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A Review of Biodegradation and Abiotic Degradation of Carbon Tetrachloride

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ABSTRACT

Volatile organochlorines (VOCs) are widely present in our environment and can be used as good solvents, paints, degreases, and various industrial and commercial products, can be detected in soil, air, and any kind of polluted water medium. Carbon tetrachloride (CT), as a typical volatile organochlorine compound, has stable chemical properties, long half-life and long residence time in polluted environment. CT is mainly produced by anthropogenic conditions and rarely directly by nature. There is currently no microbial system capable of using CT as the only carbon source. Microbes that use CT as terminal electron acceptor have not been reported, but the corresponding degradation pathways have been studied. Known modes of CT biodegradation involve a variety of microbial metabolites, mainly metal-bound coenzymes and ferriferous carriers produced by facultative or obligate anaerobic bacteria and methanogenic archaea. In this paper, biological and abiotic methods of CT degradation were reviewed, factors affecting CT dechlorination and microbial degradation in contaminated sites were discussed, and the future development direction was prospected.

KEYWORDS

Degradation; Carbon Tetrachloride (CT); Biodegradation; Abiotic Degradation

1. INTRODUCTION

1.1. Production, Utilization and Release Of CT in the Environment

Carbon tetrachloride, also known as tetrachloromethane, is one of the typical volatile halogenated hydrocarbons. It is colorless, transparent and has a unique aromatic smell under normal temperature and pressure conditions (1). CT is denser than water, volatile, very soluble in water, soluble in ethanol, ethyl ether, chloroform, petroleum ether, etc. It is an excellent non-polar solvent for non-polar organic compounds in the chemical industry, such as grease, oil, lacquer, wax, rubber, resin, etc. CT may cause pollution to the environment, especially to surface and groundwater sources, as a result of volatilisation of gases and wastewater discharge.(2) Production of CT in the United States peaked in the 1970s at 500,000 tons per year, after which production began to decline sharply from the 1980s due to environmental concerns and declining demand for chlorofluorocarbons (CFCs) (3). In China, the annual production of CT was only 57,600 tons in 2001 and declined year by year until it completely disappeared from the market in 2010 (4). Historically, the main use of CT has been as a feedstock for the production of chlorofluorocarbons (CFCs).CT also was extensively used as a fire extinguisher, degreasing agent, and pesticide, and in the dry-cleaning industry it served as a replacement for petroleum distillates but was later replaced by trichloroethylene (PCE).In the 1990s, CT disappeared from the market when it was found to have a destructive effect on stratospheric ozone (5,6). CT has been banned in the United States since the 1970s and has been included in the 'Black List of Priority Pollutants in Water' of 128 pollutants, as well as in China's 'Black List of Priority Pollutants in Water' of 68 pollutants (7).

1.2. Toxicology and Degradation Properties of CT

Due to the use and discharge of CT, it can be detected in air, water and soil. Especially near some pharmaceutical factories and landfill sites, the detection rate is very high, and the detection reproducibility is good (8). Lu Haiyan et al. found that CT was the main pollutant in the groundwater of a district in Beijing and its concentration exceeded the standard when they sampled four aquiferous layers. Zhang Xinyu found in the study of a polluted site in North China that only CT was the pollutant exceeding the standard. The vertical distribution of CT was related to the depth, and the horizontal distribution was related to the direction of water flow. People mainly consume CT through two mediums: residential water and air. There are two main ways for it to enter the human body: one is through respiration into the lungs, intestines and other human tissues, and the other is direct contact with the skin (9,10). CT can damage the liver and kidney, resulting in liver disease and kidney disease. It also has an impact on the human nervous system including the brain, inhibiting the central nervous system, and causing permanent damage to nerve cells. Studies have confirmed that CT has carcinogenic effects, the International Agency for Research on Cancer (IARC) has classified CT as Class 2B, possibly carcinogenic to humans, and the Environmental Protection Agency has identified CT as a probable carcinogen (11-14). Due to the steady nature, non-easily degradable and long half-life of CT, which can cause irreversible and serious negative impacts on groundwater, soil, atmosphere and human health, a series of studies on CT degradation have been carried out both at home and abroad yielding certain results(15).The methods of removing CT can be divided into two categories from degradation methods: one is abiotic biodegradation, mainly through chemical methods to oxidize or reduce CT, so that it can be converted into non-toxic or can be used for chemical products; the other is biodegradation, which refers to the conversion of CT into inorganic substances through microbial metabolism (16).

This paper introduces the research progress of CT degradation in two parts: one is the common methods of abiotic degradation of CT and its shortcomings; the second is the biodegradation mode and development prospect of CT. Several reviews published in the past have focused on CT removal methods, but the present work is the first review to specifically investigate the biological and abiotic degradation aspects of CT.

2. ABIOTIC DEGRADATION OF CT

The abiotic degradation of CT mainly changes its molecular structure and implements electron transfer through a series of oxidation and reduction methods, which mainly include chemical reagent, photocatalysis, metal reduction, electrochemical and other methods.

2.1. Chemical Reagent

Chemical reagent method refers to the use of mixed solution with oxidation or reduction to react with CT to change its molecular structure, so as to achieve the purpose of degradation. Common chemical reagents are Fenton reagent, activated sodium persulfate reagent, ferrous sulfide and so on. In 1894, the British H.J.H.Enton found that the mixture of ferrous ion solution (Fe^{2+}) and hydrogen peroxide (H_2O_2) solution had extremely strong oxidation performance, which could oxidative degradation of many stable and not easy to degrade pollutants and had excellent effect. In his memory, the advanced oxidation system Fe^{2+}/H_2O_2 was called Fenton's reagent (17). The main principle of Fenton reagent is that in the presence of Fe^{2+}, H_2O_2 can be catalyzed and decomposed to produce hydroxyl radical (·OH) with high reactivity. The oxidation potential of ·OH is 2.8V. Most organic substances can be oxidized and decomposed into small molecules through reactions such as electron transfer. While Fenton reagent requires simple equipment, with a relatively fast reaction speed and mild reaction conditions, it remains a cause of some problems, such as a large number of factors influencing the reaction and a poorly controlled oxidising effect. With the deepening of research, the researchers gradually combined conditions such as catalysts, photo-radiation, electro-radiation and ultrasound with the Fenton system to promote the ability of H_2O_2 to produce ·OH, creating a positive synergistic effect.

Wang Yang et al. introduced ultrasonic waves with controllable power into Fenton system and used orthogonal test to explore the influence of the core five elements on the degradation effect of CT in water. It was concluded that the synergistic effect was best when the temperature was 303 K, the ultrasonic power was 300 W, the pH was 3, and the concentration of Fe^{2+} and H_2O_2 was 2.50 mmol/L and 20 mmol/L, respectively. Under the same conditions, the degradation rate of CT was increased by 26.96 %, and the degradation rate reached 78.49 % at 45 min of reaction, which was in line with the first-order reaction kinetic characteristics (18). Gu et al. investigated the mechanism of CT degradation in aqueous solutions by protonated and nonprotonated solvents, and concluded that both protonated and nonprotonated solvents could enhance the degradation of CT in solution, and the dominant free radicals of enhancement were $CO2\cdot^-$ and $O2\cdot^-$, respectively, with accumulation of the intermediate product CF occurring in the former, and a lower concentration of the latter with a basically complete decomposition of CT (19).

2.2. Photocatalysis

Photocatalytic technology refers to the method of degradation and removal of pollutants in water catalyzed by catalysts under a certain wavelength of light, which can be divided into homogeneous photocatalytic oxidation method and heterogeneous photocatalytic oxidation method according to the form of catalysts. This method has been reported at home and abroad for CT degradation, which is relatively mature. The heterogeneous photocatalytic oxidation method usually uses semiconductor titanium dioxide (TiO_2) as catalyst. In 1972, Fujishima and others used TiO_2 semiconductor photocatalysis technology for the first time to photolysis water to produce hydrogen. Since then, more and more researchers at home and abroad have applied this technology to oxidative degradation of pollutants. The mechanism of photocatalytic technology is that when photosensitive materials are irradiated by light with energy greater than the forbidden bandwidth, the electrons on the valence band are excited into the conduction band to form highly active electrons, and concomitantly, positively charged holes will be generated on the valence band to produce hydroxyl radicals and other highly active reactive groups, so as to achieve the purpose of degradation of organic pollutants (20,21).

It is found that the photocatalytic effect can be significantly enhanced in the presence of electron donors and precious metals. Bakar loaded different types of first transition metals on TiO_2 to degrade the target pollutant solution containing methylene chloride (DCM), chloroform(CF) and carbon tetrachloride(CT). And the experimental study showed that the best degradation effect was achieved under UV light (6 W,354 nm) irradiation for 90 min with the mixed catalysts of $Zn^{2+}/Fe^{3+}/TiO_2$ and a molar ratio of 0.0005:0.0005:1, then the best degradation reaction was observed, with a degradation rate of 41.05% for DCM, 49.45 % for CF and 37.84 % for CT (22).Similarly, Gao Xia et al. synthesized regular bismuth oxybromide (BiOBr) micrometer flakes with soluble bismuth salt and sodium bromide as raw materials through one-step hydrothermal heat treatment, and concluded that the most suitable reaction conditions were 120 min irradiation with visible light with a power of 550 W when the solution pH=3 and the catalyst dosage was 2 g/L. Under these conditions, the maximum degradation rate of CT was 91.72 % (23).

2.3. Metal Reduction

The essence of metal reduction method is to dechlorinate chlorine-containing organic compounds by using some reducing metal substances and their derivatives, so as to transform them into less toxic or easily degraded substances. In 1994, Gillham/O 'Hannesin et al found that the addition of iron can effectively improve the degradation rate of chlorinated aliphatic compounds in batch and column tests, that is, the reduction dechlorination process using iron as the electron source. Subsequently, a series of studies on zero valent iron (ZVI) reduction dechlorination were carried out successively (24). ZVI stands out among many metal reducing agents because of its low toxicity, easy preparation and availability, and no secondary pollution. ZVI can be used to repair groundwater contaminated by halogenated solvents, heavy metals, nitrates and polycyclic aromatic hydrocarbons. Zhu et al. took CT as the target pollutant to explore the effects of common anions Cl^-, $SO_4^{2-}$and HCO_3^- in groundwater turbidity on the degradation of CT by ZVI. The results showed that the common anions Cl^-, $SO_4^{2-}$and HCO_3^- could promote the degradation of CT by ZVI in the order of $HCO_3^-> SO_4^{2-}> Cl^-$. HCO_3^- could regulate the pH of the system and trigger a cathodic reaction, thereby promoting the degradation of CT by ZVI. SO_4^{2-} enhanced the CT degradation rate by dissolving and removing the hydroxide on the metal surface. Cl− acted as a metal corrosion activator to accelerate the degradation of CT by corroding the surface of ZVI.The promoting effects of Cl^-, $SO_4^{2-}$and HCO_3^- ions showed a trend of first increasing and then decreasing with the increase of ion concentration (24).

2.4. Electrochemical Methods

ZVI reductive dechlorination is not effective due to the passivation of the iron surface by halocarbons produced during reductive dechlorination of zero-valent iron. Fentons oxidation, photocatalytic degradation of TiO_2 catalyst, combined use of UV irradiation and ultrasonic (sonophotolysis), all these above methods have the disadvantages of high operation cost and long reaction time. In contrast, the researchers found that the application of electrochemical treatments can be used to convert chlorinated organics in chlorinated solvents to the corresponding dehalogenated hydrocarbons by either direct or indirect methods of oxidation at the anode or reduction at the cathode. Lakshmipathiraj et al. anodized trichloroethylene (TCE) using Ti/ IrO_2-Ta_2O_5 electrodes by cyclic voltammetry. The results showed that the oxidation of TCE occurred directly on the electrode surface in the potential region above 0.3 V, and the electron conversion and oxygen precipitation occurred directly at the anode.The dechlorination rate of TCE increased with the extension of electrolysis time, and complete dechlorination was observed in all experiments, the degradation was in line with kinetic quasi-first-order reaction with a rate constant of 0.0081 $cm.s^{-1}$ (25).

3. BIODEGRADATION OF CT

As a highly volatile chlorinated organic compound, there are few researches on the degradation of CT, which can mainly be degraded by abiotic and biological methods. The former mainly includes traditional physical adsorption method, chemical oxidation method, metal reduction method and electrochemical reduction method. However, these methods cannot completely degrade CT, and can only be transferred from one medium to another. However, these methods cannot remove CT completely and can only transfer it from one medium to another, while chemical methods are generally characterised by complex procedures, insufficiently mild reaction conditions, high costs, etc., which make in-situ remediation difficult. Bioreintermediation is the process by which microorganisms degrade environmental pollutants into less toxic or non-toxic substances, aiming to use microbial catabolic diversity to degrade, transform, or accumulate a large number of compounds, including hydrocarbons (such as petroleum), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), radionuclides, and metals.

At the moment, bioremediation is considered to be one of the safest, cleanest, most economical and environmentally friendly site purification technologies. Compared to other physical and chemical method, biological remediation usually consumes less energy and resources, cheap and accord with the requirement of the sustainable development of our country (26).

3.1. Microbial Aerobic Degradation of CT

Nearly a century after the industrial production of CT began in Germany and the United Kingdom in the late 19th century, the first reports of microbial experiments capable of degrading CT were made in the early 1980s, and Regnault first reported the chemical synthesis of CT in 1839. Since then, the researchers have obtained bacterial complexes and isolates capable of degrading CT from a large number of sites (27). As a compound with a high octanol/water partition coefficient and a high redox price, CT appears to be difficult to degrade under aerobic conditions in the natural environment, i.e. groundwater, soil and wastewater. Until 2008, Liang et al. enriched and cultured the bacterial colonies in the soil contaminated by CT for a long time, selected robust bacterial colonies, isolated the dominant strains and domesticated them, and obtained the strain Ct5 that could degrade CT by consuming oxygen. The strain CT5-1 was screened out among the 13 mutant strains with the highest rate of CT degradation. And it was concluded by orthogonal experiments that the best CT degradation efficiency of 22.14 % was achieved by strain Ct5-1 at 35 ℃, pH 7.0, CT concentration of 20 μg/L, and rotational speed of 140 r/min when glucose was used as an additional carbon source at a mass concentration of 5 g/L, with the CT concentration being the most important factor influencing CT degradation by strain Ct5 (28,29). Zou et al. also isolated dominant strain SL in CT-contaminated soil in the following year (2009), and screened out Gram-negative aerobic strain SL-6 by domestication and UV mutagenic mutation. Strain SL-6 had the best CT degradation efficiency of 20.1 % when it was enriched at 35 ℃ and 150 r/min for 7 days. Physiological and biochemical characteristics showed that strain SL6 belonged to Pseudomonas (30).

However, studies on aerobic strains CT-5 and SL6 only stayed in the screening and preliminary identification stage, and there was a lack of follow-up studies on the strains. For example, studies on the physiological, biochemical, molecular mechanism and enzyme kinetics of these two microorganisms degrading CT have not been revealed. At present, CT-degraded aerobic strains have no practical application in the remediation of contaminated sites, and their degradation activity in the environment and the remediation effect of CT contaminated sites need to be further studied, and the degraded strains can also be improved and strengthened by mutagenesis breeding and other technologies.

3.2. Anaerobic Microbial Degradation of CT

CT has no C-H bond and is a tetrahedral symmetric molecule like methane. Even though the four C-Cl bonds of CT are highly polarized, its carbon atoms are still not electrophilic. The high electronegative halogen substituents and high oxidation valence carbon atoms of CT make it inert and relatively stable in the environment. In the natural environment, the aerobic degradation of CT is difficult to occur, and CT is mostly deposited in the relatively anaerobic environment such as soil and groundwater. A wide range of culture conditions have been reported for CT degradation, including sulfate reduction, nitrate reduction, iron reduction, fermentation and methanogenesis conditions. Up to 420 concentrated cultures or complexes are known to degrade CT, but few have been classified or identified as members of complexes responsible for dehalogenation (4 cases). Nevertheless, the phylogenetic diversity of CT-degrading strains is extensive: containing 12 parthenogenetic or specialised anaerobic bacterial lineages and three methanogenic archaeal lineages (31). Thermodynamic studies have shown that many chlorinated aliphatic hydrocarbons can act as electron acceptors for microbial respiration, and a number of related microbial reductive dechlorination reports exist, such as *dehalomonas spp.* strains WBC-2 and GP that dechlorinate chlorinated alkenes, and

Dehalococcus spp. KB-1, and SDC-9 that degrade properly both chlorinated olefins and chlorinated alkanes (32, 33).

In the past few decades, many studies have focused on the potential applications of aerobic and anaerobic microorganisms in converting chlorinated volatile organic compounds (Cl-VOCs) into non-toxic hydrocarbons. Many aerobic microorganisms, such as methane oxidizing bacteria, propane oxidizing bacteria, ammonia oxidizing bacteria, and toluene oxidizing bacteria, can collectively metabolize certain Cl-VOCs (34). Due to the high toxicity of most Cl-VOCs, few microorganisms can use them as the sole carbon source in the environment. Research has shown that under denitrification, heavily chlorinated hydrocarbons may undergo accidental biotransformation, converting into compounds with lower levels of chlorination that are more easily biodegradable under sulfate reduction and methane production conditions. Under conditions of stronger reducibility, the conversion rate is usually faster (35). Bouwer et al. observed the conversion of a mixture of oxygen, nitrate and sulphate as the primary electron acceptor, with bacteria as the primary substrate and trace amounts of organic chlorides as secondary substrates. The conversion of CT under sulfate-reducing conditions in a continuous-flow reactor was described but the CT conversion products were not explored (36,37).Egli et al. found in pure cultures of autotrophic *Desulfovibrio desulfuricans* that more than 70% of the CT could be converted to produce chloroform (CF) and dichloromethane (DCM), with unidentified water-soluble products being detected (38).

Best et al. explored the biotransformation of CT under sulphate-reducing conditions in an upflow packed-bed reactor filled with polyurethane foam (PUR) particles and digested sludge (20 %V/V) from a wastewater treatment plant in Kralingseveer (The Netherlands). The results of the assay revealed that CF and DCM were the main transformation products, but some CT was also completely dechlorinated to unknown products. In this packed column, it was Gram-positive sulfate-reducing bacteria that played a major role in CT conversion, reducing and dechlorinating CT to CF and DCM, but both CF and DCM accumulated without further dechlorination to CM or CH_4, which may be due to the reduced redox potential of the reductive dechlorination, and further reductive dechlorination thermodynamically unfavourable to the occurrence of the reaction. It has been previously reported that DCM can be reductively dechlorinated to CM or CH_4, but this conversion was only performed by *Acetobacterium woodii* under methanogenic and acetogenic conditions at very low conversion rates (31).Best et al. did not find evidence of DCM fermentation in their experiments, which may be due to the fact that the other product of the CT conversion, CF, is toxic to the DCM-utilising bacteria (39). Both the sulfate reduction inhibitor molybdate and the Gram-positive bacterial inhibitor vancomycin completely inhibited CT conversion. Conversion of CT by these bacteria was a co-metabolic process that depended on the type and concentration of the electron donor and electron acceptor (sulphate). Although the sulfate-reducing bacteria in this reactor did not completely dechlorinate CT, both CF and DCM were formed. The complete anaerobic bio-dechlorination of CT in groundwater containing high sulfate concentrations had the potential to be realised and was expected to be applied to in situ bioremediation of groundwater environments containing high sulfate concentrations.

3.3. Microbially Mediated Abiotic Degradation of CT

Reduction mediators (RM), also known as electron shuttles, are a class of reactive substances involved in reversible redox reactions that transform different pollutants by redox through chemical or biological mechanisms. Many microorganisms are capable of reducing redox mediators associated with the anaerobic oxidation of organic and inorganic substrates.RM can also be chemically reduced by electron donors commonly found in anaerobic environments (e.g., sulphides and ferrous iron).RM can transfer electrons to several different electron-absorbing compounds such as polyhalogenated compounds, nitroaromatic hydrocarbons, and oxidised metalloids. In addition, reducing molecules with redox properties provide the ability to support microbial reduction of electron acceptors, such as nitrate, arsenate, and perchlorate (40). Many CT-degrading bacteria synthesise a large number of redox-active low-molecular-weight compounds that enhance the reductive dehalogenation of CT, mainly as cofactors in the electron transfer reactions of central metabolic enzymes. These compounds include organometallic compounds such as cobalt-containing coagulins, iron-conjugated porphyrins (e.g., cytochromes), the nickel-containing factor F430, and key cofactors such as riboflavin or menaquinone. For instance, cochineal-like cofactors are produced during acetyl coenzyme a synthesis, methanogenesis, desalination respiration, fermentation pathways, and DNA synthesis in numerous taxonomically distinct phyla of CT-degrading strains, including the acetic acid-producing bacteria *A. woodii* and *M. thermoacetica*; the intestinal bacteria *E. coli*; the organohalogen respiratory bacteria *Desulfitobacterium hafniense* and *Dehalobacter restrictus*; and the methanogenic bacteria *Archaea Methanosarcina barkeri*, among others (41).

The degradation of CT not only occurs intracellularly. When CT is dechlorinated by co-metabolism and absorbs a large number of low molecular weight molecules, these molecules can act in extracellular processes, some even after cell death. Due to the incidental catalytic role of these cofactors in CT degradation, the greater the ability of a microorganism to produce these catalytic cofactors, the more potential it has to degrade CT as well as other chlorinated compounds. Lower concentrations of vitamin B_{12} are known to accelerate the anaerobic biotransformation of CT and CF. Guerrero-Barajas et al. presently investigated a strategy to generate vitamin B_{12} by the addition of biosynthetic precursors. One of the precursors, cholecalciferol (PB), which participated in the formation of the cochineal ring, significantly increased CT bioconversion by 2.7-fold, 8.8-fold, and 10.9-fold when 160 µM, 500 µM, and 900 µM were added, respectively. The use of 10 µM vitamin B_{12} in the positive control group resulted in a 5.9-fold increase in CT bioconversion. The experimental results confirmed that the effect of PB was due to the stimulation of vitamin B_{12} biosynthesis (42).

3.4. Thermodynamic analysis of CT reductive dechlorination

Esaac and Matsumura showed that significant reductive dechlorination occurs only when the redox potential of the environment is below 350 mV (43), and Parsons et al. (1985) showed that reductive dechlorination of chlorinated hydrocarbons may occur when the redox potential (ORP) of the sealed microcosm is below 300 mV. However, the effective redox potential for different compounds could be different, and the pseudo-primary rate constant for reductive dechlorination of CT increased with decreasing redox potential (44, 45).

No organism capable of using CT as a carbon or energy source has been isolated, and no specific related dehalogenases have been reported.The mineralisation of CT to carbon dioxide and its reductive conversion to methane are exergonic processes, and thermodynamically, the CT conversion is favourable under aerobic conditions for this phenomenon, and the stepwise dechlorination of CT is an energetically favourable conversion reaction. But some steps are more energetically favourable than others due to factors such as environmental conditions and redox potentials (46). In the course of their experiments investigating the degradation of perchloroethylene (PCE) by reductive dehalogenation, Holliger et al. discovered that desalination respiration under highly anaerobic conditions is the most favourable for the two initial steps in the production of 1, 2-dichloroethene (1, 2- DCE), but it becomes even more favourable under aerobic conditions, with 1, 2- DCE potentially acting as an energy source or as a carbon source (47). Besides, other metabolic strategies, such as sulphate reduction, Fe (III) reduction, and under methanogenic conditions, usually energy-wise competed with the reductive dehalogenation of PCE, which also set important selective limits for the survival and development of organisms that can degrade PCE in the environment (48, 49).

The most typical external metal chelate involved in CT degradation is the secondary iron carrier, pyridine-2, 6-dithiocarboxylate (PDCT), of *Pseudomonas stutzeri* KC. *Pseudomonas stutzeri* KC was found to catalyse extracellular PDCT-dependent dehalogenation of CT. Unlike other biomolecules known to mediate reductive CT dechlorination, PDTC was not able to be regenerated by electron addition after CT degradation, but was converted to a bona fide reactant of dipyridine carboxylic acid during the dehalogenation process (50, 51). In addition to low molecular weight organometallic compounds of direct biological origin, other types of chemicals present in the environment can act as electron shuttles to facilitate CT degradation, such as inorganic metal chelates, natural organic matter, humic acids, and certain organic matter. Alternatively, bacteria can provide the required electrons. Soils and aquifers contain large amounts of humic and xanthic acids, and quinones are the main electron acceptors in humic acids, providing one or more electron acceptor sites (52, 53). For example, the reduced form of the electron shuttle and humic analogue anthraquinone disulfonate (AQDS), anthraquinone disulfonate (AHQDS), catalyses CT degradation either directly or indirectly by transferring electrons to other biomolecules or inorganic compounds, acting itself as an intermediate electron shuttle to be oxidised, with the electrons generated in the process being transferred directly into the CT. In turn, oxidised AQDS are reduced to reducing AHQDS or abiotic reductants via microbially supplied electrons (54).

3.4.1 Thermodynamic profile of CT reductive dechlorination

Only a few common elements: carbon (C), nitrogen (N), oxygen (O), iron (Fe) and sulphur (S) are major players in natural aquatic reductive oxidation processes. Redox potentials of +810, +750, -220 and -240 mV in the environmental system correspond to the redox pairs: O_2/H_2O, NO_3^{-}/N_2, SO_4^{2-}/H_2S or CO_2/CH_4, respectively, in that order. In particular, chlorinated hydrocarbons can act as electron acceptors, competing with electrons from organic substrates and other electron acceptors in the microbial environment. The standard redox potential of chlorinated hydrocarbons (PCE/TCE, CT/CF) is lower than that of O_2/H_2O and NO_3^{-}/N_2,, but higher than that of SO_4^{2-}/H_2S and CO_2/CH_4.This situation implies that chlorinated hydrocarbons may gain an electron under methanogenic conditions (low redox potential) for reductive dechlorination in the presence of denitrification, sulphate reduction, and oxidative reduction. On the other hand, strong electron acceptors inhibit dechlorination in an oxidative environment, which also suggests that reductive dechlorination by microorganisms is more likely to occur under anaerobic conditions, which are thermodynamically more favourable.

3.4.2 Factors affecting CT dechlorination

There are a series of factors affecting CT dechlorination, such as environmental conditions, redox potential, extracellular influences, and the presence of other organisms and microorganisms, all of which promote or inhibit the conversion of CT dechlorination to varying degrees.

In a study of a contaminated chemical manufacturing site, effective natural attenuation of CT was limited by the in situ bioavailability of carbon and electrons and unfavourable physico-chemical conditions such as low pH and high redox potential. However, significant biodegradation of CT can occur in areas with low redox potentials and elevated pH due to the addition of lime-related organic materials in early decontamination treatments, which stimulate microbial dechlorination. Numerous studies have shown that successful in situ CT biodegradation is highly dependent on environmental conditions such as low oxygen content, low redox potential, and the presence of one or more electron donor species. In terms of CT concentration, moreover, could have a non-negligible effect on the biodegradation of CT (55).

Boopathy R et al. investigated the biotransformation of CT under different electron acceptor conditions using enriched cultures developed from anaerobic digester sludge from Thibodaux Wastewater Treatment Plant. The results showed that the CT conversion rate varied depending on the reduction conditions. The fastest rate of CT removal (100 % removal within 12 days) was observed under mixed electron acceptor conditions, followed by sulphate reduction, methanogenesis, fermentation, iron reduction and nitrate reduction conditions. Under mixed electron acceptor conditions, CT was converted to methyl chloride for further metabolism. The major metabolite produced by CT metabolism under sulfate-, iron-, nitrate-reducing, and methanogenic conditions was CF. under fermentation conditions, CT was metabolised to produce DCM. Boopathy's study demonstrated evidence of CT metabolism in a mixed microbial population system similar to that of many contaminated sites where heterogeneous microbial populations exist (56).

Doong et al. observed that the incorporation of electron donors and microorganisms significantly increased the dechlorination efficiency of CT. The addition of electron donors such as humic acid, acetate, and glucose increased the cell number of the anaerobic consortium, which led to an increase in the dechlorination rate, and if the conditions for supplementation of electron donors were properly selected, it was possible to stimulate the dechlorination capacity of the anaerobic consortium to remediate the chlorinated hydrocarbons in the nutrient-poor environment (35).

Many organochlorides are toxic to microorganisms by inhibiting their growth and development, physiological metabolism, and enzyme activity. Therefore, due to the inhibitory nature of these compounds, a major challenge for biodegradation methods is that bacteria often take a long time to acclimatise and remove the HCFCs from the contaminated site (35, 57). For example, CF is toxic to microorganisms and inhibits microbial processes (e.g., methanogenesis) and reductive dechlorination of other chlorinated aliphatic compounds. Many organochlorine compounds, to include CT, are denser than water and have low water solubility, resulting in its accumulation in groundwater aquifers as a heavy non-aqueous phase liquid (DNAPL) with slow dissolution into groundwater. In some heavily contaminated groundwater systems, a unique system of heavy non-aqueous phases co-existing with their upper aqueous phase (APL) occurs, with different transport and degradation patterns for the aqueous and non-aqueous phases. CT will be released slowly into the APL in DNAPL, which results in different CT concentrations in the two phases of the same contaminated environment, and the microorganisms' growth conditions and CT degradation products in the two phases are also different. Shan Aiqin et al. collected farmland soil contaminated with wastewater from a pesticide factory as a target pollutant, enriched and cultivated highly efficient CT-degrading bacteria, which were Gram-positive Streptococcus, and measured the growth of microorganisms under different CT concentrations by spectrophotometric method. The results showed that in the experimental concentration range, the degradation rate of CT decreased with the increase of the initial concentration, and the growth of the colony was obviously inhibited and delayed under the concentration of CT (APL and DNAPL two-phase) of >0.1 %~0.2 %, and the degradation efficiency of CT was higher when the CT concentration was <0.005 % (APL). After domestication, the colony was able to degrade target pollutants with higher initial concentrations (58, 59).

4. CONCLUSION

As mentioned above, the prevalence of CT in the environment and its potential toxicity to humans have fuelled the development of methods for its remediation. These methods can be generally categorised into abiotic and biotic methods. Abiotic methods such as ozonation, photocatalytic oxidation, Fenton oxidation and electrochemical oxidation can be successfully applied for CT removal with high removal efficiency. Non-selective oxidation of CT by free radical intermediates generating undesirable by-products, addition of expensive chemicals and high energy consumption are some of the drawbacks of abiotic methods for which they need to be overcome in the future. In general, electrochemical reduction is more effective for CT dechlorination. Further development of electrochemical reduction ought to focus on the construction and optimisation of electrochemical devices, including the development of dimensionally stable and efficient cathode materials, large-area flow cathodes, and the evaluation of the most suitable electrolysis conditions for reducing process costs. The selection of remediation technologies for contaminated sites entails a comprehensive consideration of their applicability and the actual contamination situation.

In sharp contrast, CT microbial anaerobic reductive dechlorination is the most promising in situ remediation technology. Owing to the ubiquity of microbial CT degraders, the diversity of energy metabolisms, and the diversity of biomolecules that catalyse CT conversion, virtually every ecosystem possesses CT dechlorination potential. Further studies are warranted to explore the diversity of microbial CT degradation pathways in the environment and to assess the conditions required for the most efficient degradation. Recent advances in microbial community analysis, such as real-time PCR, FISH, genotyping techniques, macro-genomics and macro-proteomics, and stable isotope probing are all technologies that will be more helpful in better assessing the unknown fate of CT and its degradation products in the environment. Inputs from the hybrid processes of different combinations of methods could also provide an interesting direction for future research, such as combining biochemical techniques with microbial in situ remediation to compensate for the limitations in CT degradation methods.

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