reagent is more appropriate for *in situ* treatment of HOCs contaminated groundwater. Since Ag is more expensive than Cu and readily deactivated in water, AgNPs+NaBH₄ may find less application in

the treatment of water contaminated with HOCs.

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