Base-activated Sodium Persulfate Degrades 1,1,1-trichloroethane in Groundwater

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Abstract

This paper studied the effect of 1,1,1-trichloroethane(TCA) in base-activated sodium persulfate(NaOH/SPS), investigated the effects of NaOH/SPS, initial pollutant concentration, oxidant dosage, and chloride release during the reaction, and deduced the degradation route of TCA in base-activated SPS system by chemical probe and radical cleaning, and verified the contribution in the degradation process of TCA. The results show that the base-activated SPS system can effectively degrade TCA in an aqueous solution, and the degradation rate and removal rate of TCA increase with the increase of NaOH/SPS molar ratio; HO• plays a main role in the degradation of TCA; under the base-activated SPS system, the overall dechlorination performance of TCA is good.

Keywords

Sodium Persulfate; 1,1,1-trichloroethane; Base-activated; Groundwater; Influencing Factors.

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1. Introduction

Trichloroethane(TCA) is an important chemical raw material and organic solvent. Due to the leakage in the process of production, use, storage and disposal, it has become one of the organic pollutants widely detected in the groundwater of the contaminated site[1]. Long-term TCA exposure can cause damage to the central nervous system liver and kidney, and possibly even death[2]. TCA is a priority pollutant in Europe, America, and China[3]. As A typical heavy non-aqueous liquid (DNAPL), in addition to dissolving groundwater, it also exists in the form of immiscibility with water and releases slowly and continuously. TCA has significantly low water solubility, low viscosity, and difficult biodegradability, so it is difficult to repair and control TCA in the actual contaminated sites.

In situ chemical oxidation (ISCO) is one of the most promising soil and groundwater pollution remediation technologies. ISCO technology can effectively and quickly control the groundwater contaminated by chlorinated hydrocarbons, which has the advantages of short treatment cycles and strong treatment effects and is conducive to underground in situ bio-remediation[4]. Sodium persulfate (SPS) is a strong oxidant, which is widely used in ISCO repair of contaminated sites. SPS is relatively stable at room temperature, but it decomposes into sulfate radicals ($SO_4^{\bullet-}$ under the activation of strong alkali, heat, excessive metal ions, or UV light−) Or further production of hydroxyl radicals (HO•) and superoxide radicals ($O_2^{\bullet-}$), These free radicals can effectively deal with refractory organic pollutants[5]. However, in practical engineering, the wide application of this technology is restricted by the rapid reaction of activated sulfate remediation technology, the narrow effective treatment range of pollution feathers, and the serious water acidification of groundwater after remediation. It is necessary to carry out further relevant research to solve the practical problems encountered in the application process of activated persulfate repair technology.

2. Materials and Methods

2.1 Reagents and Instruments

The reagents used in this test include TCA, tert-butanol (TBA), isopropanol (IPA), 1,4-benzoquinone (BQ), humic acid (HA) from Shanghai Jingchun Industrial Co., Ltd.; SPS from Shanghai Aladdin Reagent Co., Ltd. Groundwater (without TCA pollution) is taken from the campus of East China University of Science and Technology (Xuhui Campus).

The instrument used in this test includes a constant temperature magnetic stirrer (85-2, Shanghai Minhang Hongpu Instrument Factory), Electronic Analysis Balance (AL204, Swiss Mettler-Toledo Group), vortex oscillator (XW-80A, Shanghai Qingpu Huxi Instrument Factory), gas chromatograph (Agilent 7890A, Agilent Technologies, Inc.), ion chromatograph (ICS1000, American Dionex Company), UV spectrophotometer (DR-6000, HACH Water Quality Analysis Instrument (Shanghai) Co., Ltd.).

2.2 Test Method

Use a 42 mL general standard thread mouth sample bottle (PTFE / silicone cushion) as the reaction bottle. TCA liquor was stirred from light for 2 h and diluted to the desired initial concentration. Add a certain amount of SPS and NaOH to the TCA solution, mix well, and quickly fill each reaction bottle (inverted without bubbles). The reaction bottle was placed in a 20℃ constant temperature water bath oscillator (100 r/min), and two parallel samples were analyzed at the established time point, and the results were averaged. 0.1 M NaOH and 0.1 M dilute H_2SO_4 were used to adjust the initial pH value of the solution; the initial pH value of the solution refers to the pH value of the solution before the addition of SPS (the TCA is included in the solution at this time). All other experiments do not adjust the initial pH of the solution, and all solutions adopt the above groundwater configuration.

2.3 Analysis Method

The TCA concentration in the solution was determined by n-hexane extraction and enrichment. Specific steps: 1 mL of n-hexane was placed in the extraction bottle, 1 mL of the solution was added immediately, vortex shaking for 3 min, static for 5 min, and the upper organic phase was measured by gas chromatography. The gas chromatograph is Agilent 7693A (USA) with an automatic sampler, column model DB-VRX (60 m long; inner diameter 250 μm; membrane thickness 1.4 μm), inlet and electronic capture detector (ECD) temperatures are 240 and 260℃ respectively, and column temperature of 75℃. The injection volume was 1 μL and the flow of the column was 2 mL min^{-1}. The SPS concentration was determined spectrophotometrically by potassium iodide; chloride ion (Cl^-) Was measured by using an ion-chromatography instrument.

3. Results and Discussion

3.1 Feasibility Study of TCA Degradation by Base-activated SPS

Base-activated persulfate is one of the most commonly used and widely used technologies in soil and groundwater remediation projects at actual contaminated sites[6]. It has been reported in the literature that about 60% of the sites repaired by in situ sodium persulfate oxidation use alkali activation technology[7]. There are two common ways for bases to activate persulfate[8]: (1) the maintenance system pH is in the strong alkaline range (pH>10); (2) adding equal or excessive base to the persulfate system. Figure 1 shows the degradation effect of TCA in three systems of base-activated sodium super sulfate (NaOH/SPS), simple strong alkaline conditions (initial pH=12 of the adjusted solution or adding a certain amount of NaOH to the solution), and sodium persulfate (SPS, no adjusted solution pH), in which the base-activated sodium super sulfate (NaOH/SPS) system is achieved by adjusting the initial pH=12.0 of the solution and controlling the NaOH/SPS molar ratio of 10 / 1. The initial TCA concentration was 0.15 mM (20 mg L^{-1}), The initial concentration of sodium persulfate and sodium hydroxide was 75 mM (17858 mg L）,750 mM（30000 mg L−1). The initial pH of the solution was adjusted by NaOH 0.1 M and H_2SO_4 0.1 M. The initial pH of the solution is the pH of the solution obtained before adding sodium persulfate (which then contains only TCA), and the reaction temperature is 20 ± 0.5℃.

The results of the control group (no SPS, the initial concentration of TCA was 0.15 mM, 20 ± 0.5℃) showed that TCA volatilization was <5% within 21 d; after adding sodium persulfate, the TCA removal rate was 24.9%, indicating that sodium persulfate can directly oxidize and degrade some TCA. Liang et al[9]It was also found that sodium sulfate was able to slowly degrade BTEX through its oxidation at room temperature. Gu et al[10]In the actual TCA contaminated groundwater test with thermal-activated sodium persulfate, the TCA removal rate after SPS was 7.6% (10 h, 20℃, containing volatilization). Under strong alkaline conditions, many organic pollutants may be directly associated with the OH−The alkaline hydrolysis reaction occurs. After 21 d of reaction, the removal rate of TCA in pH =12 and Na OH = 75 mM (initial pH of 13.78) was 11.4% and 15.6%, respectively (with about 4.1% volatilization). And Jeffers et al[11] investigated the relationship between the alkaline hydrolysis rate and solution pH of the four chlorinated hydrocarbons, and the experimental results showed that the alkaline hydrolysis rate of these substances accelerated at room temperature as the pH increased. Liang et al[12]It is found that when no oxidant is added, the diesel oil in the contaminated soil is also removed under alkaline conditions. Therefore, it is speculated that alkaline hydrolysis may be an important way of pollutant degradation in the process of alkali activation.

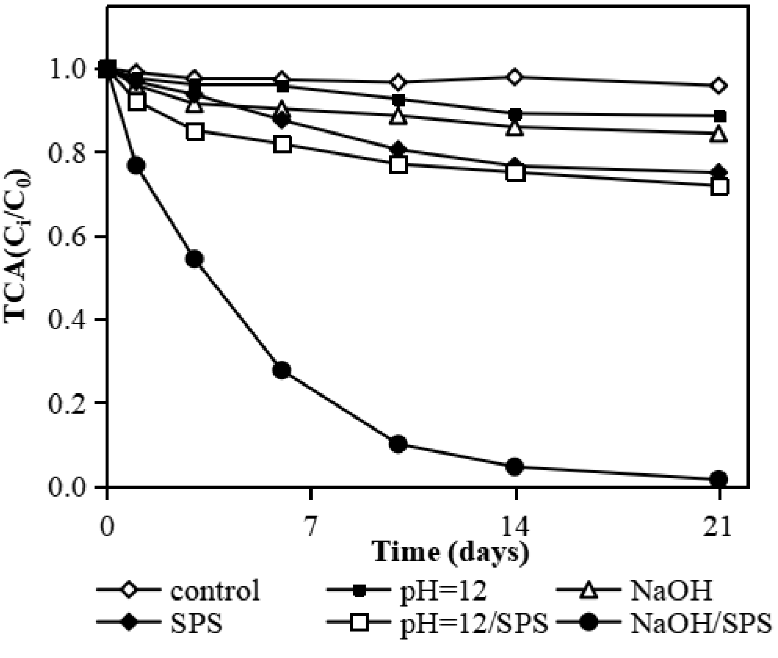


Figure 1. TCA degradation performance by persulfate activated with alkaline under various conditions (C0=0.15 mM, T=20℃)

Compared with the single sodium persulfate and the simple alkaline environment system, the TCA removal efficiency and removal rate were significantly improved in the two ways of the base-activated sodium persulfate system. In the pH=12/SPS system, 28.1% of TCA was removed within 21 d; in the stronger alkaline system with a NaOH/SPS molar ratio of 10/1, TCA was almost completely removed at 21 d, with a removal rate of 98.6%. This result shows that the base-activated sodium persulfate technique can degrade TCA is feasible, and the base activation is better by controlling the NaOH/SPS molar ratio. Liang et al[12]Found that approximately 30% of the diesel oil was efficiently removed within 7 d under NaOH/SPS and CaO/SPS.

3.2 Effect of Initial TCA Concentration, SPS Dosage, and Addition Mode on the Degradation Effect of TCA

Figure 2 shows the effect of base-activated SPS in treating different initial concentrations of TCA (0.075 to 0.75 mM) at 20℃. The results show that the TCA degradation process still fits the quasi-first-order reaction kinetic equation at different initial concentrations. After 21 d, the TCA removal rate exceeded 92.8%, which indicated that under the experimental investigation conditions (T=20℃, [SPS]0= 75 mM, NaOH/SPS=10/1), TCA of different initial concentrations could be effectively removed, but with the initial concentration of TCA, the removal rate of TCA (21 d) decreased from 99.8% to 92.8%, it is concluded that the lower the initial concentration of TCA, the higher the removal rate. Figure 3 shows the effect of different SPS doses on the effect of base activation treatment. The SPS concentration of 7.5 mM yielded 60.5% removal within 21 d. When the SPS dosage increased to 30, 75 and 150 mM, the TCA degradation rate constant gradually increased to 0.2973 d^{-1}, Among them, when the SPS dosage was 75 and 150 mM, the TCA was completely degraded within 21 d. Inferred that the SPS dosage affected more on the reaction than the initial concentration of TCA. In addition, the initial concentration of TCA was 0.15 M, T=20℃, [SPS]0=75 mM, NaOH/SPS molar ratio of 10/1, SPS consumed only 4.2% within 1 d and 42.85% after (21 d), indicating a low utilization of oxidant during base activation.

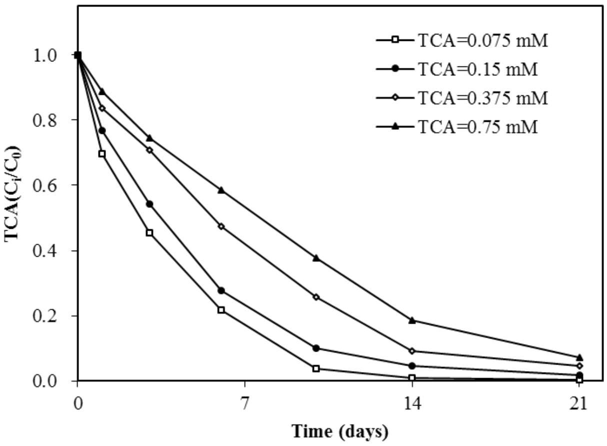


Figure 2. Effect of initial TCA concentration on its degradation performance (C0=0.15 mM , [SPS]0=75 mM , NaOH/SPS =10/1, T=20℃)

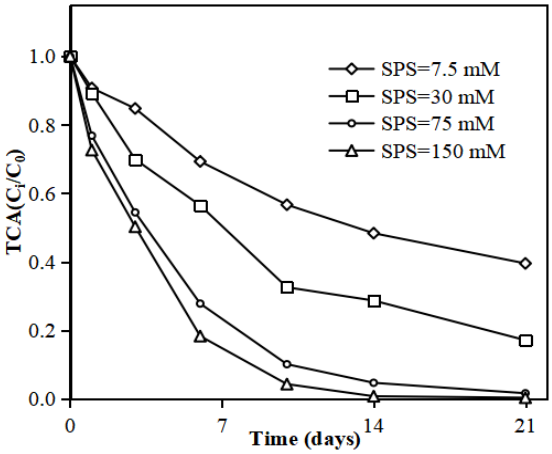


Figure 3. Effect of SPS sage on TCA degradation performance (C0=0.15 mM , NaOH/SPS =10/1, T=20℃)

The addition mode of oxidant is an important parameter in the degradation process of organic pollutants, which can affect the activity and utilization rate of free radicals, thus affecting the removal effect and rate of pollutants. To study the effect of the number of SPS injections on the degradation effect of TCA, the SPS solid powder was added into the reaction system at the reaction temperature of 20℃, the reaction time of 7 d, total SPS dose of 75 mM and NaOH/SPS =10/1. The results are shown in Figure 4. At the beginning of the reaction, the reaction rate was faster, and about 23.2% of TCA was removed after 1 d of the reaction, but gradually decreased as the reaction progressed, and the TCA removal rate within 7 d was only 76.7%. As can be seen from Figure 4, in the early stage of the reaction (within 1 d), the degradation rate of TCA is determined by the initial dosage of SPS at time 0. The greater the greater the initial dosage of SPS, the greater the TCA degradation rate, and the higher the TCA removal rate. This result is consistent with the situation reflected in Figure 3. It can be considered that the initial dosage of SPS is the dominant factor in the early reaction.

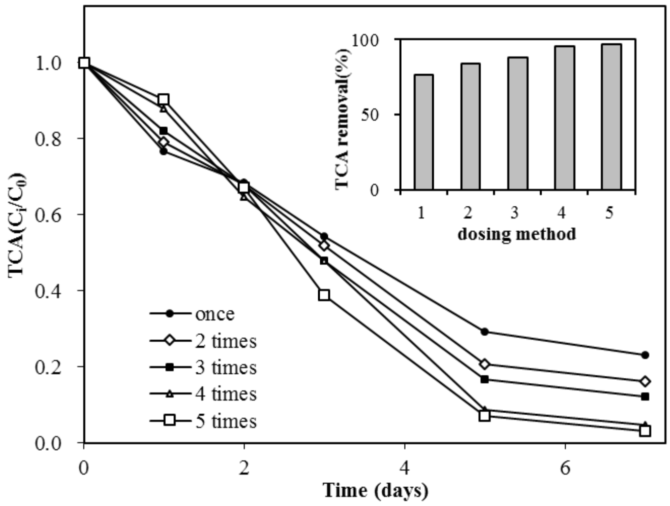


Figure 4. Effect of SPS do sing mode s on TCA degradation performance
(C0=0.15 mM , [SPS]total=75 mM, NaOH/SPS =10/1, T=20℃)

With the increase of the number of shots, the removal rate of TCA is also gradually increased. Among them, with an average of 4 and 5 shots of SPS, the TCA removal rate within 7 d can reach more than 95%. Zhu and Luo[13]Taking chlorobenzene in water as the research object, the treatment of chlorobenzene pollution by the addition of persulfate can improve the degradation rate of chlorobenzene. Increasing the number of dosages can relatively continuously supplement $S_2O_8^{2-}$, and the newly generated $SO_4^{\bullet -}$ and HO• can participate in the reaction in a timely manner. At the same time, adding persulfate in stages c an avoid excessive concentrations of $SO_4^{\bullet -}$ and HO• in aqueous solution, reduce the likelihood of quenching reaction between free radicals, thereby improving the effective utilization rate of oxidants and promoting the degradation of TCA.

3.3 Effect of the NaOH/SPS Molar Ratio on the Degradation Effect of TCA

Figure 5 shows the effect of different NaOH/SPS molar ratios on the effect of TCA treatment by the base-activated persulfate technique. At a NaOH/SPS molar ratio of 0.2/1, the TCA was removed by 48.0% within 21 d. At the time that when the molar ratio of NaOH/SPS increased to 1/1, 2/1, 5/1 and 10/1, the removal rate of TCA increased to 75.1%, 90.6%, 90.6%, 97.7% and 98.4% within 21 d. According to the experimental results, we can see that the degradation rate of TCA and the total removal rate of 21 d increased with the increase of NaOH/SPS molar ratio, and with the increase of NaOH/SPS molar ratio, the degradation effect of TCA became less and less obvious.

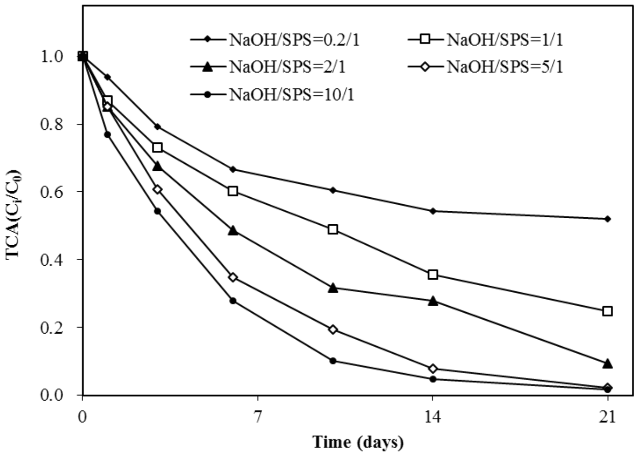
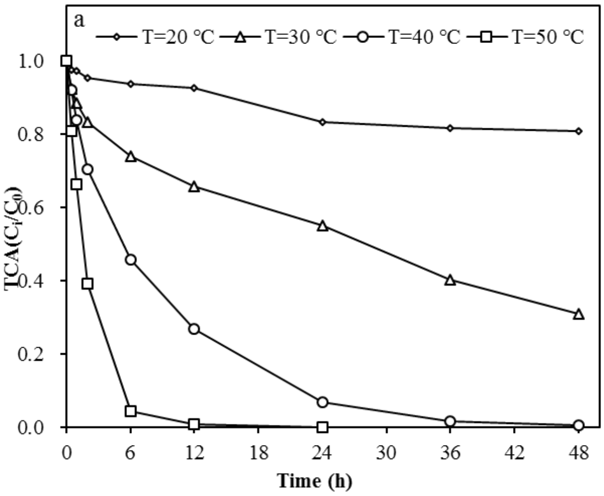


Figure 5. Effect of NaOH/SPS molar ratio on TCA degradation performance (C0=0.15 mM, [SPS]0=75 mM , T=20℃)

When NaOH/SPS is high, when sodium persulfate produces sulfuric acid and TCA degradation produces acidic intermediates, the pH drops less, which makes the effect of base activation stable to a certain extent. Therefore, with the increase of NaOH/SPS molar ratio, the removal rate and degradation rate of TCA increase successively. On the other hand, the increased NaOH/SPS molar ratio implies an increase in the alkalinity of the solution, in a strongly alkaline environment, $SO_4^{\bullet-}$Will be quickly associated with the OH−Reactions to generate the HO•, NaOH/SPS molar ratio increased from 0.2/1 to 10/1, HO• Increasing yield; meanwhile, higher concentration of OH−Also leads to the reductive radical component ($O_2^{\bullet-}$) Increasing in yield, and HO• and $O_2^{\bullet-}$ can promote the degradation of TCA. Figure 5 shows that with the increase of NaOH/SPS, the effect of TCA degradation is less obvious, because of the quenching effect between the high concentration of free radicals.

3.4 Effect of NaOH on the Reaction Activation Energy of the TCA Degradation Process

The reaction activation energy of TCA degradation by the temperature and the reaction rate constant k can be calculated from the Arrhenius equation. The degradation effect of the NaOH/SPS system on TCA at different temperatures (20, 30, 40, 50℃) is shown in Figure 6, where Figure 6(a) NaOH/SPS=10/1 and Figure 6(b) NaOH/SPS=0.2/1. Mapping with link to 1/T, the reaction activation energy of 20 to 50℃ base activated SPS for degraded TCA was 111.02 KJ/mol, respectively, at NaOH/SPS mole ratio=10/1 and 0.2/1(correlation coefficient R^2=0.9948), 117.08 KJ/mol (correlation coefficient R^2=0.9895).



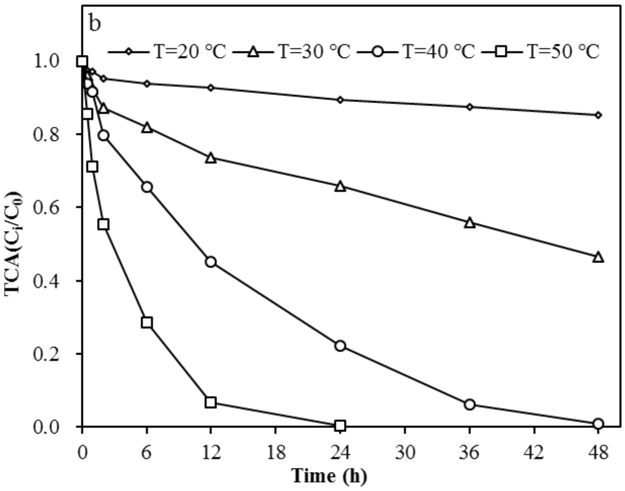


Figure 6. TCA degradation performance under different temperatures in NaOH/SPS system

Gu et al[10]Based on the effect of TCA, the reaction activation energy of 30 to 50°C was 122.44 KJ/mol (correlation coefficient R^2=0.99). Liang et al[14]Similarly, TCA was studied in aqueous solution of SPS degradation at different temperatures. The initial concentration of pollutants was 0.45 mM the SPS/TCA molar ratio was 10/1, and the reaction activation energy from 40 to 60°C was 163.86 KJ/mol. According to the comparative data, when the NaOH/SPS molar ratio=10/1 and 0.2/1, the reaction activation energy is lower than the above experimental results, indicating that adding alkali to the solution is conducive to reducing the activation energy of the reaction, which can increase the probability of material collision, conduct the reaction more quickly and effectively, and improve the degradation rate and removal efficiency of TCA to a certain extent. At the same time, according to the reaction activation energy of NaOH/SPS molar ratio =10/1 (111.02 KJ/mol) lower than NaOH/SPS molar ratio =0.2/1(1178 KJ/mol), the larger the molar ratio of NaOH/SPS, the lower the activation energy of TCA degradation by SPS; increasing the molar ratio of NaOH/SPS can effectively reduce the reaction activation energy, making the oxidative degradation of TCA reaction easier.

3.5 Identification of Reactive Oxygen Species Radicals in the NaOH/SPS System

Nitrobenzene (NB) was used as the HO• free radical probe, Anisole (AN) as the $SO_4^{•-}$ and HO• common probe of free radicals, carbon tetrachloride (CT) as $O_2^{•-}$ free-radical probe. The results showed that in the presence of NaOH or SPS alone, the removal rate of NB was 9.1% and 14.0%, respectively. Compared with the ultrapure water control experiment (NB volatilization), NB degradation was minimal, indicating that almost no HO• was produced under this condition. Conversely, in the NaOH/SPS system, NB removes 97.2% within 12 h, indicating that base-activated SPS can produce HO• during the reaction. The removal of AN within 12 h was 56.8% within 12 h, indicating the presence of at least $SO_4^{•-}$ in the base-activated SPS reaction system. On this basis, HO• was added to the AN degradation system•Of tert-butanol (200 mM), the removal rate of AN decreased from 56.8% to 23.8% at 12 h, and the degradation of AN was not completely inhibited, implying the existence of $SO_4^{•-}$ in the system. Liang and Su[121]The same method was used to verify the simultaneous presence of $SO_4^{•-}$ in the thermal-activated SPS system and HO•, And was found to be under alkaline conditions (pH=12), HO• is the dominant free radical in the system.

Based on chemical probe experiments, free radical cleaning experiments were performed to confirm $SO_4^{•-}$ during base activation of SPS, HO• and $O_2^{•-}$, and further evaluate the contribution of each radical in the TCA degradation process. Tert-butanol (TBA) was chosen as HO• discleaner, isopropyl alcohol (IPA) as $SO_4^{•-}$ and HO• of the common detergent, 1,4-benzoquinone (BQ) as the $O_2^{•-}$ the cleaning agent. The results showed that the addition of 100 mM T BA reduced the TCA removal rate by 78.4% compared with the control group, which could be considered the HO• contribution to TCA degradation was 78.4%; 100 mM IPA reduced the removal rate of TCA by 82.1% compared with the control group, indicating the $SO_4^{\bullet -}$ contribution rate is only 3.7%. The TCA degradation is assumed to be affected exclusively by the $SO_4^{\bullet -}$, HO• and $O_2^{\bullet -}$. It can be calculated as the effect of $O_2^{\bullet -}$ Contribution of 17.9%, this value with a sufficient amount of BQ sweep $O_2^{\bullet -}$. There is a slight difference in the contribution (14.1%) between this value and the sufficient amount of BQ cleaning $O_2^{\bullet -}$, which may be due to TCA volatilization, TCA hydrolysis in strong alkaline solutions, direct oxidation of TCA by SPS, or slight reactions between BQ and $SO_4^{\bullet -}$, HO•.

3.6 Analysis of SPS Mechanism of Base Activation and TCA Degradation Pathway

Figure 7 shows the release of Cl^- during the TCA degradation process. From Figure 7, it can be seen that TCA is basically completely degraded within 21 days, while the final release of Cl^- is 74.3% of the theoretical value, indicating that TCA is not completely mineralized and there are other chlorine containing products in the solution. Liang et al[14] found that after complete oxidation of TCA by thermal activation SPS method, the final release rate of Cl^- was 60%, lower than the 74.3% in this experiment. This indicates that the dechlorination effect of alkali activated sodium persulfate technology on TCA is better than that of thermal activation technology. This can be explained from three perspectives: (1) The strong alkaline environment intensifies the hydrolysis of TCA and chlorine containing intermediates; (2) HO•, as the dominant free radical in the NaOH/SPS system, has strong oxidizing properties and makes a significant contribution to the degradation process of TCA; (3) The alkaline activation of SPS process generates a strong reducing free radical $O_2^{\bullet -}$, promoting the reduction dechlorination process of TCA.

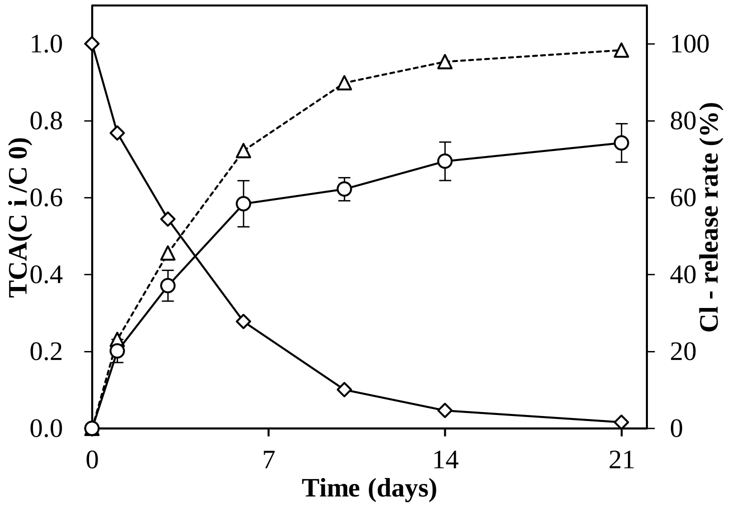


Figure 7. The release of chloride ion during TCA degradation
(C0=0.15 mM, [SPS]0=75 mM, NaOH/SPS =10/1, T=20°C)

Based on the previous discussion, a mechanistic model for the degradation of TCA by base-activated sodium persulfate was established, as shown in Figure 8. Base activation of persulfate and degradation of TCA can be roughly divided into four steps: (1) persulfate first goes through alkali-catalyzed hydrolysis to produce hydroperoxide anion (HO_2^-) and SO_4^{2-}; (2) HO_2^- reduced persulfate produces the $SO_4^{\bullet -}$, at the same time HO_2^- oxidized to a highly reducing superoxide radical ($O_2^{\bullet -}$, E0= -2.4 V); (3) most of the $SO_4^{\bullet -}$ under alkaline conditions was rapidly converted to the HO•; (4) $SO_4^{\bullet -}$,HO• and $O_2^{\bullet -}$ free radicals work together to degrade TCA in aqueous solution, and the contribution of these three free radicals to TCA degradation is 78.4%, 3.7% and 17.9%.

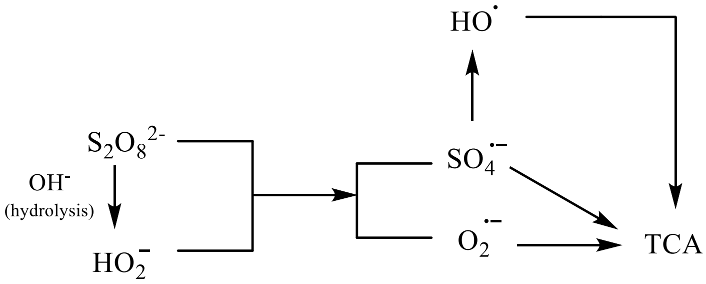


Figure 8. Schematic model of TCA degradation mechanism in base activated persulfate system

Further analysis by GC/MS revealed that the TCA degradation process in the base-activated SPS system produced three main intermediates: trichloromethane, dichloromethane, and formic acid. Thus can speculate that the alkali activation SPS degradation of TCA possible way, the results as shown in Figure 9, TCA through carbon bond break and reduction dechlorination process, respectively, 1,1-dichloroethylene and trichloromethane, 1,1-dichloroethylene carbon bond break and trichloromethane dechlorination can further produce dichloromethane, finally, the methane further dechlorination, into formic acid, the final product of the reaction is CO_3^{2-} and H_2O.

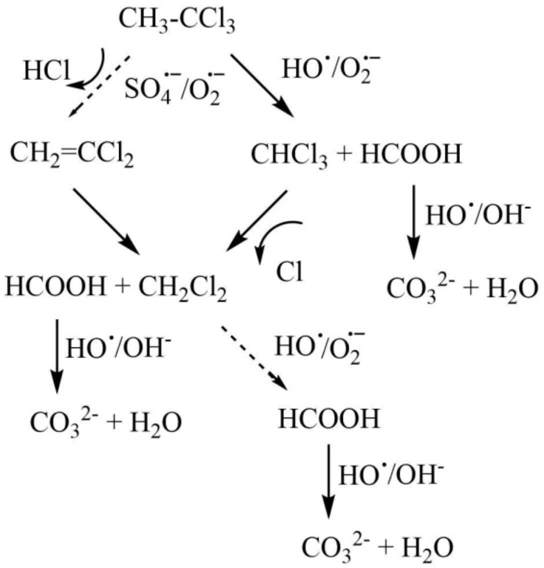


Figure 9. Proposed TCA degradation pathway in NaOH/SPS system

4. Conclusion

The base-activated SPS system can effectively degrade TCA in aqueous solution, and the degradation rate increases with the increase of SPS dosage. SPS is beneficial to the degradation of TCA; the degradation rate and removal rate of TCA increase with the increase of NaOH/SPS molar ratio; increasing NaOH/SPS mole ratio can effectively reduce the reaction activation energy, which is conducive to the degradation of TCA.

The existence of reactive oxygen radical HO• in the base-activated sodium persulfate system was verified through the chemical probe experiments,$SO_4^{•-}$ and $O_2^{•-}$. Free radical cleaning experiments showed that HO• play a major role in the degradation of TCA.

Under the action of an base-activated SPS system, TCA produces intermediates such as trichloromethane, dichloromethane, and formic acid through the process of carbon-carbon bond breaking and reduction dechlorination, and the intermediates can be further oxidized, so the overall dechlorination effect of TCA is good.

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