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Synergistic effect of zero-valent copper nanoparticles on dichloromethane degradation by vitamin B_{12} under reducing condition

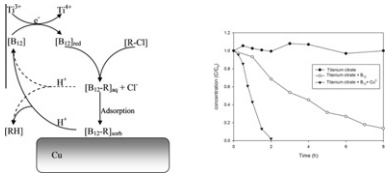
Chang-Chieh Huang [a], Shang-Lien Lo [a,*], Hsing-Lung Lien [b]

[a] Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Rd., Taipei 106, Taiwan
[b] Department of Civil and Environmental Engineering, National University of Kaohsiung, Kaohsiung 811, Taiwan

HIGHLIGHTS

- The synergistic effect of Cu^0 on DCM degradation by vitamin B_{12} was found.
- Increasing vitamin B_{12} or Cu^0 dose will increase DCM degradation rate.
- The excessive amount of copper did not increase the reactivity.
- DCM was degraded reductively to methane.
- Copper ions were lower than the WHO-specified limit for drinking water.

GRAPHICAL ABSTRACT



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ABSTRACT

While zero-valent iron (ZVI, an electron donor) can degrade many kinds of chlorinated organic contaminants and vitamin B_{12} (an electron mediator) is capable of enhancing the degradation, both are ineffective in degrading dichloromethane (DCM). In this study, we found that a combination of zero-valent copper (Cu^0) nanoparticles and vitamin B_{12} can catalyze the degradation of DCM effectively under reducing conditions when titanium citrate was used as the reducing agent. Batch experiments were performed to test the effectiveness of the Cu^0–B_{12} system in DCM degradation. Approximately 99% of 26 mg/L DCM was degraded rapidly within 2 h by the Cu^0–B_{12} system. The observed pseudo-first-order rate constant was 1.35 h^{-1}, which was five times greater than that of using vitamin B_{12} alone. A synergistic effect of Cu^0 nanoparticles on the reductive degradation of DCM by vitamin B_{12} was found. Soluble copper ions generated by the dissolution of Cu^0 nanoparticles were lower than the WHO-specified limit for drinking water. It is expected that the combination of Cu^0 nanoparticles and electron mediator system may have the potential for treating recalcitrant groundwater contaminants that cannot be degraded by ZVI technology.

1. Introduction

Dichloromethane (DCM) is widely used as a solvent in chemical processing and in many consumer products such as paint strippers and adhesives. DCM is an environmental contaminant, and its origin in the environment, for example, in soil and groundwater, can be traced to leaks and discharges from industrial sources. It has been detected in surface water and groundwater, and its concentration in these water sources in the United States has been reported to range from 0 to 3600 μg/L [1]. Recently, the concentration of DCM in groundwater in Taiwan has been reported to be 1120 mg/L, which is higher than the groundwater quality standard set by the Taiwanese Environmental Protection Administration by a factor greater than 20,000 [2]. The toxic effects of DCM in humans manifest mainly as disturbances of the central nervous system and hepatotoxic effects. In addition, DCM is potentially carcinogenic to humans. Therefore, it is important to remove DCM from the environment.

* Corresponding author. Tel.: +886 2 23625373; fax: +886 2 23928830.
E-mail address: sllo@ntu.edu.tw (S.-L. Lo).

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Zero-valent iron (ZVI) technology is a proven technology for the treatment of water containing many kinds of contaminants, such as chlorinated organic contaminants (COCs), heavy metals, nitrates, and dyes [3–8]. ZVI is an electron donor degrading contaminants through surface-mediated reductions (Eq. (1)). Previous studies have indicated that both adsorption and reduction of chlorinated organic compounds took place in the presence of ZVI or iron oxides [9–11]. Further, complicated processes including surface adsorption, reduction, precipitation, and coprecipitation are involved in the heavy metal removal [4,12–14]. In addition to the conventional ZVI, nanoscale ZVI (NZVI) particles offer additional advantages: they have a smaller size and larger specific surface area, and therefore higher reactivity than ZVI particles [15]. The presence of a catalyst such as palladium further increases the reactivity of ZVI and NZVI particles. For instance, bimetallic particles such as Pd/Fe have been developed to improve the reactivity of ZVI and NZVI [15,16].

$$C_xH_yCl_z + zH^+ + zFe^0 \rightarrow C_xH_{y+z} + zCl^- \quad (1)$$

Although the ZVI technology has shown great success in treating many types of COCs such as carbon tetrachloride and trichloromethane (chloroform), it is ineffective in degrading less-chlorinated organic compounds such as DCM [17–22]. The formation of a considerable amount of DCM as a result of the transformation of carbon tetrachloride and trichloromethane by using ZVI, Pd/Fe or Ni/Fe bimetallic nanoparticles has been reported [17,18,20,22]; however, the extent to which DCM can be degraded by using these nanoparticles is limited [17,18,20,22]. Thus, there is a need for effective remediation technologies to treat less-chlorinated organic compounds.

The poor 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 [22–24]. The carbon–chlorine bond strength of carbon tetrachloride (Cl–CCl_3), trichloromethane (Cl–$CHCl_2$) and dichloromethane (Cl–CH_2Cl) was 67.5, 75.9 and 78.8 kcal/mol, respectively [23]. The degradation of COCs on copper surfaces has been studied: the activation energy of carbon–chlorine bond scission on copper accounts for only 12–20% of the gas-phase bond dissociation energy [23]. Thus, copper may be useful to the degradation of less-chlorinated organic compounds. Nanoscale zero-valent copper supported on a cation resin was also successfully synthesized and used to reduce carbon tetrachloride [25].

Reductive dechlorination of COCs can be further enhanced by electron-transfer mediators. Extensive research has demonstrated that some naturally-occurring organic macrocycles (also known as metalloporphyrinogens) and electron mediators such as microbial transition-metal-containing coenzymes (e.g., vitamin B_{12} [26,27], coenzyme F430 [26,28] and hematin [26,29]) and quinones [30,31] can be used for the enhanced dechlorination of COCs. Vitamin B_{12} (also known as cobalamin) can be produced by anaerobic bacteria [27], and has been used as a catalyst for the reductive degradation of COCs. The center metal of vitamin B_{12} is cobalt, and its common oxidation states are 3+(B_{12}), 2+(B_{12r}), and 1+(B_{12s}). Reduced vitamin B_{12} (B_{12r} or B_{12s}) can degrade COCs through electron transfer processes to form non-volatile intermediates that subsequently dissociate into vitamin B_{12} and other products. The dissociation step determines the degradation rate, especially under neutral conditions [32–35]. The vitamin-B_{12}-mediated degradation rates of COCs increase with the vitamin B_{12} concentration [36], reductant concentration [36,37], and pH [37]. However, vitamin B_{12} lacks the capability to fast transform less-chlorinated organic compounds [37,38]. For example, the degradation rate of DCM was significantly slower than carbon tetrachloride and chloroform [38]. The accumulation of a considerable amount of DCM as a result of the transformation of carbon tetrachloride by using vitamin B_{12} has been reported [37].

In this study, a new method that combines zero-valent copper (Cu^0) nanoparticles and vitamin B_{12} for the effective degradation of DCM is presented. Although a combination of zero-valent metals (e.g., iron, zinc, and NZVI) and vitamin B_{12} has recently been reported to degrade perchloroethylene (PCE), trichloroethylene (TCE), and carbon tetrachloride [39–41], the use of such combination to directly degrade DCM alone has not been studied. In this study, zero-valent copper (Cu^0) nanoparticles were prepared and successfully degraded DCM in the presence of vitamin B_{12}. The objective was to examine the synergistic effect of Cu^0 nanoparticles and vitamin B_{12}. The dose effects of Cu^0 nanoparticles and vitamin B_{12} on DCM degradation were examined.

2. Experimental

2.1. Materials and chemicals

All chemicals were of analytical grade or better. Dichloromethane (99.8%) was obtained from LAB-SCAN Analytical Science, and methyl chloride (chloromethane, 2 mg/L) was obtained from Accu-Standard. Methanol (99.9%) was obtained from Mallinckrodt. A standard gas mixture was obtained from Supelco for use in GC analysis, and it contained ethane, ethylene, acetylene, and methane (1% each). Cupric sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, 99.5%), trisodium citrate dihydrate (99%), and ammonia solution (NH_3, 30%) were obtained from Yakuri Pure Chemicals Co. Ltd. Sodium borohydride (99%) and vitamin B_{12} (99%) were obtained from Sigma–Aldrich. Titanium(III) chloride (15% in 10% HCl) was obtained from Ferak, and ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 98%) was obtained from Nacalai Tesque.

2.2. Synthesis of zero-valent copper (Cu^0) nanoparticles

Synthesis of Cu^0 nanoparticles was carried out by adding $CuSO_4$ (0.008–0.04 M) to $NaBH_4$ (0.13 M) solution in the volume ratio 1:1 (100 mL) [42,43]. The solution was mixed at room temperature for 1 min to reduce the copper ions to zero-valent copper (Cu^0) nanoparticles (Eq. (2)) [43].

$$Cu^{2+} + 2BH_4^- + 6H_2O \rightarrow Cu^0 + 7H_2 + 2B(OH)_3 \quad (2)$$

The synthesized metal particles were then washed with a large volume (1000 mL) of deionized water and harvested via vacuum filtration. The freshly prepared nanoparticles were then immediately used to perform batch experiments. The loading mass of nanoparticles was measured by weighting the sample dried by nitrogen gas. For example, the measured value was 0.2401 g when the calculated value was 0.25 g.

2.3. Synthesis of zero-valent iron nanoparticles and Cu/Fe nanoparticles

Synthesis of ZVI nanoparticles was carried out by adding iron precursor (0.045 M) to $NaBH_4$ (0.25 M) solution [15,18]. Cu/Fe nanoparticles were prepared by soaking the freshly prepared ZVI nanoparticles with a water solution containing copper precursor ($CuSO_4$) [9,44]. The ratio of copper to iron was 2% by weight. The deposition of copper onto the surface of iron occurred through the following redox reaction:

$$Cu^{2+} + Fe^0 \rightarrow Cu^0 + Fe^{2+} \quad (3)$$

2.4. Reduction of vitamin B_{12}

Vitamin B_{12} was reduced by using titanium citrate (0.177 M), which was prepared by mixing a solution of titanium chloride