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Rapid degradation of hexachlorobenzene by micron Ag/Fe bimetal particles

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Abstract

The feasibility of the rapid degradation of hexachlorobenzene (HCB) by micron-size silver (Ag)/iron (Fe) particles was investigated. Ag/Fe particles with different ratios (0, 0.05%, 0.09%, 0.20%, and 0.45%) were prepared by electroless silver plating on 300 mesh Fe powder, and were used to degrade HCB at different pH values and temperatures. The dechlorination ability of Fe greatly increased with small Ag addition, whereas too much added Ag would cover the Fe surface and reduce the effective reaction surface, thereby decreasing the extent of dechlorination. The optimal Ag/Fe ratio was 0.09%. Tafel polarization curves showed that HCB was rapidly degraded at neutral or acidic pH, whereas low pH levels severely intensified H₂ production, which consumed the reducing electrons needed for the HCB degradation. HCB degradation was more sensitive to temperature than pH. The rate constant of HCB dechlorination was 0.452 min⁻¹ at 85°C, 50 times higher than that at 31°C. HCB was degraded in a successive dechlorination pathway, yielding the main products 1,2,4,5-tetrachlorobenzene and 1,2,4-trichlorobenzene within 2 hr.

Key words: dechlorination; hexachlorobenzene; silver-iron micron bimetallic particles; chlorinated toxic organics

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Introduction

Zero-valent iron (Fe(0)) has been found to have a strong ability to dechlorinate some chlorinated aliphatic compounds, such as tetrachloroethene, trichloroethene, carbon tetrachloride, etc. (Matheson and Tratnyek, 1994; Song and Carraway, 2005; Katsenovich and Miralles-Wilhelm, 2009). To enhance the rate of dechlorination by Fe(0), the Pd/Fe bimetal system was used first for rapid degradation (Muftikian et al., 1995), and then other bimetal particles, such as Ni/Fe, Cu/Fe, Ag/Fe, Au/Fe, Ru/Fe, and Pt/Fe, were also been respectively used in the dechlorination of chlorinated carbons (Wei et al., 2006; Feng and Lim, 2007; Tee et al., 2009; Nagpal et al., 2010; Cao et al., 2011).

Apart from chlorinated aliphatic compounds, Fe(0)-based reductants have also been applied in the treatment of chlorinated aromatic hydrocarbons (Shih et al., 2009; Zhang et al., 2011). The bioconcentration factors of the products were greatly decreased, whereas the degradation efficiency was not as effective as that for chlorinated aliphatic compounds (Zheng et al., 2009; Wan et al., 2010; Cong et al., 2010).

Hexachlorobenzene (HCB), with its highly toxic and bioaccumulation characteristics, is an animal carcinogen

and is also potentially harmful to humans (Randi et al., 2006). It has been included in the list of twelve persistent organic pollutants by the Stockholm Convention on Persistent Organic Pollution. There have been some studies on HCB dechlorination by Fe(0) previously, most of them focused on the effect of the particle size of Fe, changing from scrap iron to nano-sized zero-valent iron (Yuan et al., 2010; Zhu et al., 2010; Shih et al., 2011), others focused on additives to increase the solubility of HCB during dechlorination (Yuan et al., 2006; Zheng et al., 2009; Wan et al., 2010).

Concerning HCB dechlorination by Fe(0)-based reductants, there are two aspects needing attention: the cost is extremely high for large-scale engineering applications, and the reductive activity time of Fe(0)-based reductants is too short. In the present study, Ag/Fe micron bimetallic particles were prepared using 300 mesh Fe powder, which was more stable and cheaper than nanoscale bimetal particles. The present study investigated and revealed for the first time the relationship between Ag/Fe reduction and Fe corrosion using Tafel polarization curves, to reveal the influence of reductive activity for Ag/Fe bimetal. Moreover, the dechlorination conditions, including Ag/Fe ratio, temperature, and pH, were optimized. The research can provide technical support for project applications in

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chlorinated toxic organic disposal, and help in the detoxification of hazardous waste containing persistent organic pollutants.

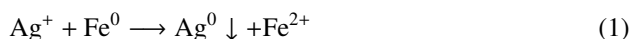
1 Materials and methods

1.1 Materials

The chemicals used were HCB (99.8%; Sigma-Aldrich), pentachlorobenzene (PeCB; 99.9%; Supelco), 1,2,4,5-tetrachlorobenzene (TeCB; 99.3%; Supelco), 1,2,3,5-TeCB (98.5%; Accustandard), 1,2,3-trichlorobenzene (TCB; 99.3%; Supelco), 1,2,4-TCB (99.3%; Supelco), 1,3,5-TCB (99.3%; Supelco), diethyl ether, *n*-hexane, acetone, AgNO₃, HCl, HAC, NaH₂PO₄, and NaOH. All chemicals used were analytically pure. Micro-Fe powders (99%+, 300 mesh). All chlorinated organics were dissolved in diethyl ether as standard samples. All aqueous solutions were prepared in deionized water. A buffer solution was prepared with acids (HCl, HAC), NaH₂PO₄ and NaOH to control the solution pH.

1.2 Preparation of Ag/Fe bimetallic particles

Ag/Fe was prepared by reduction on the Fe surface according to the following reaction:



The process was as follows: 5 g of 300 mesh Fe powder was added to 150 mL of AgNO₃ solution with different concentrations (5.95, 2.98, 1.19, and 0.59 mmol/L respectively), reacted for 1 hr and washed twice by HCl and deionized water, then filtered and blow dried with nitrogen.

The Ag ratio on the Fe particles was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo IRIS): 1 mL of the reaction solution was added to 10 mL of nitric acid for 30 min until Ag particles were completely dissolved, then 25 mL deionized water was added before measuring the Ag concentration by ICP-AES. In this study, the Ag concentrations were measured at 0, 0.26, 0.64, 1.79, and 3.29 mmol/L, and the real Ag/Fe ratios are calculated to be 0, 0.05%, 0.09%, 0.20%, and 0.45%, respectively.

The morphology of the Ag/Fe bimetallic particles was viewed under a field emission scanning electron microscope (SEM) system (Quanta 200FEG, USA). Localized elemental information from chosen regions was studied using SEM-energy dispersive spectrometer (EDS).

1.3 Dechlorination batch experiments

The initial samples were prepared from 100 mg/L HCB in diethyl ether placed in 100 mL amber serum vials. Dechlorination batch experiments were conducted in 20 mL vials containing 0.5 g Ag/Fe powder, 0.3 mL HCB initial sample, and 10 mL deionized water under different reaction conditions. Each bottle was sealed with a Teflon-

lined cap in a nitrogen box, and then reacted at a constant temperature with stirring on a rotary shaker at 250 r/min. The degradation ratio of HCB (R_{HCB} , %) was calculated as follows:

$$R_{\text{HCB}} = (1 - (C/C_0)_{\text{HCB}}) \times 100\% \quad (2)$$

where, $(C/C_0)_{\text{HCB}}$ is the observed ratio of HCB in the samples, C (mg/L) and C_0 (mg/L) are residue and initial concentration, respectively.

1.4 Sample and intermediate analyses

The samples were extracted three times at selected time intervals using an organic solvent mixture of *n*-hexane and acetone (1:1, V/V) for 15 min with constant shaking. The mixture was left undisturbed for 10 min, and then concentrated to 1 mL for analysis. The extracts were analyzed by an Agilent 6890N GC/ECD equipped with a 30 m DB-5HT capillary column. The sample injection volume was 1 μL, and the temperature conditions were programmed as follows: oven temperature of 80°C, injection port temperature of 260°C, and detector temperature of 280°C. Separation was performed with the following oven temperature program: initial 80°C held for 1 min, ramped at 10°C/min to 200°C held for 1 min, ramped at 5°C/min to 220°C, held for 1 min, and finally ramped at 10°C/min to 260°C and held for 3 min. Ultrapure nitrogen was used as the carrier gas for the GC at a flow rate of 1 mL/min.

1.5 Fe corrosion measurement

The corrosion current of Fe under different conditions was measured using a Shiruisi RST5000 electrochemical workstation (Zhengzhou Shiruisi Technology Co., Ltd., China). Two pieces of Fe and Ag each with 3 cm² surface area were used as working and auxiliary electrodes, respectively. The reference electrode was Ag/AgCl. The Tafel polarization curves were obtained to calculate the Fe corrosion current at a scan rate of 40 mV/sec with a RST 5200 (Zhengzhou Shiruisi Technology Co., Ltd., China).

2 Results and discussion

Ag depositing on the iron surface can form numerous microcells, which accelerate electron transfer to facilitate the reduction of HCB (Xu et al., 2000). The main reactions for the dechlorination of HCB by Ag/Fe bimetal particles in solution are as follows:

iron dissolution and supplied electrons occur on the anode side (Fe),



The cathode side (Ag) consumes electrons and mainly comprises two kinds of reactions, one consuming a portion

of electrons and creating H_2 ,



The other portion of electrons contributes to the dechlorination from RCI to RH ,



2.1 Effect of Ag/Fe ratio

Figure 1 shows the SEM images and EDS spectra of the surfaces of Fe(0) and Ag/Fe particles with ratios of 0.09% and 0.45%. The results show that the zero-valent iron surface is smooth (**Fig. 1a** and **b**), and Ag particles are significantly aggregated on certain iron particles with a moderately uniform distribution of gathered dots (**Fig. 1c** and **d**). The Ag atomic percentage dispersion on the surface of Fe measured by EDS in conjunction with the SEM was 1.26% and 2.78% for samples having Ag/Fe ratios of 0.09% and 0.45% (**Fig. 1e** and **f**), respectively.

The Ag/Fe bimetal microcell exhibits better reductive capacity than zero-valent iron alone. Enhancing the surface with Ag means enhancing the cathode surface of the microcells, thereby benefiting HCB dechlorination. However, too much Ag deposition will cover the Fe surface and hamper electron transfer, resulting in a negative influence on HCB dechlorination. **Figure 2** shows the effect of the Ag/Fe ratio on HCB degradation at 50°C. R_{HCB} increased with Ag/Fe ratio increasing from 0.04% to 0.09%, and decreased slightly with Ag/Fe ratio increasing from 0.09% to 0.20% and 0.45% sequentially. With greater Ag dispersion on the iron surface, the effective reaction surface decreases and dechlorination is restrained. Therefore, an appropriate Ag/Fe ratio would be beneficial to HCB

dechlorination. In this test, the optimal Ag/Fe ratio was 0.09%.

The rate constants of HCB dechlorination for different Ag/Fe ratios at 50°C within 30 min of reaction were 0.8×10^{-4} , 0.063, 0.122, 0.083 and 0.076 min^{-1} for Ag/Fe ratios 0, 0.05%, 0.09%, 0.20%, and 0.45% respectively. The degradation by zero-valent iron (only less than 1% HCB dechlorinated) could be considered negligible compared with that achieved by the Ag/Fe bimetal particles. Adding a small amount of Ag was found to enhance the dechlorination ability greatly, whereas more Ag addition had negative effects. For the 300 mesh Fe particles, the optimal Ag/Fe ratio was 0.09%. This ratio is lower than that found in previous research (Xu et al., 2000), which had synthesized Ag/Fe using nanoscale Fe particles having higher surface areas than the micro-Ag/Fe particles used in the present experiment.

2.2 Effect of pH

The influence of pH on HCB dechlorination was investigated by adjusting the solution pH to 3, 5, 7, and 9 using HCl, HAC, NaH_2PO_4 and NaOH, and the sample in deionized water had no added buffer solution. The results of HCB dechlorination for different pH at 50°C are presented in **Fig. 3**.

As shown in **Fig. 3**, the HCB degradation ratio in deionized water was 40% after 10 min reaction, which was more than that at pH 3, and HCB was hardly degraded at pH 9. Apparently, low pH levels benefit HCB degradation by Ag/Fe. HCB experienced more rapid degradation in the neutral solution (deionized water) compared with that at pH 3. This result suggests that the phosphate ion could decrease the dechlorination ability of Ag/Fe. In high-pH solution, ferrous or ferric hydroxides precipitate on the Fe

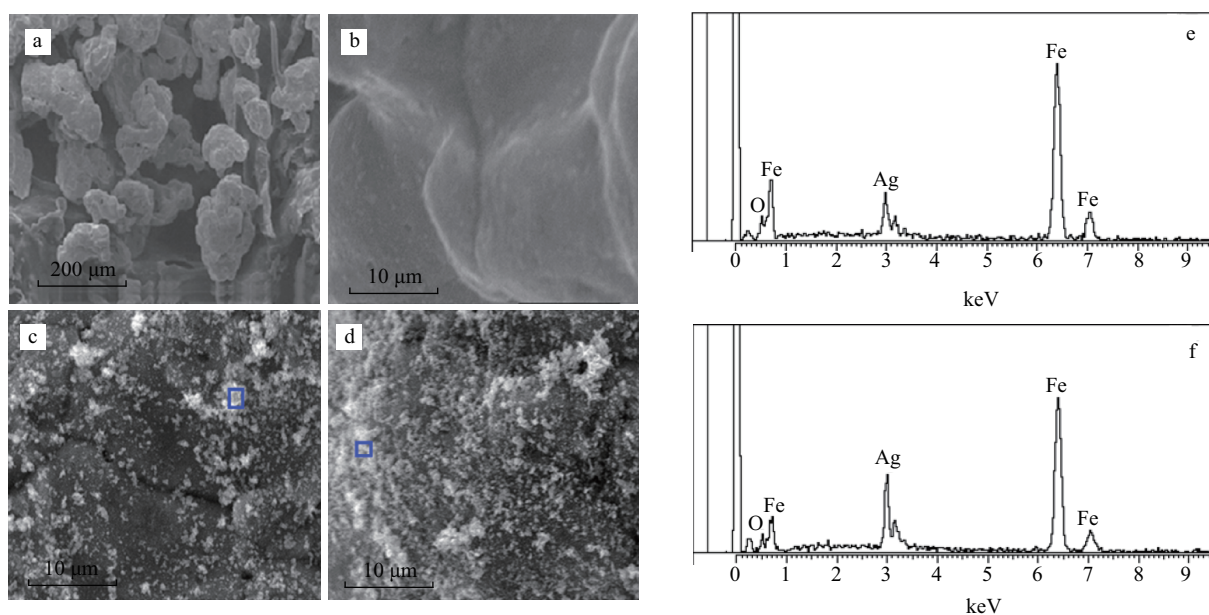


Fig. 1 SEM-EDS of Fe and Ag/Fe particles. (a) and (b): Fe; (c): Ag/Fe particles with ratio of 0.09%; (d): Ag/Fe particles with ratio of 0.45%; (e): EDS of (c); (f): EDS of (d).

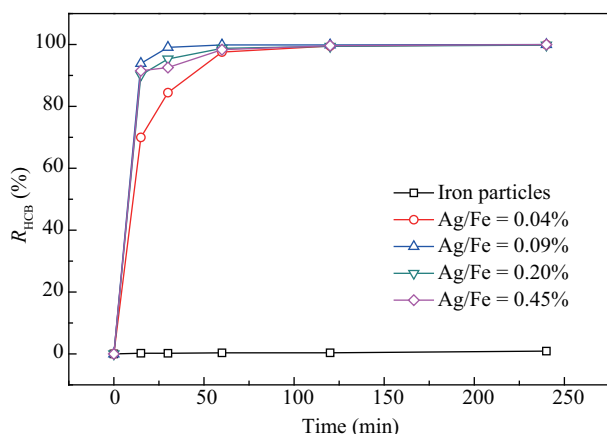


Fig. 2 Effect of Ag/Fe ratio on HCB degradation (R_{HCB}). Reaction condition: particle dosages 0.5 g; temperature 50°C; deionized water.

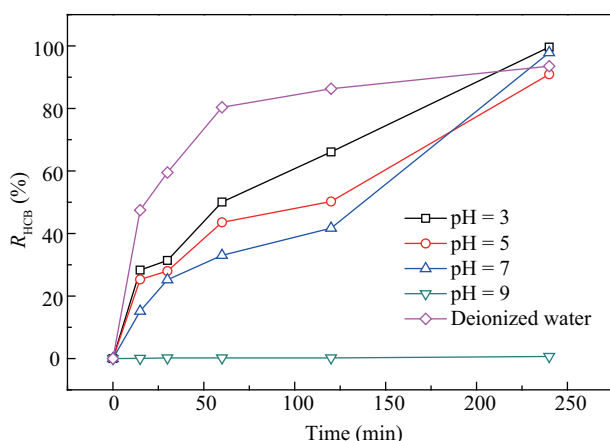


Fig. 3 Effect of pH on HCB degradation. Reaction condition: particle dosages 0.5 g, Ag/Fe 0.09%, temperature 50°C.

surface and impact Fe dissolution and electron transfer. In low-pH solution, on one hand, H^+ intensifies Fe corrosion and supplies more electrons on the cathode side, which is of benefit for dechlorination; on the other hand, H^+ ions are reductively transformed to H_2 and consume a large portion of electrons based on Reaction (5), which weakens the reaction of Reaction (6) and is disadvantageous for dechlorination. From the Tafel polarization curve in **Fig. 4**, the corrosion currents of Fe at pH 3, 5, and 7 are 363, 53.7, and 25.7 $\mu\text{A}/\text{cm}$, respectively. The Fe corrosion rate at pH 3 is about 14 times faster than that at pH 7. Although the HCB degradation rate is also accelerated with decreasing pH, the effect is smaller than that on Fe corrosion. Hence, hydrogenation rather than H_2 production is the rate-limiting step for HCB reduction by Ag/Fe.

In other words, a high-pH (> 9) solution generates Fe(II) and Fe(III) hydroxides on metallic Fe surfaces, and these deposits hamper Fe dissolution and electron transfer; a low-pH (< 3) solution severely intensifies H_2 production, consuming the reductive electrons and resulting in a disadvantage for HCB degradation (Roy et al., 2003). Thus it would be unnecessary to adjust the solution pH for HCB degradation by Ag/Fe.

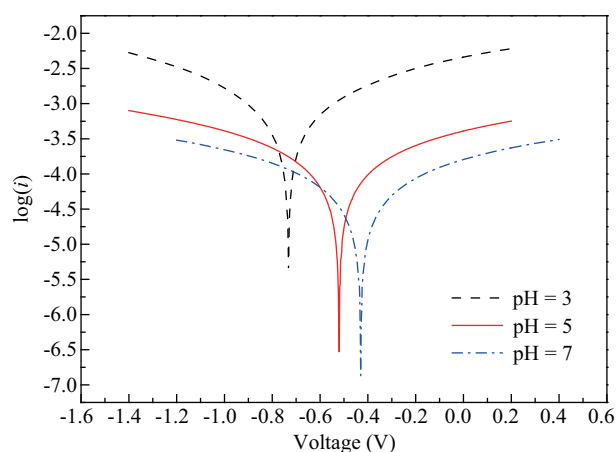


Fig. 4 Iron current density (i) at different pH values.

2.3 Effect of temperature

Figure 5 presents the degradation ratio of HCB at different temperatures by 0.09% Ag/Fe. With increasing reaction time, the degradation ratio of HCB is gradually increased at 31°C, and sharply increased with temperature increasing from 50 to 70 and 85°C. After 10 min at 85°C, HCB was almost totally removed, but only 22% HCB was removed at 31°C. The rate constant of HCB at 31, 50, 70, and 85°C was 0.009, 0.027, 0.103, and 0.452 min^{-1} within 20 min, respectively. The rate constant of HCB degradation at 85°C was more than 50 times higher than that at 31°C.

The activation energy (E_a) was calculated by the Arrhenius formula (Lien and Zhang, 2003) as follows:

$$\ln k = -\frac{E_a}{RT} + \ln A_0 \quad (7)$$

where, E_a (kJ/mol) is the Arrhenius activation energy or apparent activation energy, R is the ideal gas constant, and A_0 is the pre-exponential factor having the same dimension as k . The activation energy of HCB dechlorination by Ag/Fe calculated by Eq. (7) is 62 kJ/mol, which is less than the value of 80.0 kJ/mol found for p-dichlorobenzene with Pd/Fe bimetallic particles (Xu et al., 2005). This result indicates that increasing temperature can greatly enhance

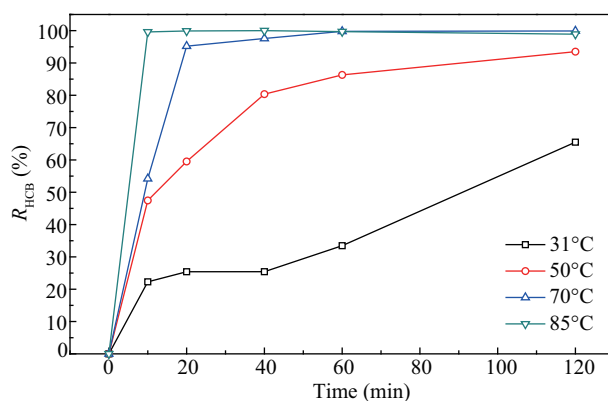


Fig. 5 Effect of temperature on HCB degradation. Reaction condition: particle dosages 0.5 g; Ag/Fe 0.09%; deionized water.

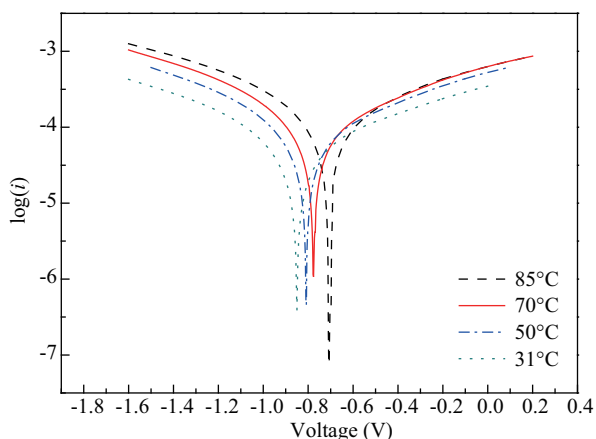


Fig. 6 Iron current density (i) at different temperatures.

HCB degradation.

Unlike pH, increasing temperature had a smaller effect on Fe corrosion. As shown in **Fig. 6**, the Fe corrosion current densities increased with increasing temperature, and the values were 26.3, 40.7, 53.7 and 61.7 $\mu\text{A}/\text{cm}^2$ at 31, 50, 70, and 85°C, respectively. The corrosion current density at 85°C was only 2.3 times higher than that at 30°C, whereas R_{HCB} at 85°C was 56 times higher than that at 31°C as mentioned in **Fig. 5**. Therefore, the HCB degradation process is highly sensitive to temperature, and the Fe utilization efficiency is also enhanced with temperature increase. Higher reaction temperatures would be more beneficial to HCB degradation.

2.4 Pathway of HCB dechlorination

The GC analysis indicated that the degradation products of HCB are lower chlorinated benzenes. **Figure 7** presents the distribution of chlorinated benzenes with reaction time at 31 and 85°C. HCB degradation is a successive chloride atom loss process (Xu and Zhang, 2000; Shih et al., 2009), and the products detected were PeCB, TeCB and TCB. **Figure 8** shows the pathway of HCB dechlorination. The first product detected by GC was PeCB, which has a uniform number of electrons in its benzene ring, assuming that the chlorides are also uniform at the benzene ring of HCB. The chloride atoms at the first and third carbon have lower

electron density, and more easily undergo nucleophilic substitution. As shown in **Fig. 7**, 1,2,4,5-TeCB was the main product of PeCB, and other TeCBs were only present in minor amounts. This finding is in agreement with the theory of nucleophilic substitution (Roy et al., 2003; Shih et al., 2011). Similarly, 1,2,4-TCB was the main product of TeCB degradation. Dichlorobenzene was not detected. In the dechlorination of HCB, chloride atom substitution by hydrogen is difficult because the benzene ring electrons resist displacement. Thus the main pathway within 2 hr is $\text{HCB} \rightarrow \text{PeCB} \rightarrow 1,2,4,5\text{-TeCB} \rightarrow 1,2,4\text{-TCB}$.

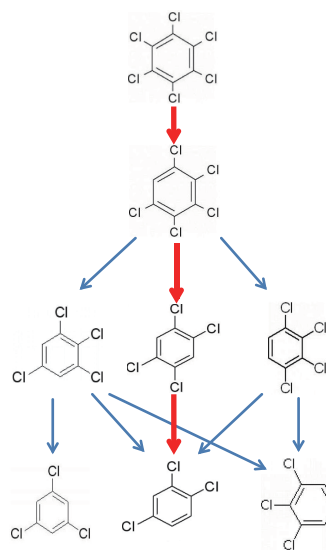


Fig. 8 Proposed degradation pathway of HCB with Ag/Fe particles.

3 Conclusions

The present study investigated HCB degradation by Ag/Fe under different conditions. The following main conclusions are drawn: Firstly, a small amount of Ag can remarkably promote the HCB degradation rate, whereas too much Ag addition decreases the effective reaction surface, and consequently decrease the degradation ratio, with the Ag/Fe ratio of 0.09% having the optimal effect on HCB degradation; Secondly, HCB was rapidly degraded in

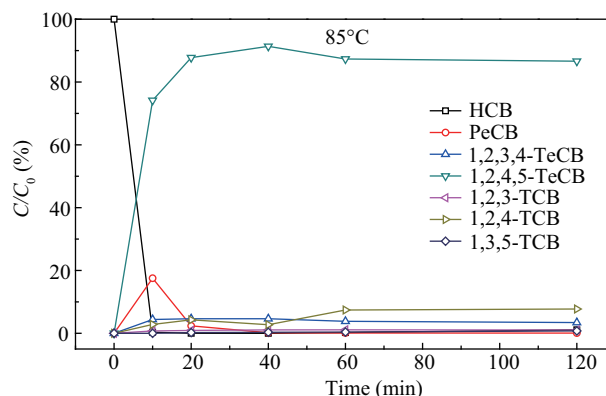
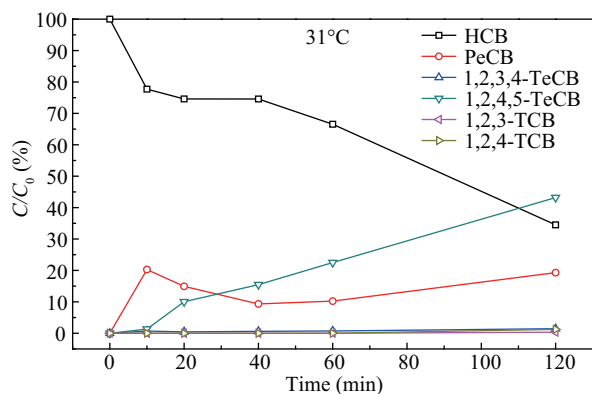


Fig. 7 Distribution of HCB and the degradation products at 31 and 85°C. Reaction condition: particle dosages 0.5 g, Ag/Fe 0.09%, deionized water.

neutral and acidic solutions and best in deionized water, so that pH does not need to be adjusted under such conditions, because most of the additional H⁺ at low pH would produce H₂ and consume a large portion of electrons that would otherwise be used for dechlorination; Thirdly, increasing temperature can decrease the activation energy and promote HCB degradation sharply. HCB was almost completely degraded in 10 min at 85°C; lastly, HCB degradation is a successive hydrodechlorination process. The main products are 1,2,4,5-TeCB and 1,2,4-TCB within 2 hr. HCB is rapidly degraded under the optimal conditions of 0.09% Ag/Fe ratio, 85°C, and in deionized water reaction medium.

Acknowledgments

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