Transformation rules and degradation of CAHs by Fenton-like oxidation in growth ring of water distribution network-A review

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Abstract. Chlorinated hydrocarbons are widely used as organic solvent and chemical raw materials. After treatment, water polluted with trichloroethylene (TCE)/tetrachloroethylene (PCE) can reach the water quality requirements, while water with trace amounts of TCE/PCE is still harmful to humans, which will cause cancers. Water distribution network is an extremely complicated system, in which adsorption, desorption, flocculation, movement, transformation and reduction will occur, leading to changes of TCE/PCE concentrations and products. Therefore, it is important to investigate the transformation rules of TCE/PCE in water distribution network. What’s more, growth-ring, including drinking water pipes deposits, can act as catalysts in Fenton-like reagent (H₂O₂). This review summarizes the status of transformation rules of CAHs in water distribution network. It also evaluates the effectiveness and fruit of CAHs degradation by Fenton-like reagent based on growth-ring. This review is important in solving the potential safety problems caused by TCE/PCE in water distribution network.

1. Introduction

Chlorinated hydrocarbons (CAHs) are widely used as organic solvent and chemical raw materials in chemical, leather, medicine and electronic industries. CAHs contaminated soil and groundwater has resulted due to past disposal directly onto land, accidental spills, and leaking storage tanks, posing a threat to human health and environment [1]. Atmosphere, water body, soil and refuse landfill have been reported of pollution of CAHs [2-4]. CHAs are common persistent organic pollutants and they are easy to be enriched in living organisms. CHAs are characterized by high stability, toxicity and "mutagenesis, carcinogenesis, teratogenesis". Besides, CHAs are especially troubling since their high densities as compared to water allow them to move downward through the water table and collect in hard to reach regions. Here they continue to contribute to contamination [5, 6]. Due to their toxicity and refractory, halogenated organic solvents are listed as priority control environmental contaminants. In 1979, United State Environmental Protection Agency (US EPA) released 129 kinds of environmental priority control pollutants and organic halogenated hydrocarbons and their derivatives
accounted for more than 60. In the "blacklist" released by European Communities, CAHs and chlorinated hydrocarbon compounds that can be formed in the environment are listed first [7]. Besides, TCE and PCE are among the most common pollutants in CAHs, and they are high-toxic substances and widely used. Both of them draw utmost attention, and the both are included in 129 kinds of environmental priority control pollutants released by US EPA in 1976 and "blacklist of priority pollutants" put forward in China [8-10].

World Health Organization (WHO)'s Drinking Water Quality Indicators (2005 year, the third edition) regulates that TCE and PCE in drinking water are not more than 0.02 mg/L and 0.04 mg/L, respectively. US EPA regulates that Maximum Contaminant Levels (MCL) of both of TCE and PCE are 5 μg/L and Superfund sites polluted by TCE amount to 336 [11]. According to the survey of shallow underground water of cities, the maximum concentrations of TCE and PCE are as high as 6000 μg/L and 200 μg/L separately [12]. PCE has become one of five kinds of the most widely distributed pollutants in the groundwater [13, 14]. 61% leach liquor samples of the toxic waste collected from 1984 to 1991 year in America were detected to contain PCE [15]. Tap Water Quality Standards promulgated in Japan regulates that the maximum concentrations of TCE and PCE are 0.03 mg/L and 0.01 mg/L separately. According to the research conducted by environmental protection bureau, a wide range of groundwater was polluted by TCE, and that amount of groundwater was polluted by high concentration of TCE and the number of polluted wells was still increasing, especially in Morioka which had a population of 300000. In Morioka, 15% tap water come from polluted groundwater [16]. After testing 5900 water samples in Japan nationwide, we found that PCE concentrations of 2.3% samples did not reach the standards of drinking water [17]. Standards for Drinking Water Quality (GB 5749—2006) promulgated in China regulates that the maximum concentrations of TCE and PCE are 0.07 mg/L and 0.04 mg/L separately. An investigation on groundwater of a city in north China indicates that TCE exceed ratio and concentration are both the highest, followed by PCE. The maximum TCE concentration reaches 1000 μg/L, 200 times higher than the standard of US EPA, with the exceed ratio 44.4% [18]. Another investigation of organic pollution in shallow groundwater of north China indicates that local areas are seriously polluted by CAHs, and the pollution of TCE and PCE is much more serious than trichloromethane (CF) and tetrachloromethane (CT). In this investigation, TCE and PCE are the main pollutants and the highest concentrations are 487.55 μg/L and 63.74 μg/L, respectively [19].

TCE is volatile organic compounds (VOCs), and it is denser and less viscous than water resulting in rapid rates of subsurface migration and eventually in the formation of non-aqueous phase liquid (NAPL) [20], which can be extremely difficult to remediate due to their inaccessibility and insolubility, potentially leading to long term contamination of aquifers. TCE and its degradation products, dichloroethylene (DCEs) and vinyl chloride (VC), are toxic carcinogenic substances, posing a great threat to human health [21]. PCE usually exists in the forms of immiscible residual liquid, dissolved phase, gas phase or adsorbed phase in vadose zone and underground water [22]. PCE gathers near the water table first, and the height provides enough pressure to overcome capillary forces at the oil-water interface and force the PCE to move downwards. Finally, PCE moves through the entire aquifer, and collects at the bottom of the aquifer or in low areas [23], leading to long term contamination [24].

With the development of relevant industries, TCE and PCE contamination will aggravate, and the contradiction between drinking water security and industrial developments will be more acute. Therefore, in order to secure water quality, it is urgent to know and control transformation rules of TCE/PCE in water treatment and conveyance processes, and it is necessary to construct TCE/PCE degradation system by advanced technology.

2. Growth-ring in water distribution network

Water distribution network is an important part of water supply system. Treated water is transported to consumers through huge complex network. Water distribution pipelines runs for years, and irregular annular mixture, “growth-ring”, forms gradually along the inner wall of pipeline [25, 26]. It is the mixture of deposits, corrosions, slimes and biofilms [27-29]. Water flows through pipelines for tens of
or even hundreds of kilometers, and the residence time can reach as high as several hours or even several days. In the process of transportation, water contacts with growth-ring. If water is polluted during the transportation, it will lead to water deterioration and a secondary pollution occurs. Therefore, the effect of growth-ring on water quality draws more and more attention.

In the early stage of the formation, “growth-ring” is loose, so it is easily washed away. When flow direction or flow rate of water suddenly changes, sediments are stripped from pipe wall, impacting water quality of consumers. Sediments stay on pipe wall deposit and harden gradually, providing a haven for bacteria. The formation mechanism of “growth-ring” is complicated, including physical deposition, electrochemical corrosion, influences of chemical and biological stability. Besides, for metallic pipe, ferrous iron forms under the function of iron bacteria and sulfate-reducing bacteria; after further oxidation, metallic pipes release ferric iron, and its volume is hundreds of times larger than before, blocking pipelines and leading to microbial corrosion. Micro-flocs of aluminum salt and Fe/Mn oxides and hydroxides attach to pipe surfaces, and a slime layer forms, providing protection for bacteria and they can regrow and reproduce. Accompany with the reproduction of iron bacteria, electrochemical corrosion occurs, leading to formation of rust tumor. In the process, impurities in water continuously adhere to the inner wall of pipes. “Growth-ring” is formed along the inner wall of pipes with time and the “growth-ring” has a thicker bottom and a thinner roof [30].

3. Analysis of growth-ring components and microbial species

Scholars make a research on the composition of corrosion products and microbial species of water supply pipelines [31-33].

Yuan Y X and Li Xin et al tested and analyzed growth-ring in cast iron pipes of actual water supply network. The results showed that growth-ring had a large surface area, which is up to 41.35~132.3 m²/g. The main components of growth-ring included Fe, O, S and Si. Besides, it also contained Mg, Al, P, Cl, Ca, Mn and K etc.. Growth-ring existed mainly in the form of goethite (α-FeOOH), lepidocrocite (γ-FeOOH) and FeS, and Fe existed mainly in the form of ferrous iron and ferric iron. Escherichia coli, iron bacteria and sulfate-reducing bacteria were also detected in growth-ring [34].

Wu J J and Jiang W C et al investigated growth-ring in grey cast iron pipes and steel pipes without coating in the actual pipelines of a mountainous city. The results showed that tuberculations of grey cast iron pipes and steel pipes had similar chemical compositions, mainly Fe and O, followed by C, Al, Si, Cl, Ca, S, Mn, P and K etc.. The main component of tuberculations was iron oxide. Corrosion products of cast iron pipe mainly contained α-FeOOH, Fe₃O₄, γ-FeOOH, γ-Fe₂O₃ and a little Fe(OH). The surface layer of corrosion products of steel pipes mainly contained CaCO₃, α-FeOOH and Fe₂O₄. The hard crust mainly contained α-FeOOH, Fe₃O₄, γ-FeOOH and γ-Fe₂O₃. The kernel layer mainly contained α-FeOOH, γ-Fe₂O₃ and γ-FeOOH [31, 35].

Zhang X Y, Yuan Y X and Li X investigated growth-ring in cast iron pipes of actual water supply network. The results showed that the main elements of growth ring are O and Fe, followed by organic functional groups and a little Si, C and S. The main components of growth-ring were goethite, lepidocrocite and FeS. Isolated bacteria included bacillus, Escherichia coli, Enterococcus faecalis, paenibacillus elgii, pseudomonas and mycobacterium [36].

Devet et al investigated bacteria diversity in underground water and filtered water. The results showed that similar to Cenarchaeum and Nitrosopumilus, ancient nitrifying bacteria largely existed in nitrated filtered water. Grenathrix polyspora, iron oxidizing bacteria, existed in groundwater which contained carbon dioxide [37]. The corrosion process of iron release process is shown in figure 1.

Li Y Q, Yuan Yi X, et al investigated biofilm community structure and biodiversity in PE, stainless steel and cast iron pipes. They got 59 strains of bacteria and found that bacillus accounted for a large proportion. They identified 47 strains of bacteria successfully, which belonged to 18 genera and 13 families, and Sphingobium, appeared most frequently. The degree of biological diversity of cast iron pipes was the highest and the bacteria in cast iron belonged to 14 genera. The bacteria in stainless steel pipes and PE belonged to 7 and 3 genera respectively. Bacteria genera isolated from those three pipes were largely different and the only genus those three kinds of pipes shared was only
Sphingomonas [38].

![Diagram](image)

**Figure 1.** Picture of corrosion process of iron release process.

Yu J X, et al investigated bacteria on biofilm in actual water supply network and got 7 strains of bacteria including Micrococcus roseus, Micrococcus uarians, white bacillus pumilus, Brevibacterium linens, arthrobacter flavescent, Microbacterium lactium and Alkalophilic Bacillus [39]. Bai X H, et al investigated biofilm in a main pipeline of actual water supply network and the relevant adjusting valve wall. The results showed that Bacillus accounted for a large part of microorganisms in pipelines. In addition, they got actinomycetes and fungus [40]. Liu X L, Liu W J, et al investigated biofilm in cement-lined steel pipes and steel pipes of actual water supply network in Beijing. They found five kinds of bacteria including Bacillus cereus, pseudomonas, Bacillus thuringiensis, Acinetobacter haemolyticus and uncultured bacteria [41]. Zhang X Y, Liu W J et al. investigated biofilm in cement-lined steel pipes and steel pipes of actual water supply network and detected 15 species of bacteria, 1 species of Streptomyces, 4 species of fungi and 1 species of yeast. Gram-positive aerobic bacillus accounted for a large part of bacteria, and Gram-negative bacteria and cocci accounted for a small part [42]. Li Jun, Zhao Xin hua et al. investigated biofilm in simulated network and they got 32 strains of bacteria belonging to 10 genera including Pseudomonas, Chryseobacterium, Xanthomonas, Bordetella, Stenotrophomonas, Burkholderia cepacia, Chromobacterium, Aeromonas and non-fermenting bacteria [43]. Other researchers also have similar results [44-46].

4. Degradation mechanism of chlorinated hydrocarbon

It is thus obvious that iron is the main element in growth-ring. Iron is active metal and has reducing capacity. So iron can displace metals which rank behind iron in Metal Active Order Form and the reduced metals deposit on the surface of iron. Iron can also reduce ions, compounds and some organics with strong oxidability. Fe²⁺ has reducing capacity, too. Fe³⁺ can be oxidized to Fe⁴⁺ when
oxidizing agent exists in water. When cast/pure iron with impurities is mixed with carbon particles in water, countless tiny primary cells will be formed between iron and carbon or other elements. When the solution is alkaline and oxygen exists, Fe$^{2+}$ and Fe$^{3+}$ can be transformed into flocculent precipitates, Fe(OH)$_2$ and Fe(OH)$_3$, respectively. Fe(OH)$_3$ may also hydrolyze, generating Fe(OH)$_2^+$, Fe(OH)$_3^2-$ and other complex ions. Those complex ions have strong flocculation performance. It is thus obvious that zero-valent iron can remove pollutants through reduction, microelectrolysis, coagulation and adsorption and combined effect [47]. Research shows that under the condition of normal temperature and pressure, zero-valent iron can reduce a variety of chlorinated organic compounds [47, 48]. After a number of studies, Gillham et al. found that zero-valent iron can dechlorinate TCE quickly.

There are three ways for TCE dechlorination: ① the metal react directly, that is, the electron on the surface of zero-valent iron is transferred to chlorinated hydrocarbon: Fe+RCl$\rightarrow$RH+Fe$^{2+}$+Cl$^-$; ② ferrous iron, the direct product of iron corrosion has reducing capacity, and it can dechlorinate a part of chlorinated hydrocarbon. But this reaction proceeds very slowly; ③ hydrogen produced by the reaction of iron can reduce chlorinated hydrocarbon. Under anaerobic condition, H$_2$O can act as electron acceptor, and the following reactions occur: 2H$_2$O$\rightarrow$H$_2$+2OH$, Fe+2H$_2$O$\rightarrow$Fe$^{2+}$+H$_2$+2OH, thus H$_2$+RCl$\rightarrow$RH$+$H$^+$+Cl$^-$. Among the reactions, the most important reaction is the first one [49, 50]. With suitable catalysts, all of the three ways are effective. The catalysts can be provided by surface of iron, impurities in iron and other solid phases in system [47].

Other researchers found that Fe/FeS nanoparticles were able to remove TCE in water quickly [51]. There are mainly two kinds of bacteria that are capable of reductive dechlorination. The one is a strain such as dehalobacter restrictus, dehalosporillum multivorans etc. that can transform PCE and TCE into dichloroethylene (DCE). The other one is a strain that can continually transform DCE and vinyl chloride (VC) into ethylene(ETH). Indigenous microorganisms that can degrade TCE include Sphaerotilus natans and Crenothrix of iron bacteria, Thiothrix in Filamentous sulfur bacteria, Rhodococcus TA1, Pseudomonas putida TA2 and Nocardia AR1, two kinds of microorganisms: P.putida DC1 and Onion pseudomonas genus GR3 [1, 21, 52].

5. Research status of Fenton-like

Similar to the traditional Fenton reagent, “Fenton-like reagent” consists of H$_2$O$_2$ and Fe$^{3+}$ salt solution, soluble iron or iron oxide minerals such as goethite, lepidocrocite, magnetite, pyrrhotite, hematite, siderite etc. [53-55]. In the system, H$_2$O$_2$ is catalyzed and decomposed into HO$,^-$ then degrade organic compound [56].

Fenton-like reaction equations are as follows:

\[
\begin{align*}
\text{Fe}^{2+}+\text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+}+\text{OH}^-+\text{OH}^+ \\
\text{Fe}^{3+}+\text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+}+\text{HO}_2^-+\text{H}^+ \\
\text{HO}^-+\text{Fe}^{3+} & \rightarrow \text{Fe}^{3+}+\text{OH}^- \\
\text{Fe}^{3+}+\text{HO}_2^- & \rightarrow \text{Fe}^{2+}+\text{O}_2+\text{H}^+ \\
\text{HO}^-+\text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^-+\text{H}_2\text{O} \\
\end{align*}
\]

The mechanism of the degradation of TCE under the catalysis of siderite, hematite and magnetite is that hydrogen peroxide produces OH under the catalysis of ferrous iron and produces HO$^-$, O$_2$, O$^-$ under the catalysis of ferric iron. The OH is added to the TCE double bond. And the chlorine of the TCE molecule are nucleophilic substituted by the O$_2$ and O$^-$, resulting in the final conversion of TCE to CO$_2$, H$_2$O and release Cl$^-$ [54].

In the case of siderite-catalyzed TCE degradation, the specific reaction equation are as follows:

\[
\begin{align*}
\text{OH}^-+\text{CCl}_3=\text{CCH}_2\rightarrow \text{CCl}_2\text{OH}=\text{CCH}_2\text{OH} \\
2\text{OH}^-+\text{CCl}_2\text{OH}=\text{CCH}_2\text{OH} \rightarrow \text{HOCCl}_2\text{OH}+\text{HOCCl}_2\text{OH} \\
\end{align*}
\]
OH + CC1₂OH-CC1HOH→ HOCC1OH-CC1HOH+Cl-
HOCC1OH→ O=CC1₂+H₂O
HOCC1HOH→ O=CHCl+H₂O
O=CC1₂+O₂→O=CC1-O-O-+Cl-
O=CHCl+O₂→O=CHO-O-+Cl-
O=CC1-O-O-+O-→CO₂+Cl⁻+O₂
O=CHO-O-+O-→O=CHO+O₂
O=CHO+HO→O=C=O(CO₂)+H₂O

Soil and aquifer systems contain plenty of natural iron minerals so that they can be used in Fenton-like reaction directly. Therefore, compared with traditional "Fenton oxidation", the advantage of "Fenton-like oxidation" is that it can effectively repair the areas polluted by TCE without additional catalyst. What’s more, “Fenton-like oxidation” can be used in a wide range of pH [53]. So in recent years, “Fenton-like oxidation” has been gradually used in soil and groundwater pollution control and repair and it has become a hot topic around the world.

In 2012, Oliveirat al. first used pipe deposits from water networks as catalysts in paraquat peroxidation to degrade the pesticide paraquat in water. The samples used as catalysts in the oxidation studies were taken from real drinking water distribution systems. The deposits were removed from old cast iron pipes that needed to be substituted. The results revealed that the deposits exhibit good catalytic performance in the pesticide degradation and mineralization. Oliveirat al. also pointed that, depending on the types of solids present in a given water network, in situ treatment can be made without insertion of chemicals apart from the oxidant, in case of a contamination event [57].

In 2013, based on the similar principle, Gosselin et al. investigated drinking water and biofilm disinfection by Fenton-like reaction which was conducted with Fenton’s reagent (H₂O₂) at pH 3 or 5 on autochthonous drinking water biofilms grown on corroded or non-corroded pipe material. These new results provide additional support for the use of Fenton’s processes for cleaning drinking water distribution systems contaminated with biological agents or organics. Gosselin et al. also pointed that Fenton-like reagent is a promising alternative to conventional water disinfection treatment and should be extended to surface disinfection and biofilm inactivation [58].

6. Conclusions and outlook
So water distribution network is a complex system. The growth-ring in pipelines consists of elements such as Fe, O, C, S etc. The main compositions of growth-ring include α-FeOOH, γ-FeOOH, γ-Fe₂O₃, Fe₃O₄, a small amount of Fe(OH)₃ and FeS etc. There are also microorganisms including iron bacteria, sulfate reducing bacteria, Sphingobium, Microbacterium, Micrococcus, Bacillus, Pseudomonas etc. Growth-ring has strong adsorption capacity because of its large specific surface area and pore structure. The surface area changes with the existing forms, causing its adsorption capacity changes. In addition, the structure of growth-ring is loose especially in the early stage of growth-ring formation so that sediments will be stripped off from the tube wall when the flow direction or flow rate suddenly changes, releasing certain elements and changing the composition of water. The main components of growth-ring and indigenous microorganisms in growth-ring can react with TCE and PCE directly or indirectly. Therefore, in the complex system, comprehensive reactions between TCE/PCE and growth-ring/biofilm will occur during water transmission including absorption, desorption, flocculation, migration, transformation, reduction etc. As a result, TCE/PCE levels changes. What’s more, incomplete degradation product of TCE/PCE such as DCE and VC could be produced which is toxic carcinogenic substance and has a great threat to human health.

Researches on TCE/PCE are concentrated in: rapid and effective removal methods of chlorinated hydrocarbons in soil and groundwater; removal efficiency and influence factors of the methods;
development of the system for removing TCE/PCE and preparation of raw materials; degradation mechanism, degradation kinetics and product analysis of TCE/PCE; migration and transformation of TCE/PCE in soil and water. However, little is known about TCE/PCE migration and transformation mechanisms and removal methods in water distribution network.

After purification, the water polluted by TCE/PCE can reach the standards of drinking water (GB5749-2006). However, water with trace amounts of TCE/PCE is still harmful to human health (US. EPA.). Long-term drinking or contacting with the water may cause cancer [59-62]. Therefore, it is vital to know migration and transformation mechanisms of TCE/PCE in water distribution network. In addition, based on the results of Oliveira et al and Gosselin et al the main components of growth-ring can act as catalysts in Fenton-like reagent (H2O2). Then chlorinated hydrocarbons could be degraded by Fenton-like reagent, and the potential safety hazards of TCE/PCE in the water distribution network could be solved.

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