



## Zero-valent copper nanoparticles for effective dechlorination of dichloromethane using sodium borohydride as a reductant

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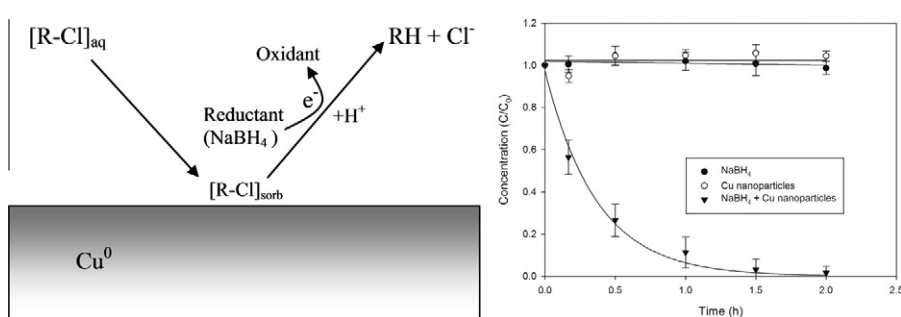
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### HIGHLIGHTS

- ▶ We synthesize Cu<sup>0</sup> as a catalyst to degrade DCM under reduction conditions.
- ▶ Increasing Cu<sup>0</sup> dose will increase dichloromethane degradation rate.
- ▶ Chloride ions appeared immediately and continued to accumulate.
- ▶ Methane was identified in the headspace.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Dichloromethane (DCM) is a recalcitrant groundwater contaminant that shows nearly no reactivity with zero-valent iron (ZVI) nanoparticles. In this study, an effective dechlorination of DCM has been demonstrated using zero-valent copper (Cu<sup>0</sup>) nanoparticles as a catalyst under sodium borohydride reduction conditions. The average diameter of Cu<sup>0</sup> nanoparticles was about 50 nm and the specific surface area was about 19 m<sup>2</sup> g<sup>-1</sup>. Batch experiments revealed that 90% of DCM (26.4 mg L<sup>-1</sup>) was rapidly degraded within 1 h in the presence of Cu<sup>0</sup> nanoparticles (2.5 g L<sup>-1</sup>) and sodium borohydride (1 g L<sup>-1</sup>). The observed pseudo-first-order rate constant ( $k_{obs}$ ) was 2.19 h<sup>-1</sup>, corresponding to a surface area normalized rate constant of 0.052 L m<sup>-2</sup> h<sup>-1</sup>, which is 2–3 orders of magnitude higher than for other zero-valent metals. The DCM degradation rate is a function of the Cu<sup>0</sup> nanoparticle dose. Increasing the dose increased the observed reaction rate. Product analysis indicated that the degradation of DCM involved hydrodechlorination. Soluble copper ions generated by the dissolution of Cu<sup>0</sup> nanoparticles are lower than the World Health Organization drinking water standard, which suggests that the use of Cu<sup>0</sup> nanoparticles under reduction conditions may be potentially useful for the treatment of recalcitrant contaminants that are unable to be degraded by ZVI technology.

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### 1. Introduction

Dichloromethane (DCM) is known to be a common environmental contaminant due to leaks and releases from industrial sources. It has been identified in industrial and municipal waste

waters from several sources at concentrations ranging from 0.08 µg L<sup>-1</sup> to 3400 mg L<sup>-1</sup> [1] and also been detected in surface water and groundwater, with concentrations ranging from 0 to 3600 µg L<sup>-1</sup> in the United States [1]. Recently, DCM was reported to contaminate groundwater at a concentration of 1120 mg L<sup>-1</sup> in Taiwan [2]. The toxicity of DCM manifests mainly in disturbances of the central nervous system and hepatotoxic effects [3]. In addition, DCM is possibly carcinogenic to humans, and has been classified by the IARC as Group 2B [3].

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Zero-valent iron (ZVI) has been widely used as a reactive reagent for the remediation of groundwater contaminated by various pollutants, such as chlorinated organic contaminants (COCs) [4–7], heavy metals [8–10], nitrates [8,11,12], and dyes [13,14]. ZVI nanoparticles, which possess a smaller particle size and larger specific surface area, enhance the reactivity of ZVI. The use of ZVI nanoparticles tends to increase the degradation rate of COCs by 1–2 orders of magnitude, compared with commercial ZVI [15]. Because the presence of a catalyst (e.g., palladium and platinum) can further increase the reaction rate, bimetallic particles (e.g., Pd/Fe, Pt/Fe) have also been developed to improve the reactivity of ZVI [5,16].

Though zero-valent metal based technology (e.g., ZVI nanoparticles and Pd/Fe bimetallic nanoparticles) has achieved great success in the treatment of many COCs such as carbon tetrachloride and trichloromethane, its performance in the degradation of less-chlorinated organic compounds such as DCM [17–19] and dichloroethane [20] has been limited. For example, a significant accumulation of DCM resulting from the transformation of carbon tetrachloride and trichloromethane by Pd/Fe or Ni/Fe bimetallic nanoparticles has been reported [17–19]. Clearly, the direct reduction of DCM using bimetallic nanoparticles is limited. Lien and Zhang used Pd/Fe bimetallic nanoparticles to degrade DCM, and reported that 78% of the initial DCM was detected after 1 h and 73% was still detected after 72 h. Because only a trace amount of methane was observed, they suggested that the initial loss of DCM was caused by sorption [17]. Wang et al. reported similar results, where about 15% of the initial DCM was transformed by Pd/Fe bimetallic nanoparticles within 480 min and the rate of DCM disappearance was very slow [19]. Consequently, developing novel remediation technologies to effectively degrade less-chlorinated organic compounds is necessary.

The low reactivity of ZVI particles toward DCM is possibly because of the relatively higher bond strength of the carbon–chlorine bond compared to the bond strength in higher-chlorinated organic compounds. The activation of DCM by some transition metals has been documented [21]. Copper is a relatively inexpensive catalyst, accordingly, it was selected in the study. Copper is known to be a mild hydrogenation catalyst. It is effective in most of the elementary reactions required in catalytic dehalogenation [22] and coupling reaction [23]. The activation energies for carbon–chlorine bond scission on copper are 12–20% of the gas phase bond dissociation energies [22]. The presence of copper on aluminum surfaces to form bimetallic Cu/Al particles was found to significantly enhance the rate of degradation of chlorinated methanes, but the reaction rate of DCM degradation was still relatively slow [24].

In this study, zero-valent copper ( $\text{Cu}^0$ ) nanoparticles were synthesized for effectively degrading DCM under reduction conditions.  $\text{NaBH}_4$  has been known as a strong reductant. It has widely been used for the preparation of ZVI nanoparticles, which has been widely used for in-situ groundwater remediation. Accordingly,  $\text{NaBH}_4$  was selected in the study. The objective of this study was to explore the potential application of  $\text{Cu}^0$  nanoparticles to the effective dechlorination of DCM under reduction conditions of  $\text{NaBH}_4$ . The characterization of  $\text{Cu}^0$  nanoparticles, analysis of the product distribution, determination of reaction rates and investigation of the effects of metal dose and electron donors on the effectiveness of DCM degradation were carried out.

## 2. Materials and methods

### 2.1. Materials and chemicals

All chemicals used were analytical grade or better. Dichloromethane (DCM, 99.8%) was obtained from LAB-SCAN Analytical Science. Chloromethane ( $2 \text{ mg L}^{-1}$ ) was obtained from AccuStan-

dard. Methanol (99.9%) was obtained from Mallinckrodt. n-hexane was obtained from ALPS CHEM CO., Ltd. Cupric sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 99.5%) was obtained from Yakuri Pure Chemicals Co. Ltd. Sodium borohydride ( $\text{NaBH}_4$ , 99%) and sodium chloride ( $\text{NaCl}$ , 99.5%) were obtained from Sigma-Aldrich. A standard gas mixture for GC analysis was obtained from Supelco, containing 1% each of ethane, ethylene, acetylene, and methane.

### 2.2. Synthesis of copper nanoparticles

Synthesis of  $\text{Cu}^0$  nanoparticles was carried out by adding a 1:1 volume ratio of  $\text{CuSO}_4$  (0.04 M) into  $\text{NaBH}_4$  (0.13 M). The solution was mixed at room temperature for 1 min. The copper ions were reduced to zero-valent copper ( $\text{Cu}^0$ ) by  $\text{NaBH}_4$ . The synthesized metal particles were then washed with a large volume (1000 mL) of deionized water.

### 2.3. Solid phase characterization

Morphological and elemental analyses of  $\text{Cu}^0$  nanoparticles were performed using a scanning electron microscope (SEM) (JEOL JSM-6500F) with energy-dispersive X-ray (EDX) at 20 kV and X-ray diffraction (XRD) (X'Pert PRO, PANalytical, Netherlands) with a Cu target operated at 45 kV and 40 mA. The specific surface area of the  $\text{Cu}^0$  nanoparticles was measured using the Brunauer–Emmett–Teller (BET)  $\text{N}_2$  method using a COULTER SA 3100 surface area analyzer. Prior to measurement,  $\text{Cu}^0$  nanoparticles were nitrogen-dried under ambient temperature.

### 2.4. Batch experiments

Batch experiments were carried out in 165 mL serum bottles containing  $26.4 \text{ mg L}^{-1}$  of DCM in a 100 mL aqueous solution. Each bottle was loaded with various amounts of fresh  $\text{Cu}^0$  nanoparticles and  $\text{NaBH}_4$  as the catalyst and the reductant, respectively. The serum bottles were then sealed with PTFE-lined, butyl rubber septa and aluminum crimp caps. Batch bottles were mixed on an orbital shaker (175 rpm) at room temperature. The batch bottles were periodically sampled by transferring aliquots (1 mL) into 0.5 mL of n-hexane and the total sampling volume did not exceed 5% of the total solution volume. The extraction was performed for 30 min. The experiments were conducted in triplicate.

### 2.5. Analytical methods

Analysis of DCM was conducted by a solvent extraction method. A  $2.5 \mu\text{L}$  extract was withdrawn for GC analysis. Concentrations of DCM were measured with a GC (HP 6890) equipped with an electron capture detector (ECD) and a DB-624 capillary column (J&W,  $30 \text{ m} \times 0.32 \text{ mm}$ ). Oven, injection port and detector temperatures were set at 50, 200 and  $250^\circ\text{C}$ , respectively. Analysis of methane was performed by a GC (HP4890) equipped with a flame ionization detector (FID) and a HP-PLOT/Q capillary column (J&W,  $30 \text{ m} \times 0.53 \text{ mm}$ ). A  $50\text{-}\mu\text{L}$  headspace gas aliquot was withdrawn by a gastight syringe for GC analysis. Oven, injection port and detector temperatures were 40, 200 and  $300^\circ\text{C}$ , respectively. Concentration of chloride ion was measured with a Metrohm 790 Compact ion chromatograph equipped with a Metrosep A Supp 5 100/4.0 column. Eluent containing  $3.2 \text{ mM Na}_2\text{CO}_3/1.0 \text{ mM NaHCO}_3$  was used. The eluent flow was set at  $0.7 \text{ mL min}^{-1}$ . The solution was filtered through a  $0.2 \mu\text{m}$  cellulose membrane filter to remove particulates prior to IC analysis.

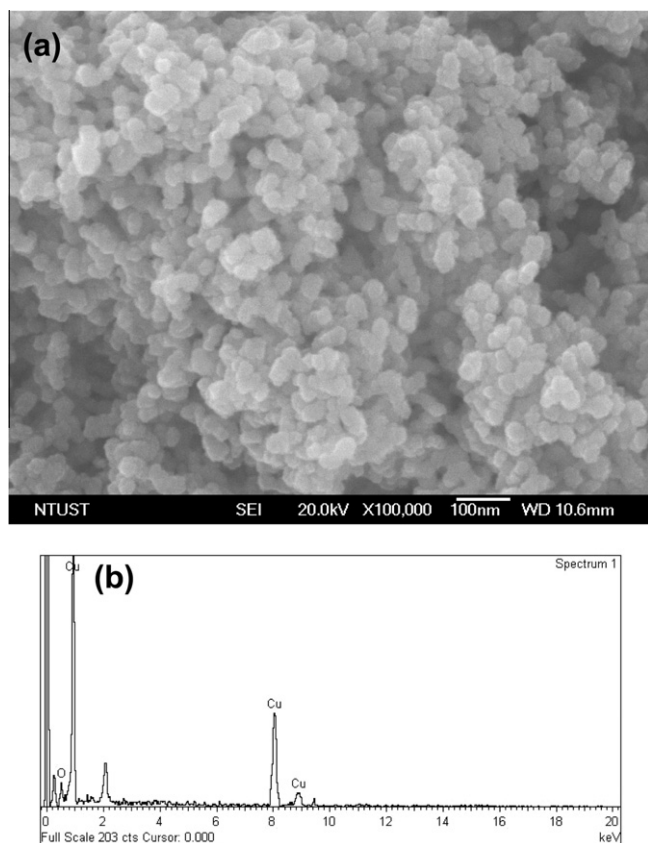


Fig. 1. (a) SEM image of  $\text{Cu}^0$  nanoparticles. (b) SEM-EDX spectrum of  $\text{Cu}^0$  nanoparticles.

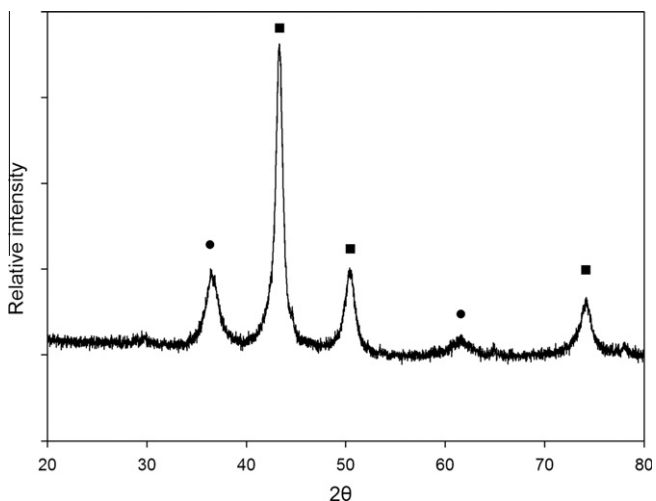


Fig. 2. XRD spectra of  $\text{Cu}^0$  nanoparticles. Solid squares and circles represent Cu and  $\text{Cu}_2\text{O}$ , respectively.

### 3. Results

#### 3.1. Characterization of $\text{Cu}^0$ nanoparticles

Fig. 1a shows a SEM image of the synthesized  $\text{Cu}^0$  nanoparticles. The SEM image shows that the particles were agglomerated in the absence of stabilizers. It was found that the  $\text{Cu}^0$  nanoparticles had an average diameter of about 50 nm. The SEM-EDX spectrum of the nanoparticles shows that copper was the major species, accounting

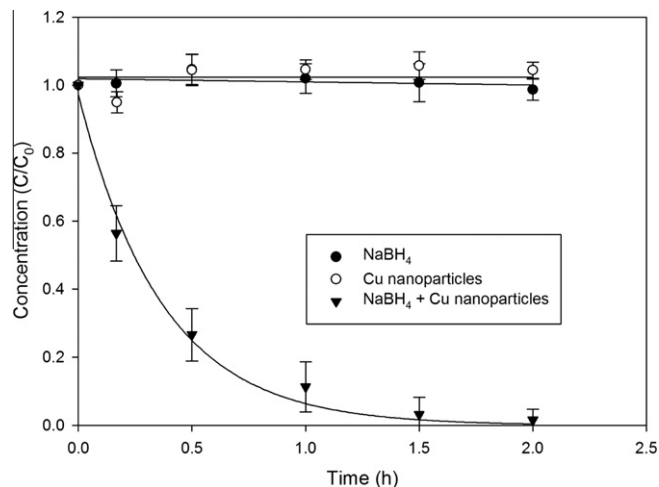


Fig. 3. Degradation of DCM ( $26.4 \text{ mg L}^{-1}$ ) in the presence of  $\text{Cu}^0$  nanoparticles ( $2.5 \text{ g L}^{-1}$ ) and  $\text{NaBH}_4$  ( $1.0 \text{ g L}^{-1}$ ).

for 96% of the mass of the sample (Fig. 1b). XRD analysis indicated that the nanoparticles contained zero-valent copper ( $\text{Cu}^0$ ) with a minor component of cuprous oxide ( $\text{Cu}_2\text{O}$ ) (Fig. 2). The characteristic peaks of zero-valent copper appeared at  $43.3^\circ$ ,  $50.4^\circ$ , and  $74.1^\circ$  ( $2\theta$ ) (JCPDS 89-2838) and the peaks of cuprous oxide were at  $36.4^\circ$ ,  $42.2^\circ$ ,  $61.3^\circ$ , and  $73.5^\circ$  ( $2\theta$ ) (JCPDS 05-0667). The specific surface area of the  $\text{Cu}^0$  nanoparticles was about  $19 \text{ m}^2 \text{ g}^{-1}$ .

#### 3.2. Degradation of DCM

Fig. 3 shows the degradation of DCM ( $26.4 \text{ mg L}^{-1}$ ) in the presence of  $\text{Cu}^0$  nanoparticles and  $\text{NaBH}_4$ . Concentrations in Fig. 3 are expressed as the molar ratio to the initial DCM concentration. The metal loading of the  $\text{Cu}^0$  nanoparticles was  $2.5 \text{ g L}^{-1}$  and the concentration of  $\text{NaBH}_4$  was  $1 \text{ g L}^{-1}$ . DCM was rapidly degraded by  $\text{Cu}^0$  nanoparticles under  $\text{NaBH}_4$  reduction conditions; approximately 73% of DCM was reduced within 0.5 h, and 90% within 1 h. No degradation of DCM was observed in the presence of  $\text{Cu}^0$  nanoparticles alone, nor under  $\text{NaBH}_4$  reduction conditions alone.

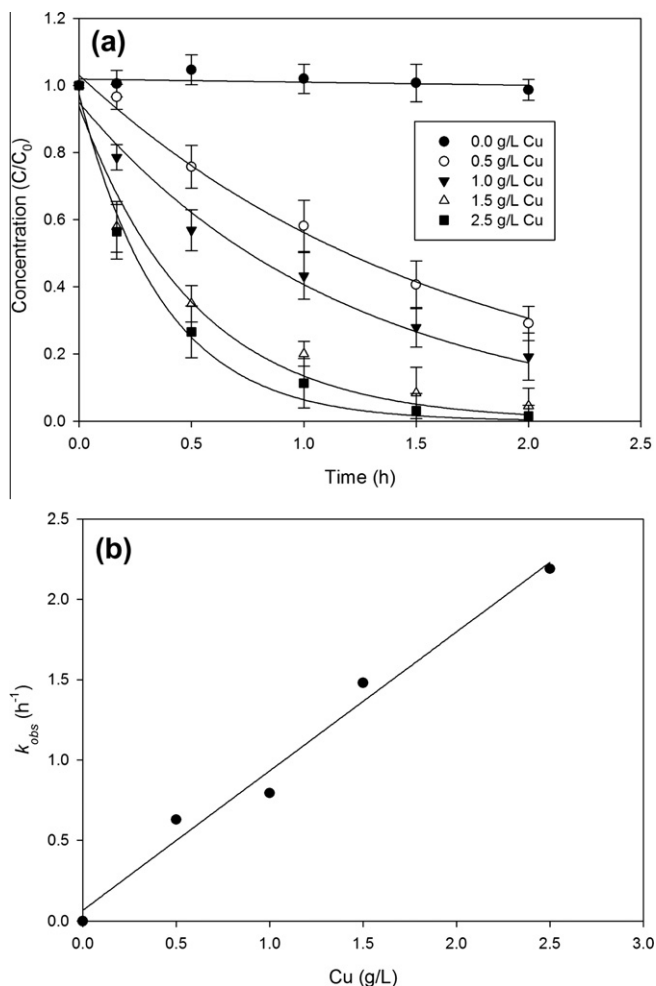
In the previous literature, a pseudo-first-order kinetics model has been frequently used to describe the degradation rate of COCs by using zero-valent metal. Therefore, the reaction kinetics of DCM degradation were modeled using a pseudo-first-order rate equation:

$$\frac{dC}{dt} = -k_{\text{obs}}C \quad (1)$$

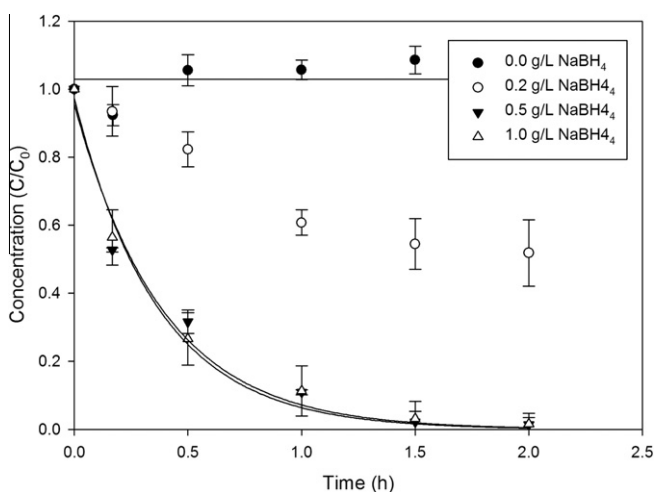
where  $C$  is the concentration of DCM ( $\text{mg L}^{-1}$ ),  $k_{\text{obs}}$  is the observed rate constant ( $\text{h}^{-1}$ ) and  $t$  is time (h). Plots of the natural logarithm of DCM concentrations versus time through linear regression analysis gave straight line results. Linear regression analyses were used to obtain experimentally-determined first-order rate constants ( $k_{\text{obs}}$ ). Data analysis indicated that the disappearance of DCM by  $\text{Cu}^0$  nanoparticles under  $\text{NaBH}_4$  reduction conditions exhibited pseudo-first-order behavior ( $R^2 > 0.98$ ). The first-order rate constant ( $k_{\text{obs}}$ ) was  $2.19 \text{ h}^{-1}$ . Control test indicated that DCM cannot be degraded in the presence of ZVI nanoparticles ( $2.5 \text{ g L}^{-1}$ ) under  $\text{NaBH}_4$  reduction conditions ( $1 \text{ g L}^{-1}$ ). It shows the catalytic effect of  $\text{Cu}^0$  nanoparticles on DCM degradation.

#### 3.3. Effects of $\text{Cu}^0$ nanoparticle dosage

Fig. 4a illustrates the effect of  $\text{Cu}^0$  nanoparticle dose on DCM degradation under reduction conditions ( $1 \text{ g L}^{-1} \text{ NaBH}_4$ ). An increase in



**Fig. 4.** (a) Effect of Cu<sup>0</sup> nanoparticles dose on DCM degradation rate under NaBH<sub>4</sub> reduction conditions (1.0 g L<sup>-1</sup>). (b) Correlation for the observed pseudo-first-order rate constant ( $k_{obs}$ ) and Cu<sup>0</sup> nanoparticle dose.



**Fig. 5.** DCM degradation under various reduction conditions in the presence of 2.5 g L<sup>-1</sup> Cu<sup>0</sup> nanoparticles.

Cu<sup>0</sup> nanoparticle dose tended to increase the DCM degradation rate. The nanoparticle doses were 0.5, 1.0, 1.5 and 2.5 g L<sup>-1</sup>, corresponding to rate constants ( $k_{obs}$ ) of 0.63, 0.79, 1.48 and 2.19 h<sup>-1</sup>, respectively. This indicated that the DCM degradation rate is a function

of the Cu<sup>0</sup> nanoparticles dose (Fig. 4b), with the slope of the linear regression line equal to 0.865 ( $R^2 = 0.98$ ).

### 3.4. Dosage effects of electron donors

The effect of reductant concentration on DCM degradation is illustrated in Fig. 5. At a low concentration of NaBH<sub>4</sub> (0.2 g L<sup>-1</sup>), only 40% of the DCM was degraded. However, after the degradation of DCM had stopped, repetitive spiking of NaBH<sub>4</sub> (1 g L<sup>-1</sup>) into the batch bottle showed that a rapid degradation of DCM resumed after the addition of NaBH<sub>4</sub>. This indicated that the electron donor was insufficient to cause the reaction to proceed at low reductant concentration. However, at higher concentrations of NaBH<sub>4</sub> (>0.5 g L<sup>-1</sup>), the DCM degradation rate was nearly independent of reductant concentration, suggesting the electron donor was no longer a limiting factor at higher reductant concentrations. The rate constants ( $k_{obs}$ ) were 2.18 and 2.19 h<sup>-1</sup> for NaBH<sub>4</sub> concentrations of 0.5 and 1.0 g/L, respectively.

### 3.5. Dissolution of copper

The dissolution of Cu<sup>0</sup> nanoparticles may raise concerns regarding copper ion contamination of the environment. Therefore, the concentration of copper ion in the aqueous solutions DCM was measured and found to be about 0.13 mg L<sup>-1</sup> following DCM degradation and was still 0.1 mg L<sup>-1</sup> after 1 year. Thus, the concentration of soluble copper ions caused by the dissolution of Cu<sup>0</sup> nanoparticles was still lower than the allowed levels in drinking water stipulated by the World Health Organization (WHO) of 2 mg L<sup>-1</sup>.

## 4. Discussion

### 4.1. Reaction kinetics

As mentioned above, DCM degradation is a first-order reaction with respect to the DCM concentration and is also dependent on the Cu nanoparticle concentration. As shown in Fig. 4b, the slope of linear regression line is 0.865 ( $R^2 = 0.98$ ). The reaction order with respect to Cu<sup>0</sup> nanoparticle dose can be determined by using

$$\frac{dC}{dt} = -k' \rho_m^N C = -k'' \rho_m^N \quad (2)$$

$$\ln \left( -\frac{dC}{dt} \right) = N \ln \rho_m + \ln k'' \quad (3)$$

where  $\rho_m$  is the Cu<sup>0</sup> nanoparticle doses, N is the reaction order with respect to nanoparticle dose, and  $k'$  and  $k''$  are the rate constants. It was found that the reaction order with respect to Cu<sup>0</sup> nanoparticle dose is 0.81, which is close to unity. As a result, the overall reaction rate can be expressed as:

$$\frac{dC}{dt} = -k' \rho_m C \quad (4)$$

Because the surface area of Cu<sup>0</sup> nanoparticles is essentially a constant, this is in good agreement with the surface area normalized rate constant proposed by Johnson et al. [25] where the observed rate constant is directly proportional to the metal dose:

$$k_{obs} = k' \rho_m = k_{SA} \rho_m a_s \quad (5)$$

where  $k_{SA}$  is the rate constant normalized to the specific surface area concentration (L m<sup>-2</sup> h<sup>-1</sup>),  $\rho_m$  is the dose of Cu<sup>0</sup> nanoparticles (g L<sup>-1</sup>), and  $a_s$  is the specific surface area of the nanoparticles (m<sup>2</sup> g<sup>-1</sup>). The surface area normalized rate constants at nanoparticle doses of 0.5, 1.0, 1.5 and 2.5 g L<sup>-1</sup> were determined to be 0.066, 0.042, 0.052, and 0.046 L m<sup>-2</sup> h<sup>-1</sup>, respectively. The average value

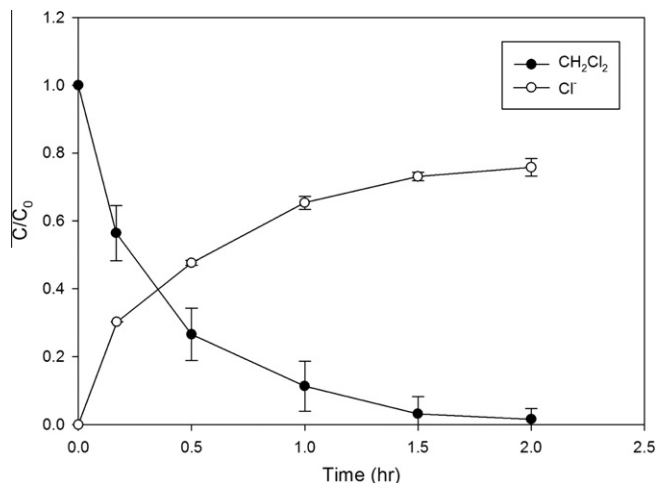


Fig. 6. Transformation of DCM using  $\text{Cu}^0$  nanoparticles ( $2.5 \text{ g L}^{-1}$ ) under  $\text{NaBH}_4$  reduction conditions ( $1.0 \text{ g L}^{-1}$ ).

of the surface area normalized rate constants was  $0.052 \text{ L m}^{-2} \text{ h}^{-1}$ . No systematic differences among the values of  $k_{\text{SA}}$  means the reaction exhibits the characteristics of being surface-mediated.

#### 4.2. Reaction pathways

Product analysis was carried out to examine the reaction pathway. Concentration of chloride ion, which is the product of reductive dechlorination, was measured by ion chromatograph. Fig. 6 shows the transformation of DCM using  $\text{Cu}^0$  nanoparticles under  $\text{NaBH}_4$  reduction conditions. Concentration in Fig. 6 is expressed as the molar ratio to the initial DCM concentration ( $\text{Cl}^-:\text{CH}_2\text{Cl}_2 = 2:1$ ). Chloride ions appeared immediately and continued to accumulate during the disappearance of DCM, about 75% of the initial DCM was transformed within 2 h, suggesting that the degradation of DCM involved reductive dechlorination.

Methane, which is the final product of reductive dechlorination, was identified in the headspace while a small amount of chloromethane was also detected. The product analysis indicated that the degradation of DCM involved hydrodechlorination. The increased quantity of chloride ion in excess of the amount estimated from DCM hydrogenolysis to chloromethane also confirmed the production of non-chlorinated products. In this study, the reduction conditions created by  $\text{NaBH}_4$  lead to the solution having a pH of 9. Under alkaline conditions, it may be favorable for DCM to undergo base-catalyzed hydrolysis during degradation. The hydrolysis of some chlorinated organic contaminants (COCs) by

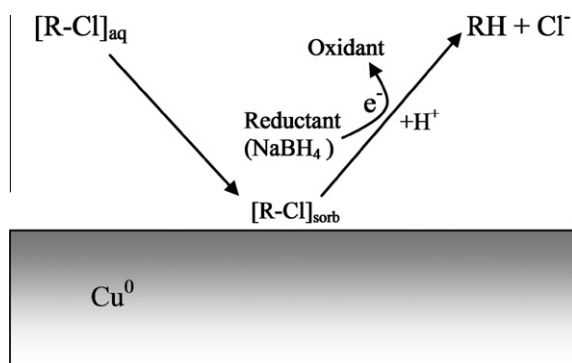
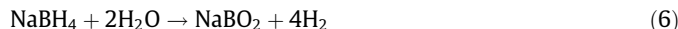
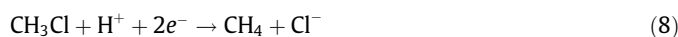
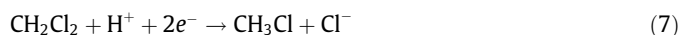


Fig. 7. Mechanism for DCM catalytic degradation using  $\text{Cu}^0$  nanoparticles under  $\text{NaBH}_4$  reduction conditions.

zero-valent metals has already been reported in literature [18,24,26]. The hydrolysis of DCM may result in the formation of formic acid or carbon monoxide. However, no formic acid or carbon monoxide was identified in this study by ion chromatograph and a GC equipped with a thermal conductivity detector (TCD). Nevertheless, hydrogen evolution occurred via the hydrolysis of  $\text{NaBH}_4$  in reaction with water.



The differences between surface area normalized rate constants for various doses of  $\text{Cu}^0$  nanoparticles were insignificant. This suggested that the DCM degradation was a surface-mediated reaction. As shown in Fig. 7, DCM was transformed by hydrodechlorination occurring at the  $\text{Cu}^0$  metal surface, yielding chloromethane (Eq. (7)), methane (Eq. (8)) and chloride ions:



#### 4.3. Potential application of $\text{Cu}^0$ nanoparticles

Effective degradation of DCM was observed in the presence of  $\text{Cu}^0$  nanoparticles under  $\text{NaBH}_4$  reduction conditions. As shown in Table 1, extensive studies have pointed out that DCM is nearly unreactive towards ZVI and many other bimetals even at very high metal doses. Though Pd/Fe nanoparticles were reported to be capable of degrading DCM, the surface area normalized rate constant ( $k_{\text{SA}}$ ) was very low ( $3.53 \times 10^{-5} \text{ L m}^{-2} \text{ h}^{-1}$ ). The use of Cu/Al increased the  $k_{\text{SA}}$  value by one order of magnitude compared to Pd/Fe nanoparticles. In this study, the  $k_{\text{SA}}$  value of the DCM degradation ( $5.2 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$ ) was further increased by two orders of magnitude.  $\text{Cu}^0$  nanoparticles coupled with  $\text{NaBH}_4$  is therefore a very powerful system for DCM remediation. Furthermore, due to the agglomeration of  $\text{Cu}^0$  nanoparticles in the absence of stabilizers was observed (Fig. 1a), the use of stabilizers to disperse the particles may increase the reactivity of  $\text{Cu}^0$  nanoparticles.

There was no significant change of pH value. XRD analysis indicated that no further oxidation occurring at the surface of  $\text{Cu}^0$  nanoparticles was observed during the experimental period, suggesting the surface passivation is insignificant. Furthermore, soluble copper ions generated by the dissolution of  $\text{Cu}^0$  nanoparticles are lower than the drinking water standard of the WHO, which suggests that the use of  $\text{Cu}^0$  nanoparticles under reduction conditions of  $\text{NaBH}_4$  may be a potentially useful technology for the treatment of recalcitrant contaminants that are unable to be degraded by ZVI technology.

$\text{NaBH}_4$  has widely been used for the preparation of ZVI nanoparticles, which has been widely used for in-situ groundwater remediation. Under this  $\text{NaBH}_4$  reduction conditions,  $\text{Cu}^0$  nanoparticles may increase the degradation rate of COCs. However,  $\text{NaBH}_4$  is a relatively strong, non-specific reductant. Therefore, it's quite likely

Table 1  
Observed and surface area normalized rate constants for DCM degradation.

Metal	Dosage ( $\text{g L}^{-1}$ )	$k_{\text{obs}}$ ( $\text{h}^{-1}$ )	$k_{\text{SA}}$ ( $\text{L m}^{-2} \text{ h}^{-1}$ )
Fe particles [18]	125	NR <sup>a</sup>	NR <sup>a</sup>
Zn particles [18]	125	NR <sup>a</sup>	NR <sup>a</sup>
Fe nanoparticles [18]	2.5	NR <sup>a</sup>	NR <sup>a</sup>
Ni/Fe nanoparticles [18]	2.5	NR <sup>a</sup>	NR <sup>a</sup>
Pd/Fe nanoparticles [17]	12.5	NR <sup>a</sup>	NR <sup>a</sup>
Pd/Fe nanoparticles [19]	10	0.018	$3.53 \times 10^{-5}$
Cu/Al particles [24]	20	0.066	$6.2 \times 10^{-4}$
Cu ( $\text{NaBH}_4$ )	2.5	2.19	$5.2 \times 10^{-2}$

<sup>a</sup> NR: no reaction.

that concentrations well in excess of  $1 \text{ g L}^{-1}$  will be required if multiple contaminants are present. Another potential environmental application can be achieved by immobilizing  $\text{Cu}^0$  nanoparticles onto the surface of reducing metals (e.g. iron, aluminum) to form bimetallic structure. The reducing metals can act as electron donor to substitute  $\text{NaBH}_4$ .

On the other hand, zero-valent copper ( $\text{Cu}^0$ ) nanoparticles supported on a cation resin has been successfully synthesized by Lin et al. for carbon tetrachloride degradation from contaminated water [27]. Moreover, the cation resin recycles the copper ions resulting from the reaction between carbon tetrachloride and  $\text{Cu}^0$  by simultaneous ion exchange. Immobilization of  $\text{Cu}^0$  nanoparticles offers an opportunity for applying this nano-material.

## 5. Conclusions

In this study, we demonstrated that using  $\text{Cu}^0$  nanoparticles as a catalyst can effectively degrade DCM under  $\text{NaBH}_4$  reduction conditions. The average diameter of the  $\text{Cu}^0$  nanoparticles was 50 nm, and the specific surface area was about  $19 \text{ m}^2 \text{ g}^{-1}$ . The major component of the nanoparticles was copper, accounting for 96% of the total mass. The particles consisted of mainly zero-valent copper ( $\text{Cu}^0$ ) and small amounts of cuprous oxide ( $\text{Cu}_2\text{O}$ ). Degradation of DCM using the  $\text{Cu}^0$  nanoparticles under  $\text{NaBH}_4$  reduction conditions was very fast. An increase in  $\text{Cu}^0$  nanoparticle dose increased the DCM degradation rate. IC analysis indicated that chloride ions appeared immediately and continued to accumulate during the disappearance of DCM. Product analysis indicated that the degradation of DCM involved hydrodechlorination. The dissolution of  $\text{Cu}^0$  nanoparticles into soluble copper ions was insignificant. This system is potentially of use for treating recalcitrant groundwater contaminants that cannot be degraded by ZVI technology.

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