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Vitamin B_{12}-mediated hydrodechlorination of dichloromethane by bimetallic Cu/Al particles

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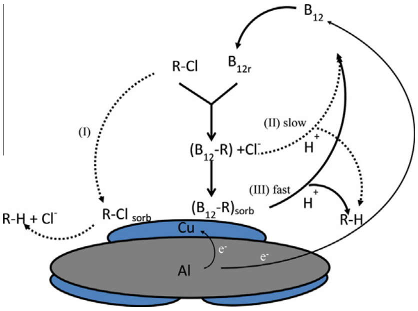
HIGHLIGHTS

- A synergistic effect of copper and vitamin B_{12} on DCM degradation was found.
- About 98% of the DCM was degraded rapidly within 2 h by Cu/Al and B_{12}.
- The B_{12}-mediated DCM degradation is involved in the formation of B_{12}-R complexes.
- Cu/Al is the most effective type of ZVMs for the B_{12}-mediated DCM degradation.
- Copper and aluminum ions were lower than the WHO limit for drinking water.

GRAPHICAL ABSTRACT



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ABSTRACT

Vitamin B_{12}-mediated hydrodechlorination was carried out to effectively transform dichloromethane (DCM) to methane with bimetallic copper/aluminum (Cu/Al) particles. DCM is known as a recalcitrant chlorinated organic contaminant unable to be degraded by many reductive technologies including zero-valent iron (ZVI), bimetallic palladium/iron (Pd/Fe) nanoparticles, and many other zero-valent metals. Cu/Al bimetal is a low-cost and high effective reactive material. Unlike expensive borohydride-synthesized copper nanoparticles, Cu/Al bimetal particles prepared by reduction of cupric ion using zero-valent aluminum offers high surface areas (>100 $m^2\,g^{-1}$) and strong reducing conditions at a low cost. In this study, though the degradation of DCM by Cu/Al alone was relatively slow, an order of magnitude increase in reaction rates was observed when vitamin B_{12} was added into the Cu/Al reaction system. Approximately 98% of the DCM was degraded rapidly within 2 h by Cu/Al and vitamin B_{12}. Reaction mechanisms of DCM degradation in this B_{12}–Cu/Al system were proposed. UV/Visible spectra showed that vitamin B_{12} (Co(III)) was reduced to vitamin B_{12r} (Co(II)) without further reduction to vitamin B_{12s} (Co(I)) in the presence of Cu/Al. A synergistic effect of copper and vitamin B_{12} facilitating the carbon–chlorine (C–Cl) bond scission on the copper surface enhanced the reductive dechlorination of DCM.

1. Introduction

Chlorinated organic solvents (COSs) were in widespread use in various areas including dry cleaning operations, organic synthesis for several decades, and consequently have become among the most widespread organic contaminants present in the groundwater and subsurface soils of many contaminated sites [1].

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Zero-valent metal (ZVM) technology, which represents a broad range of using various metals and bimetals for COSs and other contaminants remediation including zero-valent iron (ZVI) [2,3], zinc [4], silicon [5,6], aluminum [7], and bimetals such as palladium-iron (Pd/Fe) [8,9], nickel–iron (Ni/Fe) [8,10], iron–aluminum (Fe/Al) [11,12], copper–aluminum (Cu/Al) [7], palladium–aluminum (Pd/Al) [13,14], and some trimetals such as Pd/Fe/Al [11], Pd/Ni/Fe, and Pd/Cu/Fe [15,16], has been extensively studied. It has been demonstrated that ZVM is capable of effectively degrading a wide array of chlorinated contaminants including hexachloroethane [17], pentachloroethane [18], trichloroethylene [19], carbon tetrachloride [9,20], pentachlorophenol [21], 2,4-dichlorophenol [22], hexachlorobenzene [23,24], lindane and other hexachlorocyclohexanes [25], and polychlorinated biphenyls (PCB) [26]. Using a generalized chlorinated organic compound, R-Cl, as an example, ZVM-mediated reaction of R-Cl to the corresponding hydrocarbon, R-H can be represented as:

$$R - Cl + H^+ + M^0 \rightarrow R - H + M^{2+} + Cl^- \qquad (1)$$

These ZVM-degradable COSs are all in general higher chlorinated compounds. For those that are lesser chlorinated such as 1,2-dichloroethanes [17] and dichloromethane (DCM) [5,9–11,20,27], ZVM shows either very low or no reactivity towards them. The direct reduction of DCM using ZVI nanoparticles, Pd/Fe, Ni/Fe bimetallic nanoparticles, or Pd/Fe/Al trimetallic particles is limited [9,10,13,21,27]. In addition, the formation of a considerable amount of DCM as a result of the transformation of carbon tetrachloride by using ZVI, Pd/Fe or Ni/Fe bimetallic nanoparticles has been reported [9,10,21,27]. It has been reported that the ZVM-mediated degradation rate of COSs is a function of the bond strength of carbon–chlorine (C–Cl) bond [9,28]. Increase in C–Cl bond strength decreases the degradation rate. As a result, the lesser chlorinated COSs are more recalcitrant because of the higher bond strength of C–Cl bonds.

Among many ZVMs, copper has been known as one of a few reagents that are able to catalyze DCM dechlorination in the presence of proper reductants [29]. For example, we have demonstrated the effective dechlorination of DCM using borohydride-synthesized copper nanoparticles under reducing conditions of sodium borohydride [30]. A synergistic effect was further observed when the combination of copper nanoparticles with vitamin B_{12} was implemented in the DCM degradation [31]. Nowadays, synthesis and application of zero-valent copper and copper nanoparticles have been the focus of intensive study [32–34]. In addition, Cu/Al bimetal dechlorinated DCM (27 mg L^{-1}) to monochloromethane and methane in a slow reaction rate was reported [7]. It is believed that copper serves a key role that weakens the bonding energy of the C–Cl bond for the DCM degradation.

Extensive studies have documented that the ZVM-mediated reaction of COSs is a surface reaction that may undergo either direct or indirect reduction [2]. Direct reduction involving the electron transfer on the metal surface is generally observed in the use of the metal with the high hydrogen overpotential (e.g., iron, copper, and zinc) while indirect reduction involving the formation of atomic hydrogen usually occurs at the surface of the metal with the low hydrogen overpotential such as palladium and platinum. It is likely that the direct reduction is involved in the degradation of DCM with copper. Hence, an increase in the surface area of copper should enhance the DCM degradation rate.

Copper nanoparticles synthesized by sodium borohydride possess the surface area of about 19 $m^2\,g^{-1}$ [35]. Though borohydride-synthesized copper nanoparticles offer relatively high surface areas, they are expensive. In addition, the reducing capacity of copper alone is too weak to dechlorinate DCM [30,31]. Cu/Al bimetal, on the other hand, is prepared by reduction of cupric ions using zero-valent aluminum that offers high surface areas at a low cost [7]. Unlike copper nanoparticles requiring external reductants for dechlorination, Cu/Al bimetal utilizes its own support, zero-valent aluminum, as the electron donor that makes itself feasible for the treatment of contaminants. However, compared with higher chlorinated compounds that can be degraded rapidly, the use of Cu/Al bimetal for the DCM degradation is still rather ineffective [7].

The use of electron mediators (also known as electron shuttles. e.g., quinoid-type compounds and transition metal complexes) to facilitate the electron transfer process in redox reactions has widely been investigated [36,37]. For example, vitamin B_{12} is a microbial transition-metal-containing coenzyme that can be produced by bacteria, and is a well-known electron mediator and has been demonstrated to effectively catalyze COSs dechlorination under reducing conditions [38–40]. Vitamin B_{12}, also known as cobalamin, consists of a cobalt metal at the center surrounded by a porphyrin-like structure of tetrapyrrole rings. Based on the state of oxidation of the cobalt, vitamin B_{12} can be specified as cyanocob(III)alamin (vitamin B_{12} Co(III)), cob(II)alamin (vitamin B_{12r} Co(II)) and cob(I)alamin (vitamin B_{12s} Co(I)) [41]. The reduced (vitamin B_{12r}) and superreduced cobalamin (vitamin B_{12s}) have been found to play a key role in the vitamin B_{12}-mediated reduction of COSs [38,39]. Reduced vitamin B_{12} can degrade COSs through electron transfer processes to form non-volatile intermediates, cobalamin complexes (B_{12}-R) that subsequently dissociate into vitamin B_{12} and other products. However, vitamin B_{12} is ineffective in transforming DCM [39].

In this study, a combination of Cu/Al bimetal and vitamin B_{12} is carried out to dechlorinate DCM using batch experiments. The objective is to examine the catalytic effects of vitamin B_{12} on the DCM degradation by Cu/Al bimetal. The effects of the copper loading at Cu/Al bimetal and the dose of vitamin B_{12} on the DCM degradation were investigated. Speciation of vitamin B_{12} was identified by UV/Vis analysis during the reaction. Reaction mechanisms involved in the DCM degradation in the presence of both vitamin B_{12} and Cu/Al bimetal were proposed.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade or better. Dichloromethane (99.9%) was obtained from Merck. Chloromethane (methyl chloride, 200 mg L^{-1}) was obtained from Supelco. Methanol (99.9%) was obtained from Aldrich. A standard gas mixture was obtained from Supelco, which contained ethane, ethylene, acetylene, and methane (1% each). Cupric sulfate (97.5%) and sodium hydroxide (96.0%) were obtained from Showa, Japan. Aluminum powder (99.5%) was obtained from Alfa Aesar. Vitamin B_{12} (cobalamin, 99%) was obtained from Aldrich.

2.2. Synthesis of bimetallic Cu/Al particles

Bimetallic Cu/Al particles were prepared by mixing the solution of copper precursor (copper ion gel) with aluminum metal particles at a fume hood, similar to the previous study [7]. Copper ion gel was prepared by adding 1.5 g of sodium hydroxide into a 30 mL of cupric sulfate solution. Then, 5 g of aluminum particles were added into the copper ion gel. Surface oxides of aluminum such as Al_2O_3 layer were removed by sodium hydroxide. Subsequently, cupric ions underwent a fast reduction to metallic copper (zero-valent copper) by zero-valent aluminum and deposited onto the aluminum surface (Eq. (2)). In this study, the content of the copper on the aluminum applied in the study including three Cu/Al compositions, namely, 10, 20, and 40 wt%, based on theoretical calculation:

$$3Cu^{2+} + 2Al^0 \rightarrow 3Cu^0 + 2Al^{3+} \qquad (2)$$