

Research Article

Remediation of Chlorinated Alkanes by Vitamin B₁₂ and Zero-Valent Iron

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Chlorinated alkanes were heavily used in a wide range of industrial applications including as degreasers, paint strippers, chemical intermediates, and soil fumigants. These compounds are an environmental concern due to the adverse health effects associated with them and have been detected in environmental matrices including soils and groundwater. Chlorinated alkanes are recalcitrant, and current remediation methods that employ zero-valent iron (ZVI) are unable to directly dehalogenate these compounds, limiting the available approaches for *in situ* remediation of these widely utilized chemicals. This study employed a novel approach for the remediation of 1,2,3-trichloropropane (TCP), 1,2-dichloropropane (1,2-DCP), 1,3-dichloropropane (1,3-DCP), 1-chloropropane (1-CP), and 1,2-dichloroethane (1,2-DCA) in the presence of ZVI and vitamin B₁₂, a naturally occurring electron mediator. Batch reactions were performed in order to determine a kinetic model for the associated degradation mechanisms. Dechlorination byproducts were confirmed through gas chromatography-mass spectrometry (GC-MS) coupled to a purge and trap. Free chloride was quantified by ion chromatography (IC) utilizing suppressed conductivity detection. In the absence of vitamin B₁₂, reductive dechlorination of chlorinated alkanes was observed to not occur when exposed to only reactive ZVI particles (<5 μm). However, in the presence of ZVI combined with vitamin B₁₂, complete reductive dechlorination was observed and followed a pseudo-first-order reaction.

1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) were heavily used until the mid-1980s as solvents in industrial applications such as dry cleaning, pharmaceutical synthesis, adhesive manufacturing, metal component cleaning, and many others [1, 2]. These compounds have been inadvertently released into the environment through various activities including spills, leaks, and improper disposal, or intentionally released [3]. Chlorinated solvents have been detected at roughly 80% of US Superfund sites and at over 3,000 US Department of Defense sites [4]. Common physical properties of Cl-VOCs include higher densities and lower viscosities than water, high volatility and low water solubility. Due to these characteristics, these compounds are able to migrate

vertically beneath the water table and persist as dense nonaqueous phase liquids (DNAPLs). In subsurface environments, after penetrating the saturated zone, DNAPL contamination can exist as free phase, in pools, or in a residual phase, that is sorbed onto soils. Any of these forms can then act as long-term sources of groundwater contamination and are also known as contaminant “source areas” in the environmental remediation industry. Remediation of Cl-VOCs such as 1,2,3-trichloropropane (TCP), 1,2-dichloropropane (1,2-DCP), and 1,2-dichloroethane (1,2-DCA) is of great concern due to their environmental persistence. These substances pose serious health risks to humans and are all currently classified as anticipated human carcinogens [5–7]. More information on these compounds is shown in Table 1. Chlorinated

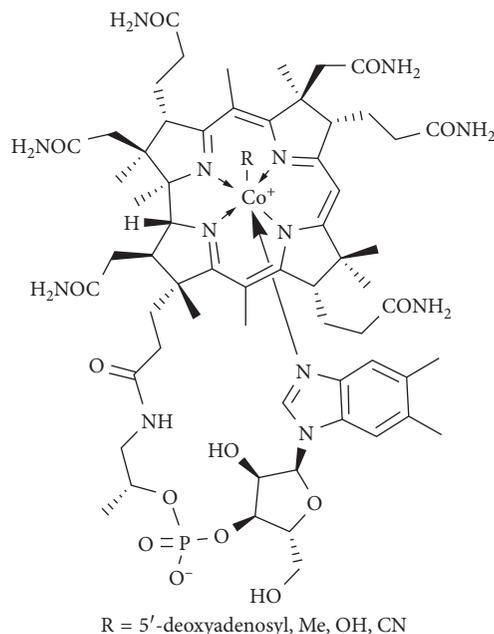
TABLE 1: Summary of environmental risks of chlorinated alkanes.

| Compound | Notes |
|-----------|--|
| 1,2,3-TCP | (i) No defined maximum contaminant level (MCL) but California has a notification level of 0.005 ppb (ii) Has been detected in more than 300 drinking wells in California at concentrations that exceed the notification level [8] |
| 1,2-DCP | (i) MCL of 5 ppb (ii) Contaminant of concern at over 100 superfund sites (iii) Has been found at concentrations exceeding 24 parts per million (ppm) at well sites in Louisiana [9] |
| 1,2-DCA | (i) MCL of 5 ppb (ii) Of the 1,585 national priorities list (NPL) sites, 1,2-DCA has been detected in at least 570 locations [10] (iii) Recalcitrant to abiotic destruction in the presence of ZVI or bimetallic systems [11] |

propanes and ethanes were heavily used as soil fumigants, cleaning/degreasing agents, and as precursors in the synthesis of other chlorinated compounds. Contamination of environmental matrices with Cl-VOCs, such as 1,2,3-TCP, has occurred at industrial and agricultural sites, all of which have the potential to contaminate groundwater.

Chlorinated aliphatics have been shown to be recalcitrant to a number of commonly employed remediation techniques, such as in the presence of zero-valent iron (ZVI) [12]. In the case of chlorinated propanes, studies have shown little to no degradation under reductive conditions [13, 14]. The recalcitrant nature of chlorinated propanes and ethanes is attributed to their chemical and physical properties. The oxidation state of each carbon atom contributes to whether a molecule will be susceptible to reduction or oxidation. Typically, the higher the oxidation number of the carbon atom, the more likely it is to undergo reduction; conversely, lower carbon oxidation numbers favor oxidative processes. Chloropropanes and chloroethanes such as 1,2,3-TCP, 1,2-DCP, and 1,2-DCA all have relatively low average oxidation states compared to chlorinated alkenes, which is why these compounds show little to no abiotic degradation under reducing biogeochemical conditions [13, 14]. In addition, alkenes are inherently more reactive due to the presence of pi-bonds. However, in anaerobic conditions, bacterial degradation has been seen for some chlorinated propanes [15–17]. Due to the adverse health effects associated with these chlorinated alkanes and their wide spread use, it is important to ascertain an environmentally friendly method to remediate them, preferably utilizing an *in situ* approach. Current methods available to remediate Cl-VOCs are either ineffective for the degradation of 1,2,3-TCP, 1,2-DCP, and 1,2-DCA, or are not suitable for *in situ* applications.

Scientists have always been inspired by nature, such as in the case of understanding naturally occurring catalysts. For instance, in 1948, vitamin B₁₂ (cobalamin, or simply B₁₂) was discovered to be a crucial cofactor for a wide range of biological processes. Cobalamin is one of a few naturally occurring organometallic molecules and is a water-soluble

FIGURE 1: Vitamin B₁₂ chemical structure.

vitamin. It is essential in the human body for metabolism and DNA synthesis, is a naturally occurring electron mediator, and plays a vital role in nervous system functions [18]. The structure of B₁₂, as shown in Figure 1 contains a cobalt (Co) atom in the +3 oxidation state situated in the center of a corrin ring and is a nontoxic cobalt complex. Cobalamin is also known to catalyze enzymatic process including isomerization, methyl transfer, and dehalogenation [19]. Reduced states of cobalamin have been shown to be able to dehalogenate organic compounds in the presence of reducing agents such as titanium citrate. These strong reducing agents act as bulk electron donors to ensure the complete reduction of cobalamin to the +1 oxidation state, known as the super-reduced B_{12s} state. Reduced forms of cobalamins have been shown to successfully reduce chlorinated compounds in the presence of these bulk electron donors [20–22]. However, these reducing agents are not feasible for use in environmental applications.

It is hypothesized that reduced forms of B₁₂ will act as an electron transport to facilitate the dechlorination of chlorinated alkanes in the presence of ZVI. This research explored the reductive dechlorination of the following chlorinated alkanes 1,2,3-TCP, 1,2-DCP, and 1,2-DCA in neat samples in the presence of μ ZVI and B₁₂.

2. Experimental Procedures

2.1. Materials. Standard solutions of 1,2,3-TCP, 1,2-DCP, 1,3-DCP, 1-CP, and 1,2-DCA were purchased from Sigma-Aldrich; saturated solutions of each standard were prepared by adding each standard to ultrapurified deionized water until it no longer dissolved. Solutions were thoroughly mixed on a stir plate for 24 hours and then allowed to settle prior to each use. Microscale (μ) ZVI and vitamin B₁₂ were

provided by Provectus Environmental Products. Check standards for propane and propene were purchased from Fischer Scientific, and cyclopropane was purchased from Synquest Laboratories.

2.2. Neat Samples. Ultrapure deionized water was deoxygenated by purging with argon for 30 minutes prior to spiking it with the chlorinated standard. The final concentration of the solution was calculated based on the solubility of the particular chlorinated compound in water at 25°C. For the experiments containing B₁₂, solutions were prepared with the appropriate concentration of B₁₂ and were then deoxygenated. The neat experiments used 0.50 ± 0.01 g of μZVI and were weighed into 20 mL glass crimp-top vials. Immediately before starting the experiments, the iron was washed with 10 mL of 1% sulfuric acid solution for 5 minutes then rinsed 3 times with 10 mL of ultrapure deionized water. Vials were then filled to zero head-space with the stock solution, and the vials were crimped with an aluminium ring over a butyl rubber septum. Samples were then placed on a Lab Companion Series K-57013 reciprocating shaker table (50 rpm) until the desired time point, at which point they were removed from the shaker table and placed in a Crest bench-top sonicator for 10 minutes. After sonication, samples were removed from the vials via a Hamilton gas-tight syringe into a 40 mL VOA vial with septum. The volume removed depended upon the dilution factor of the time point. The internal standard was chlorobenzene.

2.3. Analysis. Analysis of samples was performed on a Teledyne Tekmar Atomx Purge and Trap feeding an Agilent 6850 gas chromatograph (GC) coupled to an Agilent 5975c mass spectrometer (MS) with an RTX-VMS column (30 m, 0.25 mm i.d., 1.40 μm d_f). Ultrapure helium acted as the carrier gas with a constant flow of 1.0 mL/min. The GC/MS had a split flow with a ratio of 20:1 with the injector temperature set to 140°C and the ion source temperature at 230°C. All samples were run on the following GC-MS method with the exception of 1,2-DCP. The oven temperature was initially held at 32°C for 8 minutes, then increased to 60°C using a rate of 5.00°C/min, held at 60°C for 5.00 minutes, then increased to 180°C using a rate of 15°C/min, and held at 180°C for 1 minutes. The method for 1,2-DCP: the oven temperature was initially held at 35°C, then increased to 60°C using a rate of 5.00°C/min, held at 60°C for 5.00 minutes, then increased to 180°C using a rate of 15°C/min, and held at 180°C for 3 minutes. The purge and trap parameters were as follows: transfer line temperature 140°C, trap type #10, purge ready temperature 40°C, purge time 11 minutes with a flow of 40 mL/min, dry purge 0.50 minutes with a flow of 40 mL/min, desorb preheat 245°C, desorb time 1 minute at 250°C, and bake 2 minutes at 280°C. Both instruments were equipped with autosamplers.

Samples were run on an Agilent 8453 UV-visible spectrophotometer and diluted by a factor of 10.

In addition, a Thermo-Fischer Dionex ICS-1100 ion chromatograph with suppressed conductivity detection was utilized for the analysis of free chloride in solution. The 30-minute isocratic method employed a sodium carbonate (4.5 mM) and sodium bicarbonate (0.8 mM) eluent with a flow of 1 mL/min.

The Gaussian 09 software package was used to perform all DFT calculations in this research. The geometries and energies of each molecule were optimized and calculated with B3LYP functional and LANL2DZ basis set in order to achieve balanced accuracy and cost. DFT calculations were applied to provide theoretical evidence of reaction mechanism and energy profiles. During the simulation, the optimized structures were confirmed via frequency analysis. For all molecules simulated, the frequency analysis showed there is no imaginary frequency. In addition, PCM solvent model was also applied for all calculations and temperature was set to 298 K. For vitamin B₁₂, side chains in the structure were eliminated during calculation. The results of these calculations were also confirmed using M06-L functional, which has been demonstrated to be adequate for transition metal complexes.

3. Results and Discussion

3.1. Degradation of Chlorinated Propanes. Studies were conducted to assess whether the addition of B₁₂ (1 mM) would facilitate the reductive dechlorination of chlorinated alkanes (e.g., 1,2,3-TCP, 1,2-DCP, 1,3-DCP, and 1-CP) in the presence of μZVI (0.5 g). For the control group, no degradation was observed in the presence of only μZVI (Figure 2), and no observable degradation byproducts were formed. Any slight decrease in concentration can be attributed to sorption onto the iron surface. Additionally, reactions with only vitamin B₁₂ and chlorinated alkanes showed no sign of degradation during a 3-month time frame. However, in the presence of B₁₂ and μZVI, degradation was observed for 1,2,3-TCP, 1,2-DCP, 1,3-DCP, and 1-CP (Figure 3(a)) with the formation of degradation byproducts. Propene was the only observable byproduct for 1,2,3-TCP and 1,2-DCP, which is a common byproduct when degradation is abiotically mediated with ZVI or other reduced forms of iron. The observed byproduct for 1,3-DCP was cyclopropane, and the byproduct for 1-CP was propane. Byproduct peaks were checked with analytical gas standards.

The reactions followed pseudo-first-order reaction kinetics (Figure 3(b)) and the following equation:

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

where “C” is the concentration of the chlorinated propane and “t” is time. Reactions with zero-valent metals (ZVM) and cobalamin to degrade halogenated methanes and ethenes have been similarly reported to follow pseudo-first-order reactions [22, 23]. Table 2 displays the observed rate constants (k_{obs}) and half-lives for each chlorinated propane that was studied in the presence of 1 mM-B₁₂ and 0.5 g μZVI. 1,2,3-TCP had the fastest observed rate constant of 0.287 day⁻¹, and 1-CP had the slowest observed rate constant of 0.0182 day⁻¹. In the presence of just μZVI, no observable

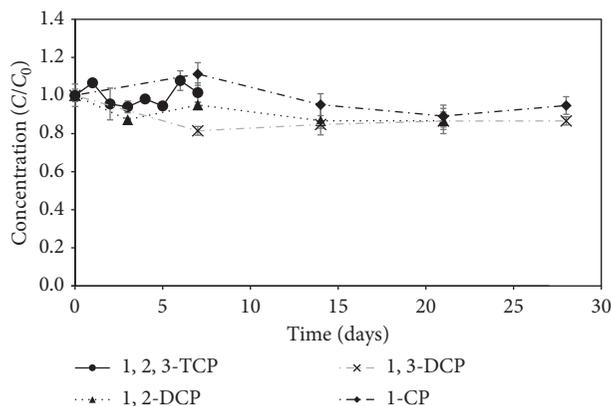


FIGURE 2: Degradation of 1,2,3-TCP (12.1 mg/l), 1,2-DCP (9.55 mg/L), 1,3-DCP (24.79 mg/L), and 1-CP (26.49 mg/L) in the presence of 0.5 g of μ ZVI.

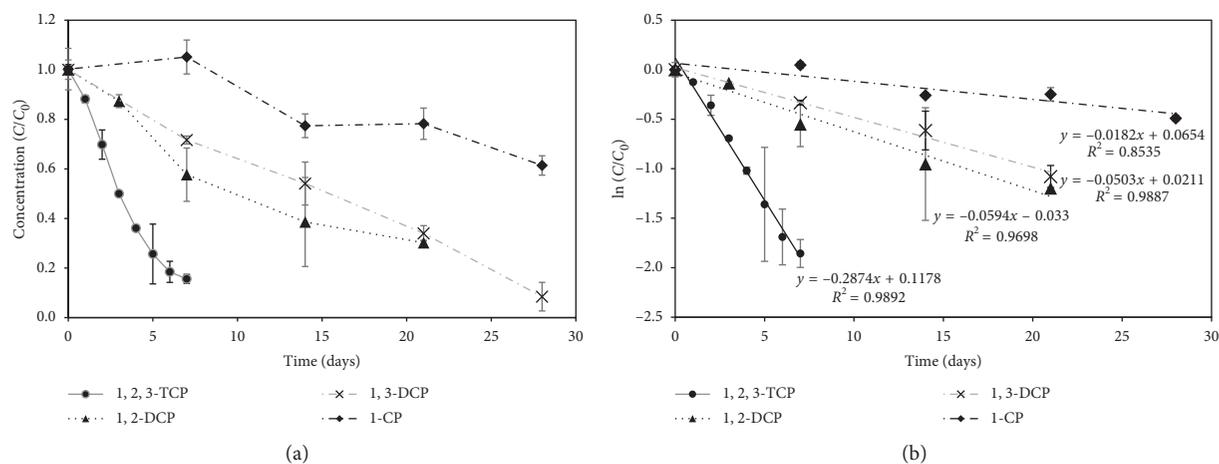


FIGURE 3: (a) Degradation of 1,2,3-TCP (12.27 mg/l), 1,2-DCP (9.48 mg/L), 1,3-DCP (24.79 mg/L), and 1-CP (20.89 mg/L) in the presence of 1 mM·B₁₂ and 0.5 g of μ ZVI; (b) degradation rates of 1,2,3-TCP, 1,2-DCP, 1,3-DCP, and 1-CP.

TABLE 2: Pseudo-first-order reaction *observed rate constants and half-lives*.

| Chlorinated propanes | k_{obs} (day ⁻¹) | Half-life (days) |
|----------------------|---------------------------------------|------------------|
| 1,2,3-TCP | 0.287 ± 0.012 | 2.4 |
| 1,2-DCP | 0.0594 ± 0.0060 | 11.7 |
| 1,3-DCP | 0.0503 ± 0.0038 | 13.8 |
| 1-CP | 0.0182 ± 0.0044 | 38.1 |

byproducts were formed, which indicates that vitamin B₁₂ had a catalytic effect on the reaction process.

As an additional indicator for reductive dechlorination of 1,2,3-TCP, 1,2-DCP, 1,3-DCP, and 1-CP, samples were analyzed using a Thermo-Fisher Dionex ICS-1100 ion chromatograph with suppressed conductivity detection to quantify increased chloride concentrations in solution. The concentration of chloride in solution was monitored over time in the presence of μ ZVI and B₁₂, and the release of chloride from the chlorinated propane compounds was documented as chloride concentration increased with time (Figure 4).

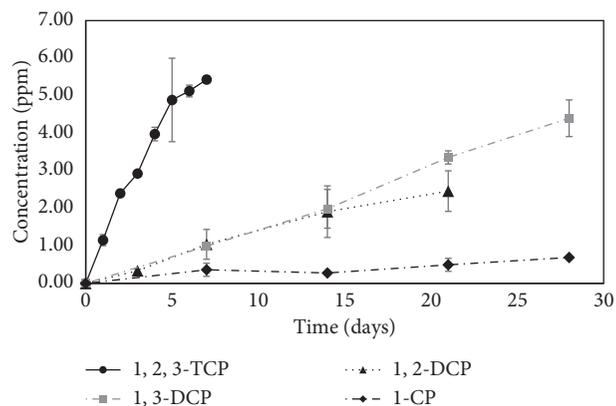


FIGURE 4: Increase of free chloride in solution of 1,2,3-TCP (12.27 mg/l), 1,2-DCP (9.48 mg/L), 1,3-DCP (24.79 mg/L), and 1-CP (20.89 mg/L) in the presence of 1 mM·B₁₂ and 0.5 g of μ ZVI.

3.2. *Degradation of 1,2-DCA*. Studies were conducted to determine if 1,2-DCA would degrade in the presence of 0.5 g μ ZVI and 1 mM·B₁₂. Experiments were also conducted to determine if μ ZVI alone could remediate 1,2-DCA. Over a

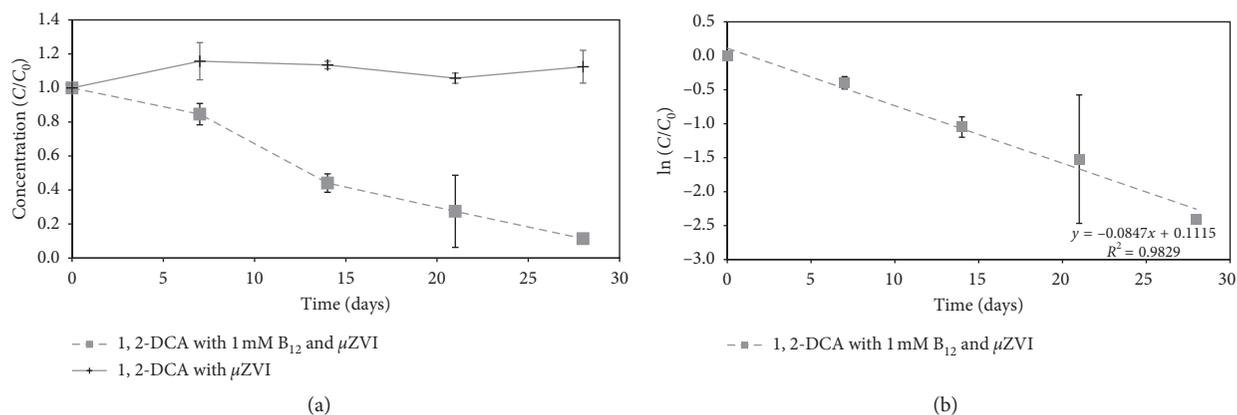
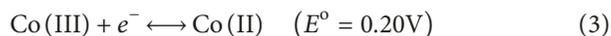
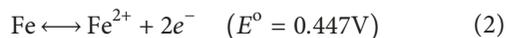


FIGURE 5: (a) Degradation of 1,2-DCA (13.52 mg/l); (b) degradation rate of 1,2-DCA.

28-day period, no significant degradation of 1,2-DCA was observed in the presence of μ ZVI alone. However, over a 3-week period of time, a significant decrease of 1,2-DCA was observed in the presence of μ ZVI and B_{12} and also followed a pseudo-first-order reaction process (Figure 5). As the reaction progressed, an increase of free chloride was observed over the 3-week time frame (Figure 6). This further supports that vitamin B_{12} provided a catalytic effect on the reductive dechlorination of these compounds.

3.3. Mechanistic Study. Prior to the start of the initial dechlorination experiments, studies were conducted to determine whether μ ZVI would be able to reduce cobalamin from Co(III) to Co(II), which is supported by the literature. The redox potentials of ZVI and B_{12} explain how this reduction proceeds to the Co(II) oxidation state without reaching the Co(I) state. Coupling the reduction of B_{12} to B_{12r} with iron's redox potential gives a calculated potential of +0.647 V. The reduction of B_{12} occurs in the presence of iron because the redox potential for this reaction is positive, indicating a favourable spontaneous reaction (see Redox potentials and half reactions (equations (2)–(4))). Redox potentials also explain why iron is not suitable to completely reduce B_{12} to B_{12s} : the calculated potential for that reduction is -0.163 V, which indicates this is not a spontaneous reaction [22, 24]:



Vials were set up to monitor the conversion of cobalamin to B_{12r} over a 48 hr time period. A review of the literature indicates Co(III) has several characteristic absorbance peaks at the following wavelengths: 361 nm and 550 nm, whereas Co(II) has characteristic absorbance peaks at 312 nm and 474 nm [22]. The UV-Vis spectrum of the reduction of cobalamin by μ ZVI over the course of the experiment is shown in Figure 7.

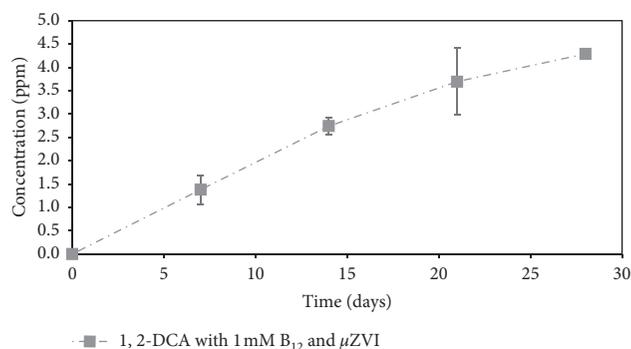


FIGURE 6: Increase of free chloride in solution of 1,2-DCA (13.52 mg/l) in the presence of 1 mM B_{12} and 0.5 g of μ ZVI.

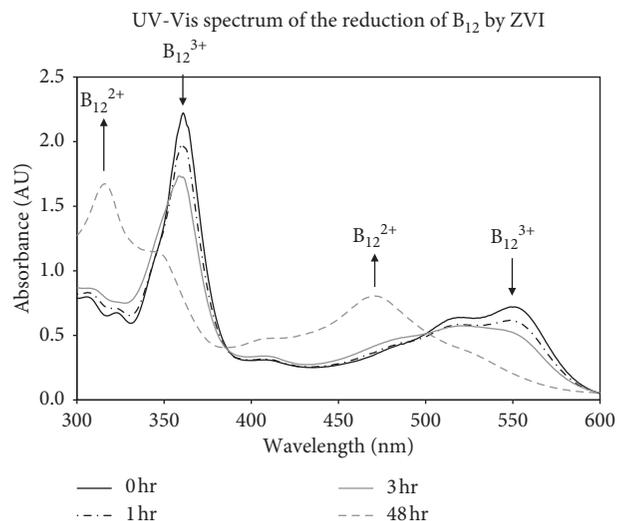


FIGURE 7: Cobalamin reduction in the presence of μ ZVI.

It was hypothesized that the reduced form of cobalamin can facilitate the transfer of electrons to chlorinated alkanes and therefore induce the processes of reductive dechlorination. For this work, direct reduction of chlorinated alkanes was demonstrated by a measurable decrease in the compound of interest with a concurrent increase in chloride concentration in solution.

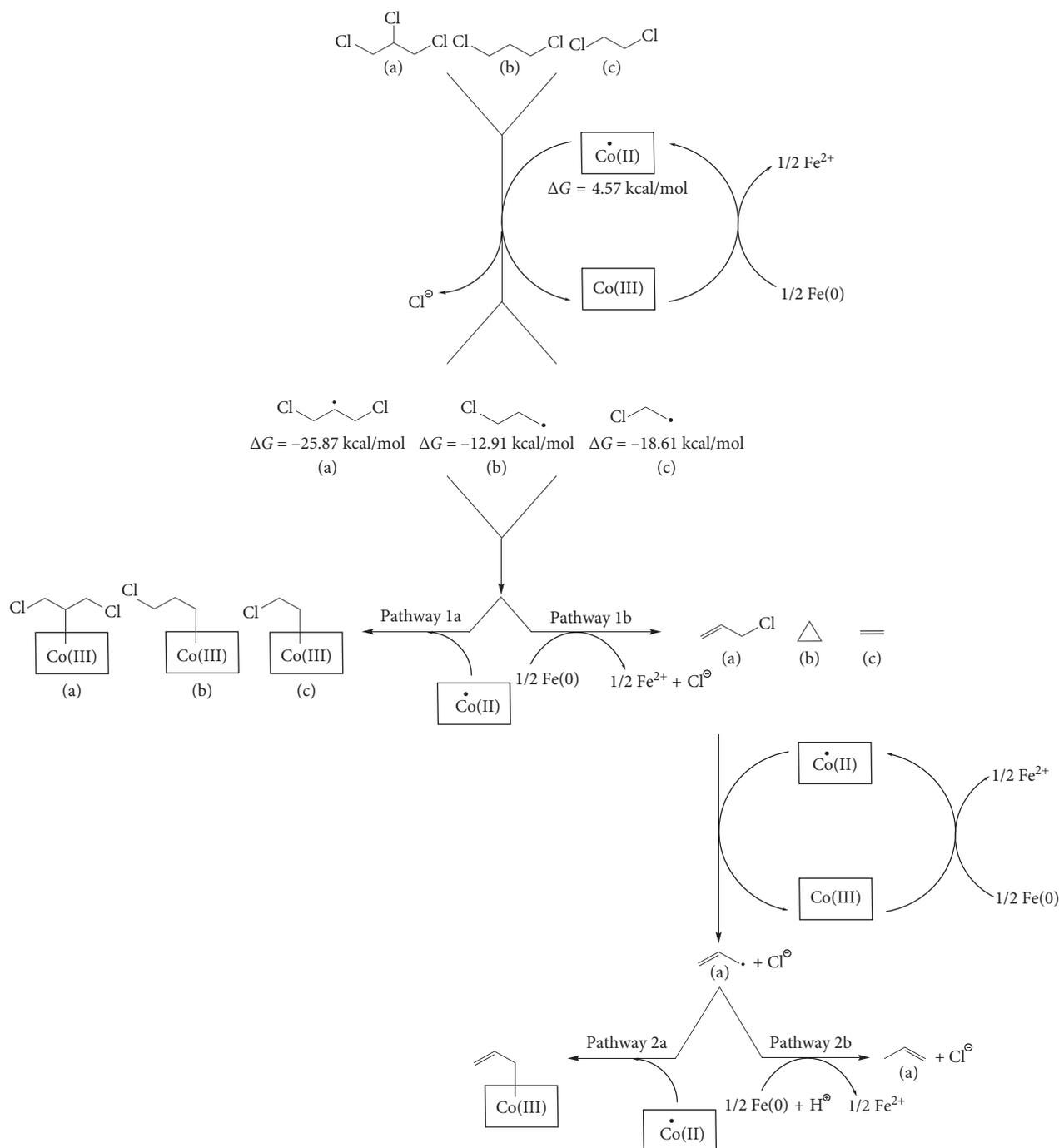


FIGURE 8: Mechanistic pathway for (a) 1,2,3-TCP, (b) 1,3-DCP, and (c) 1,2-DCA.

Figure 8 shows the mechanistic pathway for 1,2,3-TCP, 1,3-DCP, and 1,2-DCA and their respective byproducts. The proposed mechanism centers on a single electron transfer from the ZVI surface to cobalamin, reducing the cobalt center from Co(III) to Co(II). Once in this reduced state, cobalamin can transfer an electron to the chlorinated compound due to favourable reaction potentials. This transfer is accomplished by a net halogen exchange from the chlorinated alkane to B_{12r} , which may occur via a halogen-bridge transition state, yielding an alkyl radical and

chlorocobalamin [25, 26]. It is also important to note that the Co(III) center of chlorocobalamin can be reduced to Co(II) by a single electron transfer from ZVI or have its chlorine displaced by water to form aquacobalamin (B_{12a}) [25, 27, 28]. This is an important step because it regenerates the catalytic B_{12} to the Co(II) oxidation state for additional available reactivity. The alkyl radical can then react either with another B_{12r} to produce a very stable alkyl-cobalamin derivative, or it can accept an electron from ZVI to be further reduced.

The observed byproducts for 1,2,3-TCP and 1,2-DCP were propene, 1-CP formed propane, and 1,3-DCP formed cyclopropane. Cyclization byproducts with reduced forms of B₁₂ have been shown to occur and were observed by Petrović with tetrachloroalkanols [29]. These byproducts were further supported due to favourable reaction potentials. Based on energetic calculations, the proposed byproduct for 1,2-DCA was ethene, which could not be observed due to analytical instrumentation parameters.

4. Conclusions

Chlorinated propanes and ethanes are recalcitrant compounds that pose an environmental concern due to their persistence in groundwater and soil matrices. The following research focused on neat studies in order to determine whether vitamin B₁₂ could facilitate the dechlorination of 1,2,3-TCP, 1,2-DCP, 1,3-DCP, 1-CP, and 1,2-DCA in an aqueous environment with μ ZVI. Complete dechlorination was observed for chlorinated propanes and ethane in the presence of B₁₂ and, μ ZVI and the reactions followed pseudo-first-order kinetics. Studies conducted without B₁₂ showed no observable degradation over the reaction time frame (e.g., months). The reaction is initiated by a single electron transfer from B₁₂ to the chloroalkane, forming a radical intermediate which undergoes further reduction by ZVI. Degradation byproducts were observed for 1,2,3-TCP, 1,2-DCP, 1,3-DCP, and 1-CP with an increase of free chloride in solution. Even though byproducts were not resolved for 1,2-DCA, an increase of free chloride into solution was observed which supports its dechlorination. Vitamin B₁₂ is indicated to be a promising catalyst in the reductive dechlorination of recalcitrant chloroalkanes and potentially other halogenated compounds. Utilized in conjunction with ZVI, this system shows promise for expanding the scope of ZVI-treatable contaminants.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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