

Article

Study on the Inactivation of *Pseudomonas* sp and the Degradation of Trichloroethylene by Fenton-Like Reaction

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Abstract: The present work intended to use goethite, one of the main compositions of pipe deposit, to combine with H_2O_2 to degrade TCE or disinfect drinking water. Goethite exhibited excellent degradation performance for TCE, outstanding inactivation ability for *Pseudomonas* and the disinfection effect for filter water of water treatment plants. The TCE degradation efficiency could reach 87.4%, while the inactivation efficiency of *Pseudomonas* and the bacterial mortality rate in filtered water were more than 99.9% in this study. In order to effectively reduce the disinfection by-products (chlorine-resistant bacteria) and conduct permanent disinfection, the Fenton-like and chlorine combined disinfection method was also investigated. Experimental results indicated that the bacteria could be effectively killed by this combined method and the chlorine residual was 0.41 mg/L, ensuring sustainable disinfection. This work verified that the pipe deposit from the water distribution network is multifunctional, which is a potential candidate for pollutant removal and sterilization. The results could also offer theoretical support for water quality security in water distribution networks in the future.

Keywords: water distribution network; growth ring; Fenton-like; disinfection; trichloroethylene

1. Introduction

The water distribution network (WDN) is vital for transporting safe, clean and ideal drinking water. However, these networks are huge, complex and can be influenced by nature and operational conditions. The microbial communities in WDN also vary [1]. Microorganism contamination of WDN could damage the water services and the safe use of drinking water. It is also harmful to the human body [2]. Disinfection is an essential step to protect people from waterborne diseases [3]. At present, the addition of chlorine-containing disinfectant and maintaining a certain amount of chlorine residual is the most common method for controlling the regrowth of bacteria in WDN [4]. However, some bacteria still survive even under the condition of a high chlorine residual level. These bacteria can form biofilm on the wall of the network, which is a source of microbial contamination, and slowly release microorganisms into the WDN, posing a serious threat to human health. And when the water quality and hydraulic conditions change, the biofilm may fall off and enter the water resulting in pollution. In addition, exfoliated biofilm can accelerate the corrosion of growth ring and form red water, causing deterioration of water's smell and taste [5,6].

In recent years, volatile organic compounds (VOCs) have become dangerous to the environment and human health, including alcohols, mercaptans, ketones, and halogenated hydrocarbons [7]. Trichloroethylene (TCE) is widely used as a cleaning and degreasing agent in industries. TCE is

considered one of the most toxic and carcinogenic VOCs, and it has been easily found in the waste byproducts of chemical processes, dumping grounds, the indoor air and even in groundwater remediation sites [8]. The removal of TCE has been an urgent problem to explore. Several methods have been used to reduce VOCs, including TCE, such as combustion [9], adsorption [10], advanced oxidation processes [11] and biological methods [12].

Advanced oxidation processes (AOPs) is an effective way for water purification and recovery [13–17]. The Fenton reaction is an effective, inexpensive and environmentally friendly method to degrade pollutants [18–20]. In 2012, Oliveira et al. successfully used pipe deposits from water networks as novel catalysts to remove the pesticide paraquat in water by Fenton reaction [21]. In 2013, Gosselin et al. added H_2O_2 into the actual pipe network, and the corrosive growth ring combined with H_2O_2 to form Fenton-like system for the disinfection of drinking water and biofilm, and it has achieved a good disinfection effect. Gosselin et al. believed that the Fenton-like reaction is a promising alternative disinfection method [2]. However, very few studies simultaneously focus on the pollutant degradation and the disinfection of drinking water.

In this study, we analyzed the actual pipe growth ring and prepared one main composition of the actual pipe growth ring and characterized it by X-ray diffraction (XRD), X-ray fluorescence (XRF), Automatic Specific Surface Area and Porosity Analyzer (BET) and so on. These results demonstrated that the main composition of the pipe growth ring, goethite, could be used as a catalyst in active H_2O_2 to produce $\bullet\text{OH}$ radical. The ability of goethite to facilitate the Fenton-like oxidation of TCE and bacteria inactivation were tested under varying conditions. The Fenton-like and chlorine combined disinfection method and the related mechanism were also discussed.

2. Materials and Methods

2.1. Preparation of Goethite

According to the alkaline precipitation method [22], the prepared process of goethite ($\alpha\text{-FeOOH}$) was as follows: First, 1 mol/L KOH (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was added dropwise to $\text{Fe}(\text{NO}_3)_3$ (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) solution (20 mL, 1 mol/L), and was stirred with a magnetic stirrer until the pH reached 7. Then, the mixed solution was centrifuged (4000 r/min, 4 min; Eppendorf, Shanghai, China) to obtain goethite, and the goethite was washed several times with deionized water. Finally, the prepared goethite was dissolved into a certain amount of deionized water and dried in a drying oven at 333 K for 12 h. The goethite crystal was ground uniformly and preserved for next use.

2.2. TCE Degradation Experiments by Fenton-Like Reaction

50 mL deionized water, 50 μL TCE, 3.33 g/L goethite and 11.5 g/L H_2O_2 were added into a 100 mL beaker, which formed a Fenton-like system. The residual TCE at different times was measured by using the gas chromatography-headspace sampling method. In order to study the degradation efficiencies at different conditions, adjusted pH, changed goethite dosage and H_2O_2 concentration were used. 25 mL methanol was used to terminate the Fenton-like reaction for better TCE concentration detection. All the catalytic degradation experiments were conducted in triplicate.

2.3. Microbiology Experiments

2.3.1. Microbial Enrichment Culture

The microorganism culture operation steps were as follows: (1) the contained bacteria samples were cultivated by the streak plate method (303 K, 24 h) and the target colonies were selected; (2) the target colonies were inoculated into the R2A liquid medium, which has been sterilized at high temperature; (3) the conical flask containing the culture medium was shaken into an oscillation

incubator for fostering (303 K, 5–7 days); (4) a small amount of the liquid medium was taken and cultured by the streak method (303 K, 24 h).

2.3.2. Bacterial Counting Method

The method for counting bacteria in the microbiology experiment was the flat colony counting method. The specific steps were as follows: (1) sample dilution: Dilute the bacterial sample until the bacterial concentration was about 105 CFU/L (CFU, Colony-Forming Units); (2) bacterial inoculation: Use a pipette to draw a certain amount of bacterial dilution into the plate, and then coat it evenly with a coating bar; (3) constant temperature culture: Place the plate in a 303 K constant temperature incubator and incubate for 2–3 days; (4) colony count: Observe the growth of bacterial colonies in the plate and calculate the number.

2.3.3. Sterilization Experiments by Fenton-Like Reaction

The bacteria were inoculated into an Erlenmeyer flask containing about 40 mL of R2A liquid medium using an inoculating loop. The conical flask was placed in a constant temperature shaking incubator and cultured at 303 K for 3–4 days. The culture was dealt with using a high-speed centrifuge (5000 r/min, 5 min). Then the supernatant was removed, followed by washing the precipitate three times with a phosphate buffer solution (pH = 7.2). Finally, it was diluted to the required concentration for the next experiment.

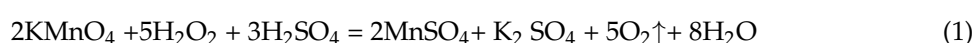
The sterilization experiments were performed in a dark test tube. A certain amount of above-prepared bacterial suspension, goethite and H₂O₂ (Shanghai Aladdin Bio-Chem Technology Co., LTD, Shanghai, China) were added into the test tube. 1 mL reaction solution was quenched by 9 mL, 1.5% Na₂S₂O₃ (Tianjin Guangfu Technology Development Co., Ltd., Tianjin, China). The mixed solution was diluted several times, then 0.5 mL sample was inoculated into R2A solid medium, inverted, and incubated at 303 K for 48 h. The colonies in the culture dish were counted, then positive control experiments and parallel experiments conducted. The experimental sample was cultured at 303 K for 48 h in a constant temperature incubator. The obtained data by counting were the final result of the experiment. Experimental procedures for disinfection of filtered water by Fenton-like reaction were similar to the abovementioned processes.

2.4. The Fenton-Like and Chlorine Combined Disinfection Method

90 mL filtered water added into a dark conical flask, then a certain amount of goethite and H₂O₂ solution was added. In order to terminate the reaction, 1 mL reaction solution mixed with 9 mL, 1.5% Na₂S₂O₃. 0.5 mg/L chlorine was put into the above system and repeated with a quenching operation. The Fenton-like and chlorine disinfection mixture was diluted several times. 0.5 mL sample mixture was pipetted, inoculated into R2A solid medium, inverted, incubated at 303 K for 48 h. The colony growth was observed and the number calculated.

2.5. Determination Method of H₂O₂ Concentration

10 mL H₂O₂ transferred into a 50 mL Erlenmeyer flask, then added 10 mL of 20.0% H₂SO₄ (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China). Titrating with KMnO₄ (C_{KMnO4} = 0.1 mol/L, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) standard solution until the solution was light pink and kept at 30 s. According to the equation to calculate the concentration of H₂O₂, the equation was as the following [23]:



$$C_{\text{H}_2\text{O}_2} = 0.025V_{\text{KMnO}_4}$$

C_{H₂O₂}—the concentration of H₂O₂, mol/L

V_{KMnO4}—used KMnO₄ volume, mL

2.6. Characterization

The crystal structures of the pipe growth ring and goethite were obtained by X-ray diffraction (XRD (Rigaku Corporation, Japan) Rigaku D/max-RB with Ni-filtered Cu K α radiation ($\lambda = 1.54056$)). The BET method was used to calculate the specific surface area. The pore-size distribution was measured by using ASAP 2020M analyzer (Micromeritics Instrument Corp, Beijing, China). The type and content of each element in growth ring were confirmed by X-ray fluorescence spectrometer (XRF, AXIOS-PW4400, PANalytical B.V. Beijing, China). TCE concentration was detected by Gas chromatography (Agilent 6890, Agilent Technologies Inc., Shanghai, China).

3. Results and Discussions

3.1. Characterization of the Actual Growth Ring And Goethite

3.1.1. Composition Analysis of the Growth Ring of WDN

A section of pipe was taken, which was from an actual WDN in a certain city in Heilongjiang Province. The pipe growth ring was stripped. The compositions of the pipe growth ring were analyzed through the following methods. The specific conditions of the pipe: Cast iron pipe, the pipe age was 20 years, and the disinfectant was chlorine dioxide.

The major compositions of the stripped growth ring were detected by XRD. Figure 1a was the relevant spectra. The main compositions were lepidocrocite (γ -FeOOH) and goethite (α -FeOOH), and their diffraction peaks were consistent with the previous published result [24]. The contents of lepidocrocite and goethite were 55.9% and 44.1%, respectively, closing to 1:1.

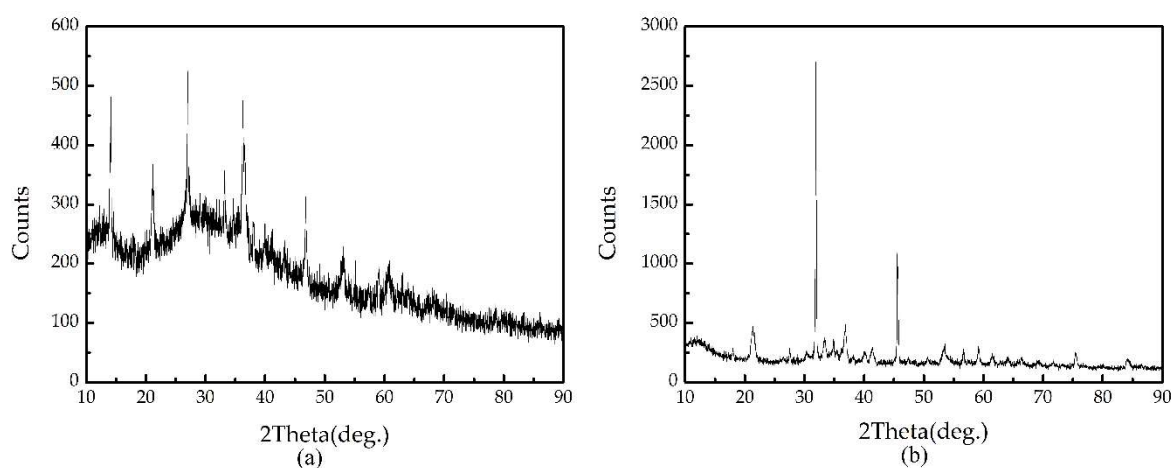


Figure 1. XRD patterns of (a) the actual pipe growth ring and (b) the prepared goethite.

The types and contents of each element contained in the pipe growth ring were determined by quantitative analysis and semi-quantitative analysis. According to Table 1, the elements and compounds in the growth ring accounted for 55.6% and 50.4%, respectively, closing to 1:1. The main chemical elements in the growth ring were Fe and O, in which the proportions are 24.0% and 29.3% of the total weight of the growth ring, respectively. It was verified that the main composition of the growth ring is iron oxide. There was a small amount of Si (1.2%) and Al (0.2%) in the growth ring. The main existent forms of Si and Al were SiO₂ and Al₂O₃. The main reason for the existence of SiO₂ might be that the water plant uses a sand filter, the fine particles and the SiO₂ in the soil can enter WDN to form a section of pipe growth ring. The reason for the existence of Al₂O₃ could be attributed to trace amounts of coagulant.

Table 1. The analysis result of XRF.

Analytical Element	Concentration (%)	Analytical Compound	Concentration (%)
O	29.320	-	-
Cl	0.042	-	-
Na	0.138	Na ₂ O	0.212
Mg	0.121	MgO	0.231
Al	0.224	Al ₂ O ₃	0.491
Si	1.211	SiO ₂	3.018
P	0.060	P ₂ O ₅	0.163
S	0.028	SO ₃	0.083
K	0.031	K ₂ O	0.044
Ca	0.212	CaO	0.358
Ti	0.057	TiO ₂	0.116
Mn	0.091	MnO	0.151
Fe	24.021	Fe ₂ O ₃	45.365
Zn	0.058	ZnO	0.103
Sum	55.614	Sum	50.335

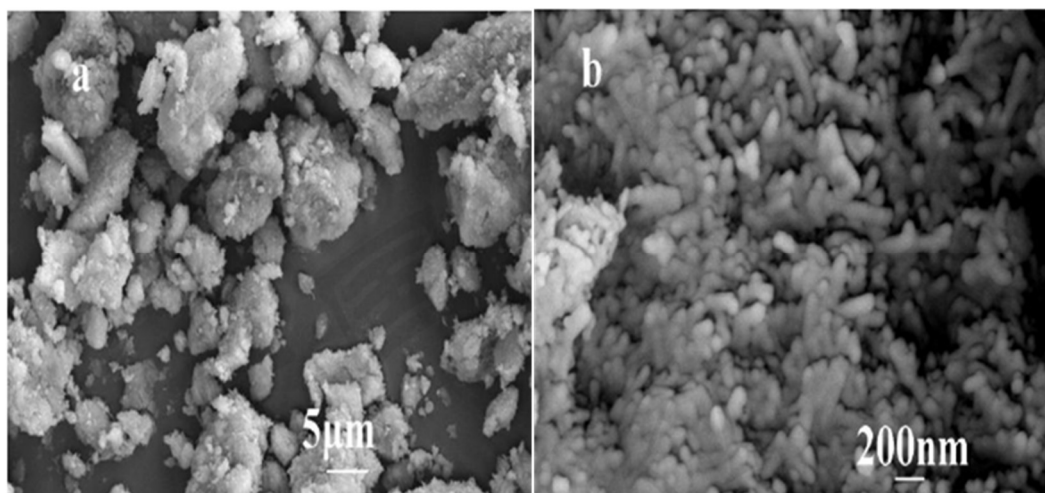
The catalytic activity of the catalyst is related to the active site on the surface of the catalyst. The amount of active site directly determines the catalytic activity. Specific surface area, pore volume and pore size of the growth ring were confirmed by the BET method. It can be seen that the growth ring has a large specific surface area, which led to its good catalytic capacity. The detailed data is shown in Table 2.

Table 2. Specific surface area, pore volume and pore size of the growth ring and goethite.

Samples	Specific Surface Area	Pore Volume	Pore Size
The growth ring	397.06 m ² /g	0.51 cm ³ /g	44.52 Å
Goethite	146.85 m ² /g	0.15 cm ³ /g	35.38 Å

3.1.2. Morphology Analysis of the Prepared Goethite

Scanning electron microscopy (SEM) was used to observe the prepared goethite morphology at different magnification, as shown in Figure 2a,b. Goethite showed a flocculent-like structure. This structure has a large specific surface area, which is beneficial for enriching pollutants.

**Figure 2.** SEM images of the prepared goethite, (a) 5 magnification, (b) 200 magnification.

3.1.3. Composition Analysis of the Prepared Goethite

The crystal form of the prepared goethite was analyzed by XRD, and the XRD spectrum was shown in Figure 1b. Compared the diffraction peaks with the standard card (JCPDS 29-0713) [24], it could be seen that the prepared goethite had good crystallinity, and its composition was indeed mainly goethite.

Table 2 summarized the results of the pore structure analysis of the prepared goethite. The specific surface area of the actual growth ring was much larger than the prepared goethite. This might be that the growth ring contains pipe rust, and the rust structure is loose and porous.

3.2. TCE Degradation by Fenton-Like Reaction

3.2.1. The Contrast of Removal Efficiency of TCE by Adsorption and Degradation

According to the previous research reports of our group [25], goethite has an adsorption capacity to pollutants. The removal efficiency of TCE by adsorption and Fenton-like degradation was 15.6% and 58.5%, respectively. The detailed conditions were shown in Figure 3. The removal efficiency of TCE by Fenton-like was almost four times as much as adsorption. After 100 min, adsorption reached saturation, but the Fenton-like degradation was still effective. The removal efficiency of TCE by Fenton-like was almost six times as much as adsorption after 480 min. Therefore, Fenton-like reaction was a more effective method to remove TCE.

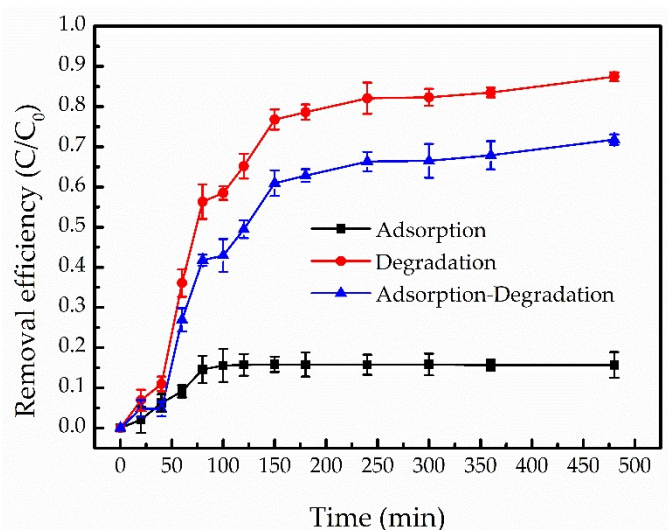


Figure 3. The contrast of adsorption and degradation. Reaction conditions: $[\text{H}_2\text{O}_2]_0 = 11.5 \text{ g/L}$, $[\text{Goethite}] = 3.33 \text{ g/L}$, $\text{pH} = 4$, $T = 293 \text{ K}$.

3.2.2. TCE Degradation by Fenton-Like Reaction under Different Conditions

1. Effect of the initial pH

pH is an important influencing factor of the Fenton reaction. The effect of pH was investigated at pH values at 3, 4 and 5 (Figure 4a). The degradation efficiency decreased with the pH increasing. This may be attributed to two reasons: Firstly, H_2O_2 is not stable with the pH increasing. Secondly, the leaching iron ions can gradually form iron hydroxide sludge, which reduces the production of $\bullet\text{OH}$ radical. The optimum pH for degradation TCE was 3.0, which was in agreement with the previous classical Fenton reaction studies [26,27].

2. Effect of the H_2O_2 concentration

The effect of H_2O_2 concentration on the degradation of TCE was shown in Figure 4b. When the dosage of H_2O_2 was in the range of 1.7–11.5 g/L, the removal efficiency of TCE increased gradually,

and the TCE removal efficiency could attain 91.3%. It could be seen that the dosage of H_2O_2 has a significant effect on the removal of TCE in water. However, when the concentration of H_2O_2 was 16.7 g/L, the removal efficiency went down. This was because the H_2O_2 concentration was increased to a certain extent, and the generated $\bullet\text{OH}$ cannot react with the TCE in time, which led to self-quenching of $\bullet\text{OH}$. And the inhibition of iron corrosion by H_2O_2 , which had the same effect [28,29].

3. Effect of the catalyst dosage

According to the previous study [25], the catalyst dosage was set at 1.67 g/L, 3.33 g/L and 6.67 g/L to study the effect of catalyst dosage on the TCE degradation, Figure 4c. As the catalyst dosage increased from 1.67 g/L to 3.33 g/L, the TCE removal efficiency increased from 28.75% to 95.9%, but when the catalyst dosage exceeded 6.67 g/L, the TCE removal efficiency was only 42.2%. More goethite could increase the total area of the solid-liquid contact surface, increase the enrichment rate of TCE and H_2O_2 , accelerate the decomposition rate of H_2O_2 and generate a large number of $\bullet\text{OH}$ radical, leading to a better degradation effect. However, excessive catalyst would consume $\bullet\text{OH}$, which was harmful to degrading TCE [30]. The decrease of degradation efficiency of TCE may be attributed to the agglomeration of catalyst and the $\bullet\text{OH}$ self-quenching or quenching of $\bullet\text{OH}$ by excess Fe^{2+} [28,31].

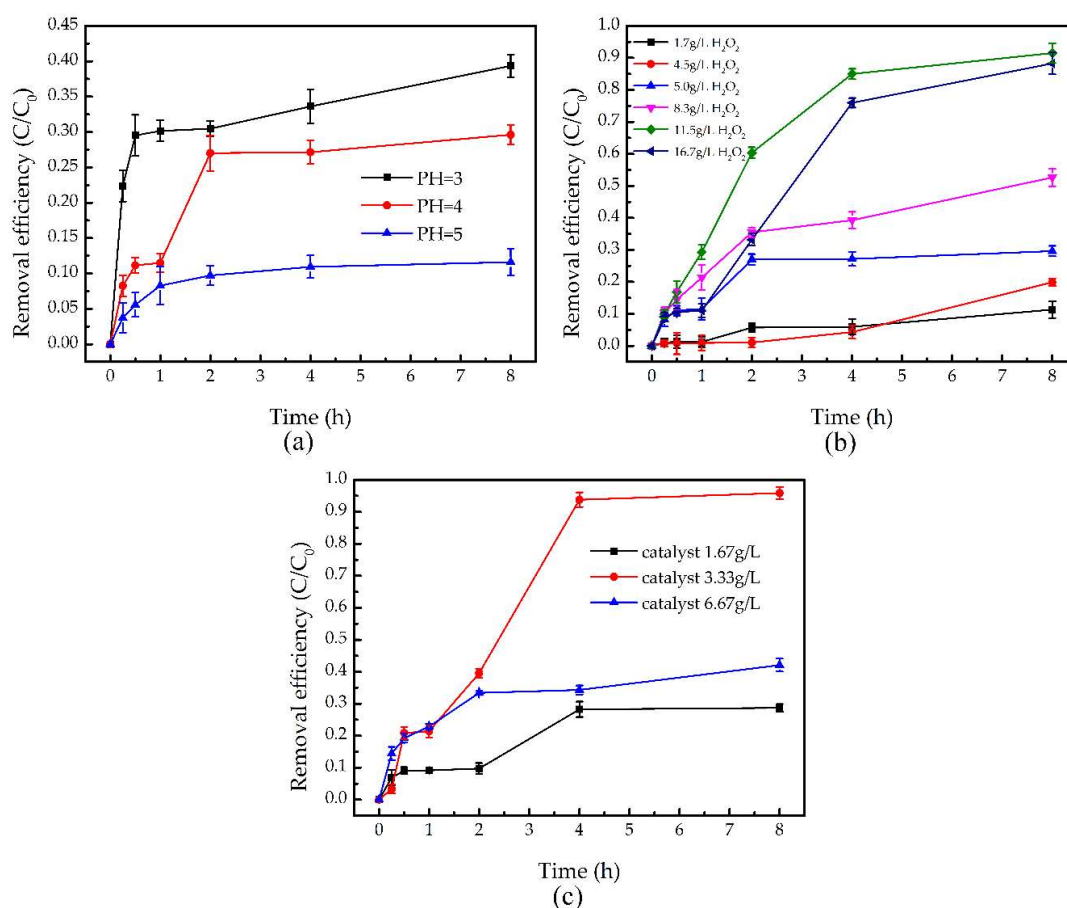


Figure 4. Effect of (a) the initial pH, (b) the H_2O_2 concentration and (c) the catalyst dosage on TCE degradation. Reaction conditions: (a) $[\text{TCE}]_0 = 1.46$ g/L, $[\text{Goethite}] = 3.33$ g/L, $[\text{H}_2\text{O}_2]_0 = 8$ g/L, $T = 293$ K; (b) $[\text{TCE}]_0 = 1.46$ g/L, $[\text{Goethite}] = 3.33$ g/L, $\text{pH} = 4$, $T = 293$ K; (c) $[\text{TCE}]_0 = 1.46$ g/L, $[\text{H}_2\text{O}_2]_0 = 8$ g/L, $\text{pH} = 4$, $T = 293$ K.

3.3. The Microorganism Identification Results of Filtered Water in a Water Plant

Six strains of bacteria were isolated from the filtered water of a water plant, and one of them failed to be identified, while the 16S rDNA sequences of the other five strains were obtained. The phylogenetic tree of related bacteria and comparison result were shown in Figure 5 and Table 3. The obtained microorganisms could be divided into two major categories. One major is γ -proteobacteria including 1-2, 1-5, they were all *Pseudomonas*. The other category included 1-1, 1-3, and 1-4. 1-1 belongs to the Bacteroides. 1-3 and 1-4 belong to Proteobacteria. According to Figure 5 and Table 4, the relative abundance of Proteobacteria was 80% when microorganisms were classified by phylum. The relative abundance of *Pseudomonas* was 40%.

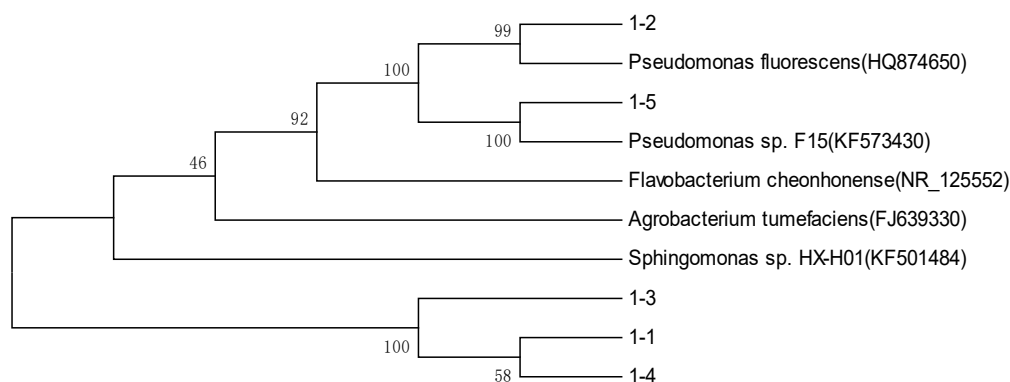


Figure 5. The phylogenetic tree of related bacteria.

Table 3. Comparison of bacteria isolated from filtered water in a water plant and related microorganisms.

No.	Sequence Length/bp	Related Bacteria Name	Related Strain Number	Similarity/%
1-1	1403	<i>Flavobacterium cheonhonense</i>	NR_125552	98
1-2	1438	<i>Pseudomonas fluorescens</i>	HQ874650	98
1-3	1452	<i>Sphingomonas sp. HX-H01</i>	KF501484	99
1-4	1418	<i>Agrobacterium tumefaciens</i>	FJ639330	99
1-5	1459	<i>Pseudomonas sp. F15</i>	KF573430	99

Table 4. Filtered water microorganisms.

No.	Phylum	Class	Order	Family	Genus
1-2	Proteobacteria	γ -proteobacteria	<i>Pseudomonas</i>	Pseudomonadaceae	<i>Pseudomonas</i>
1-5	Proteobacteria	γ -proteobacteria	<i>Pseudomonas</i>	Pseudomonadaceae	<i>Pseudomonas</i>

3.4. Inactivated *Pseudomonas* by Fenton-Like Reaction

The typical chlorine resistant bacteria, *Pseudomonas*, was separated from the water distribution network and studied *Pseudomonas*'s inactivated effect by Fenton-like reaction. According to the Figure 6, the rapid sterilization stage occurred at 0–60 min and the relative number of *Pseudomonas* declined from 1 to 0.867, the inactivation rate was 86.7%. The inactivation rate slowed down at 60–180 min because H_2O_2 was consumed. After 180 min, the inactivation rate attained 99.9%. This result indicated that Fenton-like reaction has outstanding effects on the *Pseudomonas* that are inactivated.

1. Effect of the catalyst dosage on *Pseudomonas* inactivated

The control variate method was used to study the effect of catalyst dosage on *Pseudomonas* that were inactivated. The catalyst dosage was 0.89, 4.45, 8.9 g/L (Figure 7a) and the concentration of H_2O_2 was 5 g/L. The inactivation rate of *Pseudomonas* increased with the increase of catalyst dosage, and the

inactivation time shortened. The increased inactivation efficiency may be attributed to introducing more active sites, which allow for producing more $\bullet\text{OH}$ radical that promotes the inactivation reaction.

2. Effect of H_2O_2 concentration on *Pseudomonas* inactivated

The effect of H_2O_2 on the inactivation rate of *Pseudomonas* was shown in Figure 7b. The inactivation rate of *Pseudomonas* in the Fenton-like system increased with the increase of H_2O_2 concentration. However, when the dosage exceeded a certain amount, the inactivated effect gone down. Because H_2O_2 concentration was over-high, the generated $\bullet\text{OH}$ radical cannot react with *Pseudomonas* in time which leads to a self-quenching of $\bullet\text{OH}$. At the rapid sterilization stage (0–90 min), *Pseudomonas* were rapidly killed, and the total number of bacteria decreased rapidly. 90–180 min was the slow sterilization stage, that because H_2O_2 was consumed. At same time, when the H_2O_2 was higher, the *Pseudomonas* inactivation rate was faster. The inactivation efficiency of *Pseudomonas* could reach 99.9% or more.

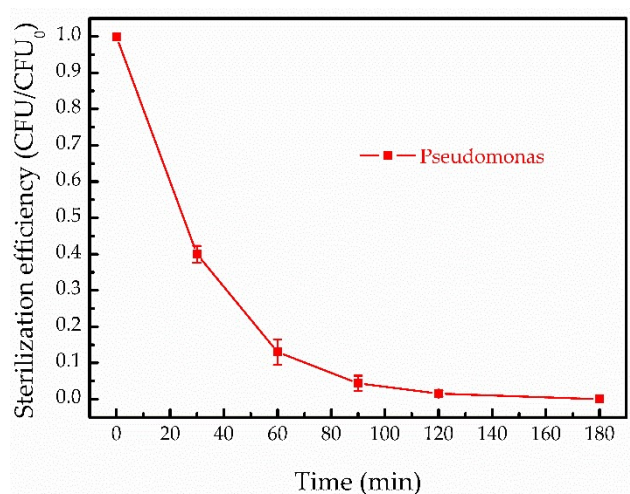


Figure 6. Inactivated effect of Fenton-like reaction on typical chlorine-resistant bacteria. Reaction conditions: $[\text{Goethite}] = 0.89 \text{ g/L}$; $[\text{H}_2\text{O}_2]_0 = 0.50 \text{ g/L}$.

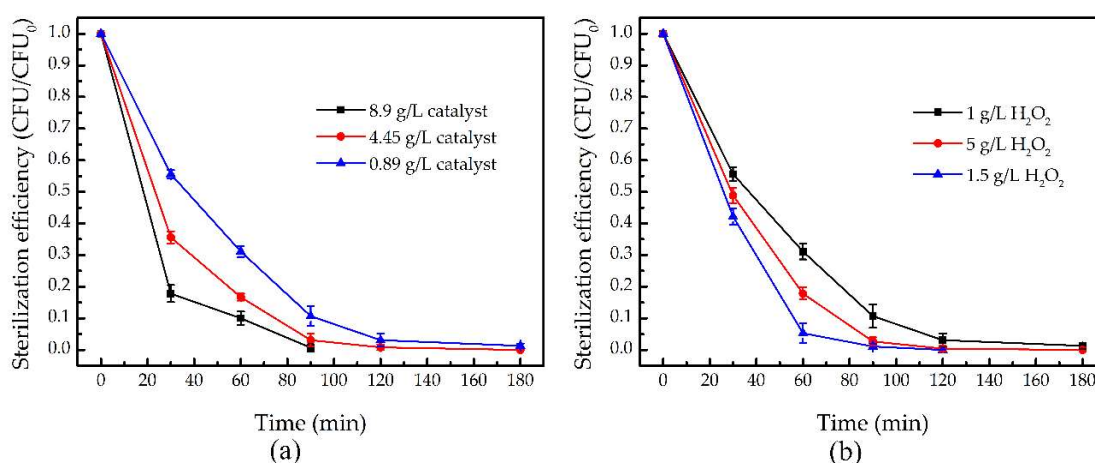


Figure 7. Effect of (a) the catalyst dosage and (b) the H_2O_2 concentration on *Pseudomonas* inactivated. Reaction conditions: (a) $[\text{H}_2\text{O}_2]_0 = 5 \text{ g/L}$; (b) $[\text{Goethite}] = 0.89 \text{ g/L}$.

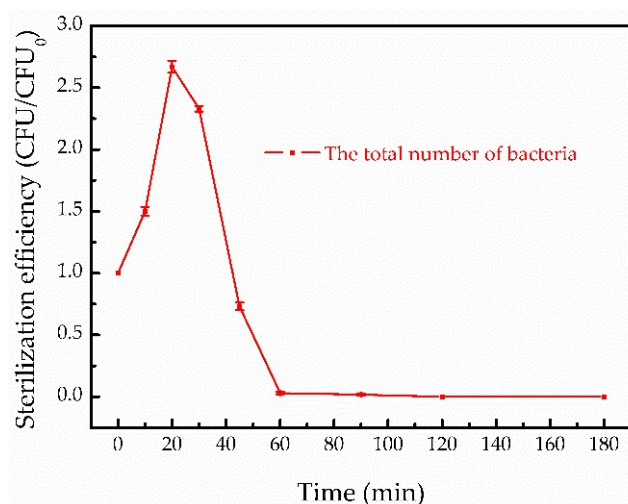
3.5. Study on Bacteria Inactivation in Filtered Water by Fenton-Like Method

Actual water quality after filtration was shown at Table 5.

Table 5. Actual water quality after filtration.

Temperature (K)	Turbidity (NTU)	pH	NH ⁴⁺ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	TOC (mg/L)	Total Iron (mg/L)	Total Alkalinity (CaCO ₃ , mg/L)
302	0.51	6.83	0.17	8.36	3.49	2.12	0.16	22.3

Disinfection experiments were carried out by adding goethite and H₂O₂ into the actual filtered water. The experimental results were shown in Figure 8. The total number of bacteria increased rapidly at the initial 20 min, and the relative bacteria total number increased from 1 to 2.67. Because the main catalytic species was Fe³⁺, while the catalytic efficiency of Fe³⁺ to H₂O₂ was low, this resulted in producing less •OH radical. The bacteria had adapted to the environment to enter the logarithmic growth period, so the total number of bacteria had increased at the beginning of the reaction. 20–60 min was the rapid sterilization stage, the total number of bacteria decreased rapidly, and the total number of bacteria decreased to 0 at 60 min. This result illustrated that the Fenton-like reaction has a good disinfection effect on actual filtered water, and the bacteria inactivation rate was over 99.9% [32].

**Figure 8.** Fenton-like system for disinfection of filtered water.

3.6. Fenton-Like and Chlorine Combined Disinfection Method

Due to •OH being easily quenched, the Fenton-like disinfection method does not have the continuous disinfection characteristic. A new method is proposed, which puts the Fenton-like reaction and chlorine disinfection together. According to Figure 9, The total number of bacteria increased rapidly at the beginning, because only Fe³⁺ was present in the solution at the initial stage, and ferric oxide was less efficient in catalyzing H₂O₂. The transition of Fe³⁺ into Fe²⁺ was the control step, resulting in the amount of generated •OH radical being smaller than the growth rate of bacteria. It was not enough to kill the bacteria, so the total number of bacteria increased. At 20–45 min, the relative total number of bacteria decreased rapidly from 1.15 to 0.03. Fe²⁺ irons appeared in the solution at the moment, which could catalyze H₂O₂ to decompose. A large number of •OH were generated, so the bacteria were quickly killed. At 45 min, •OH was consumed in a large amount, the sterilization rate of •OH was less than the rate of bacteria growth, and the total number of bacteria began to increase slowly. The total number of dead bacteria was very small through the Fenton-like system, so the total number of bacteria grew slowly. At 60 min, 0.5 mg/L chlorine was added into above sterilization reaction, and total bacteria rapidly decreased. At this stage, chlorine participated in the disinfection process. The total number of bacteria was 0 at 180 min, the bacteria were completely killed, and the chlorine residual in water was 0.41 mg/L. These results demonstrated that the Fenton-like and chlorine combined disinfection method could by continuous disinfection, reduce the disinfection by-products.

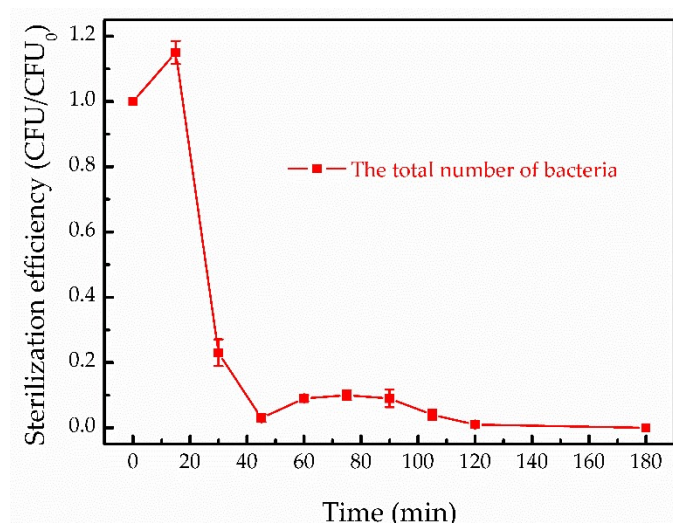


Figure 9. Fenton-like and chlorine combined disinfection experiment results.

3.7. The Disinfection Mechanism of Fenton-Like Reaction

H_2O_2 can destroy the barrier structure of bacteria and change the osmotic pressure and permeability of bacteria, which is conducive to the other substances entering the bacteria [33]. The $\bullet\text{OH}$ can oxidize amino acids, proteins, sugars, lipids, and nucleic acids in bacterial cells by addition reaction, electron transfer, and dehydrogenation to attain the aim of killing the bacteria. Bacteria inactivation involved the following several processes [34]:

First, when $\bullet\text{OH}$ radical entered the bacteria, it could inhibit the synthesis of alanine aminotransferase. The protein could be destroyed by oxidizing the unsaturated functional group in the protein, and $\bullet\text{OH}$ could also directly act on the hydrogen atom on the surface of the polypeptide chain to inactivate the protein. The $\bullet\text{OH}$ radical could also cause polymerization between macromolecular proteins to form an acid, which loses a metabolic function, resulting in bacterial metabolic disorder and achieving the purpose of sterilization. Second, $\bullet\text{OH}$ could take away the hydrogen atoms pentose sugars and basic groups of the DNA to form free radicals, resulting in the DNA pentose and basic groups becoming unsaturated, destroying the DNA backbone. The genetic information was destroyed, eventually leading to bacterial lysis and death. Third, $\bullet\text{OH}$ could also oxidize unsaturated fatty acids in bacteria. Because the phospholipids of the cell membrane composition contain unsaturated acids, $\bullet\text{OH}$ could destroy the structure of the cell membrane, causing the cell membrane to lose the selective permeability, the osmotic pressure of the bacteria to become unbalanced, and the toxic and harmful substances entering the bacteria, thereby destroying the bacterial metabolism, finally causing lysing and death.

4. Conclusions

The main compositions of the actual pipe growth ring were analyzed and prepared with one main composition, goethite. Goethite was used as catalyst or bactericidal agent to degrade TCE or purify water distribution network by the Fenton-like reaction. Studies on the degradation efficiency of goethite for TCE showed that goethite has a good ability to remove pollutants. $\text{pH} = 3$, 3.33 g/L goethite and 11.5 g/L H_2O_2 were the best degradation conditions. Moreover, goethite could activate H_2O_2 to generate $\bullet\text{OH}$, which could kill bacteria. Nearly 100% of *Pseudomonas* could be inactivated at the conditions of 0.5 g/L H_2O_2 and 0.89 g/L goethite. Goethite was also used to disinfect the actual filter water from a water plant, which obtained outstanding effects. These results indicated that the pipe growth ring had great potential to repair water pollution and disinfect drinking water in situ.

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