

DECHLORINATION OF HEXACHLOROBENZENE IN CONTAMINATED SOILS BY CU/FE MEDIATED BY NONIONIC SURFACTANTS

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Abstract

Site soils contaminated with polychlorinated aromatic compounds such as polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) has been a very serious problem. This study investigated the dechlorination of HCB in contaminated soils (50 mg/kg) by Cu/Fe mediated with nonionic surfactant of TritonX-100 (TX-100) in a slurry system. Results showed that the largest destruction rate was reached with 1 mM TX-100 in the range of 0–6 mM, although the aqueous concentration is far less than its critical micelle concentration. It was interpreted that low concentration of TX-100 facilitated HCB transport to Cu/Fe reactive sites via its adsorption on nonreactive sites, and high concentration of TX-100 covered reactive sites and facilitated HCB partition in solution regardless of its enhancement on HCB desorption from soils. About 98% HCB was destructed for 96 h treatment with 1 mM TX-100, and all HCB was transformed to pentachlorobenzene and tetrachlorobenzenes. Cu/Fe reduction could decrease the biotoxicity and increase the biodegradability of HCB contaminated soils, and could be used as an effective pretreatment unit prior to bioremediation.

Introduction

Polychlorinated aromatic hydrocarbons (PAHs), such as polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB), have attracted global attention because of their high toxicity, extensive existence and long-term persistence¹. The contamination of soils and sediments by PAHs is still a great environmental problem because the successful remediation is quite difficult. The toxicity of PAHs generally decreases with the decrease of chlorine substitution, so reductive dechlorination provides an alternative approach to the remediation of PAHs contaminated sites. Microscale and nanoscale zero-valent iron (ZVI) and modified ZVI (Cu/Fe, Ni/Fe, Pd/Fe, etc) has been proven to be promising for the reductive dechlorination of chlorinated organics in groundwater and surface water²⁻⁴. However, much less work has been done using ZVI for the remediation of contaminated soils^{5,6}. With respect to heterogeneous soil matrix, the successful remediation involved the desorption of adsorbed contaminants from soils to solution, the transport of dissolved contaminants in solution to ZVI surface, and the subsequent reduction on surface. So, the quick dechlorination of PAHs in aqueous solution and sustainable desorption from soils determines the remediation efficiency.

We previously found that HCB desorption from soils can be greatly enhanced by nonionic surfactants⁷, and HCB dechlorination by microscale Cu/Fe particles was significantly increased in the presence of low concentration of nonionic surfactant⁸. So, this study investigated the dechlorination of HCB in soils by Cu/Fe in the presence of nonionic surfactant of TritonX-100 (TX-100). Emphasis was put on the partition of TX-100 and HCB between soils and solution in the dechlorination process. The objectives are to evaluate the influence of surfactant on the dechlorination of HCB in soils by Cu/Fe, and to clarify the mechanism for the influence.

Materials and Methods

Chemicals. HCB (99.0%) was purchased from Shanghai General Reagent Factory, China. TX-100 (analytical purity, 99.0%) was from Amresco 94. All chlorobenzenes were provided by Sigma-Aldrich or Fluka. Cu/Fe bimetal was prepared by the deposition of Cu^{2+} into acid-washed Fe particles⁸. The percentage of Cu in Cu/Fe bimetal was 5%. Kaolin, a representative soils commonly used as model soil in laboratory experiments^{7,9}, was selected in this study. It is weakly acidic (pH 5.75), negatively charged (zero point of charge (ZPC) 3.36) and contains low content of organic matters (0.28%) and low cation exchange capacity (171 mmol kg^{-1})⁷. kaolin was spiked with HCB at 50 mg kg^{-1} dry soil as previously described⁷.

Procedures. All the reduction and adsorption/desorption experiments were carried out in 11-mL glass vials sealed with Teflon screw caps. For the dechlorination experiments, 0.5 g of as-prepared Cu/Fe particulates was mixed with 1 g of HCB contaminated soils and the mixture were further mixed with 10 mL of aqueous solution containing different TX-100 without headspace (120 rpm , $30 \pm 2 \text{ }^\circ\text{C}$). The slurry pH was kept at 3.0 by 0.4 M acetic buffer. At different time intervals, three vials were sacrificed for analysis of aqueous and solid distribution of HCB and dechlorination products. The likewise procedure as previously reported⁸ was used to investigate the dechlorination of various chlorinated benzenes in aqueous solution with and without TX-100. No attempt was used to purge O_2 contained in the solution and vial. Each run was performed at least in triplicate.

For the adsorption of TX-100 on soils and the corresponding desorption of HCB, 1 g of HCB contaminated soil was equilibrated with 10 mL of TX-100 solution at 0, 0.5, 1, 4, 6, 10, 20 mM without pH conditioning (120 rpm , $30 \pm 2 \text{ }^\circ\text{C}$). At certain time intervals, three vials were sacrificed for analysis of aqueous concentration of HCB and TX-100. The solid concentrations of HCB and TX-100 were obtained from the difference of total and aqueous concentration. Each run was performed at least in triplicate.

Analysis. Upon the completion of experiments, the sacrificed vials were centrifuged to separate solution with soils. The solution was first filtered with $0.45 \text{ }\mu\text{m}$ filtration membrane, and 2 mL of solution was extracted with 2 mL of hexane to give aqueous HCB and dechlorination products concentration. Three mL of hexane and 2 mL of deionized water were mixed with the reacted soils to extract the solid HCB and dechlorination products. HCB and dechlorination intermediates in the supernatant were analyzed by a Hewlett-Packard 6890 GC equipped with an electron capture detector (ECD) and a ZB-5 capillary column (Phenomenex, USA). The oven was heated from 160 to $240 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C min}^{-1}$, held for 2 min. The flow rate of carrier gas (nitrogen 99.999%) was 1.5 mL min^{-1} . The injector and detector temperature was 250 and $300 \text{ }^\circ\text{C}$, respectively. The split ratio was 2 and injection volume was $1 \text{ }\mu\text{L}$. The recovery of HCB in the extraction was proved to be above 90%. TX-100 in aqueous solution was measured at 280 nm by a Cary 50 ultraviolet visible spectrophotometer (Varian, USA). The correlation coefficients (R^2) of the fitted line were above 0.990.

Results and discussion

Partition of TX-100 and HCB on solid and solution. The sorption isotherm of TX-100 on soils and the corresponding desorption of HCB from soils were first investigated. Fig. 1a shows that all TX-100 in solution was adsorbed at TX-100 concentration below 2 mM, and the maximal adsorption reached about 38 mmol kg^{-1} . Fig. 1b reveals that HCB desorption became significant when TX-100 concentration exceeded 2 mM. This is in accordance to our previous result that HCB desorption was attributed to the presence of aqueous surfactant micelles⁷. Also, HCB desorption increased with the

increase in aqueous TX-100 concentration, and the maximal desorption achieved 47.5%.

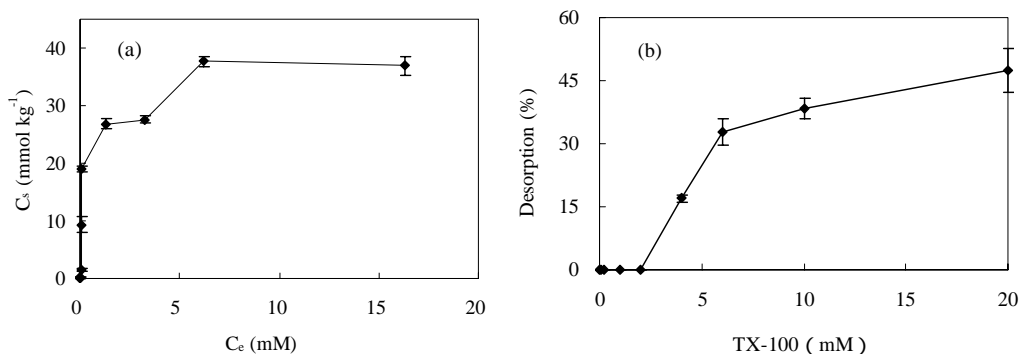
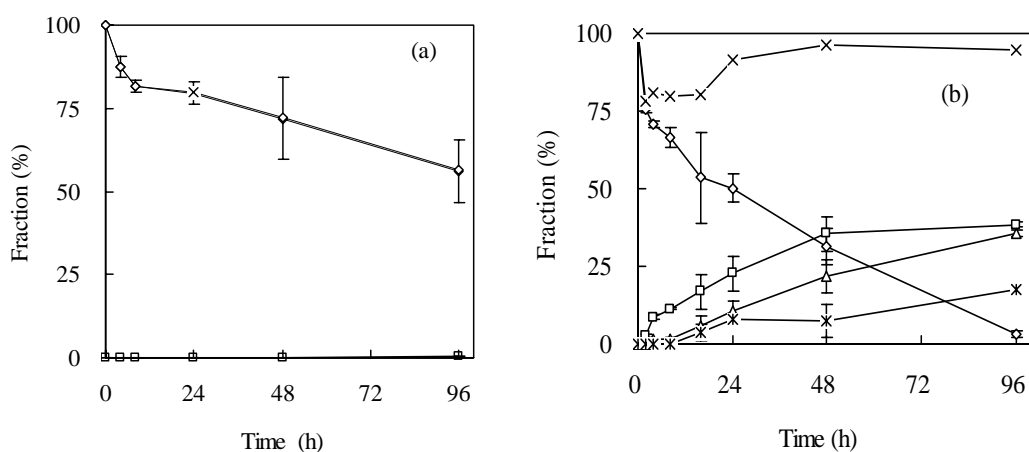


Fig. 1 (a) Sorption isotherm of TX-100 on soils; (b) the corresponding desorption of HCB from soils

Dechlorination of HCB by Cu/Fe in the presence of TX-100. Fig. 2 shows the profiles of HCB dechlorination in the slurry with 0, 1, 4 and 6 mM TX-100. For dechlorination in the slurry, HCB should be desorbed from soil particles and dissolved into solution, transported from solution to Cu/Fe reactive surface, and reduced on the surface. In the absence of TX-100, HCB desorption was rather difficult due to its very weak solubility (1.65×10^{-5} mmol/L⁹). And the small quantities of HCB were preferentially adsorbed on the hydrophobic nonreactive sites of Cu/Fe without TX-100, so a very low dechlorination efficiency was achieved (Fig. 2a). Similarly, Park et al.⁶ also detected minimal destruction of HMX in slurry by ZVI without surfactant.



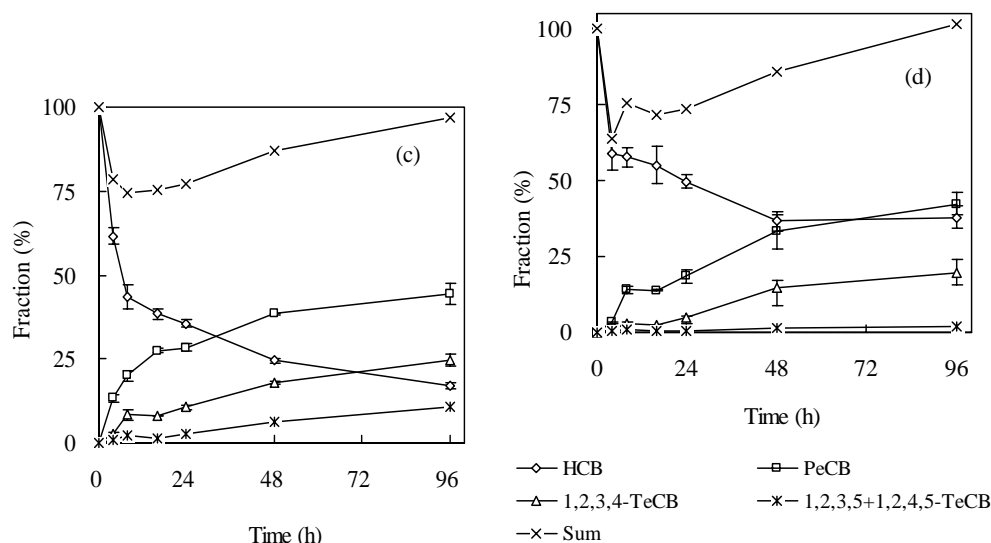


Fig. 2. Dechlorination of HCB with (a) 0 mM; (b) 1 mM; (c) 4 mM and (d) 6 mM TX-100

In the presence of 1 mM TX-100, HCB dechlorination rate was increased from 0.0045 h^{-1} to 0.0332 h^{-1} (74 times) (Table 1), and dechlorination intermediates of pentachlorobenzene (PeCB) and tetrachlorobenzenes (TeCB) were increasingly accumulated (Fig. 2b). From the sorption isotherm of TX-100 (1 mM) on soils (Fig. 1a), the equilibrium aqueous concentration of TX-100 was around 0.06 mM. The aqueous TX-100 concentration was calculated as 0.036 mM provided an individual adsorption of TX-100 on soil and Cu/Fe. This aqueous TX-100 concentration was far less than its CMC (0.11 mM), which had no positive influence on HCB desorption. Thus, it can be deduced that the enhanced HCB dechlorination with 1 mM TX-100 was not attributed to the increased HCB desorption. We have obtained that low concentration of TX-100 significantly increased HCB dechlorination in aqueous solution via facilitated sorption of HCB on the reactive sites of Cu/Fe⁸. So, it can be inferred that the sorption of low concentration of TX-100 on the hydrophobic nonreactive sites of Cu/Fe facilitated HCB transport from solution to the reactive sites of Cu/Fe, led to the decrease of aqueous HCB concentration, and resulted in the replenish desorption of HCB from soils. The continuous dechlorination of HCB on the reactive sites 'dragged' the continuous replenish desorption from soils. Park et al.⁶ also found that cationic surfactant of didecyl greatly increased HMX destruction only at its aqueous concentration below CMC. The facilitated destruction was assumed to be resulted from the increased HMX concentration near reactive ZVI surface by adsorbed didecyl⁶.

When TX-100 concentration rose to 4 mM, the dechlorination of HCB and production of PeCB and TeCB were fast in the initial 24 h and became slower in later stage (Fig. 2c). Similarly, the aqueous equilibrium concentration of TX-100 was calculated as 1.05 mM when individual sorption on soil and Cu/Fe were assumed. This aqueous concentration was much higher than its CMC, and could increase the partition of HCB in solution. Compared with 1 mM TX-100, the fractions of HCB and dechlorination intermediates in solution were markedly increased in the presence of 4 mM TX-100. When aqueous TX-100 concentration exceeded its CMC, it may benefit HCB desorption from solid, including soil and Cu/Fe particles, to solution, and cover the reactive sites on Cu/Fe surface. Facilitated HCB desorption from soils was beneficial to its dechlorination in the slurry, while facilitated desorption from Cu/Fe and TX-100 coverage on Cu/Fe reactive surface exerted negative influence on the dechlorination^{4,8}. As a comprehensive influence, HCB dechlorination at 4 mM TX-100 (0.0124 h^{-1})

was decreased compared with 1 mM (0.0332 h^{-1}) and was increased compared with 0 mM (0.0045 h^{-1}) (Table 1). At TX-100 concentration of 6 mM, the negative influence became more pronounced and HCB dechlorination was further lowered compared with 4 mM (Fig. 2d). The dechlorination rate constant was decreased to 0.0047 h^{-1} , close to that without TX-100. However, the decrease in HCB dechlorination at high TX-100 concentration was far less significant than the decrease in HMX destruction at high concentrations of didycel⁶.

As a consequence, the influence of TX-100 on HCB dechlorination in the slurry by Cu/Fe can be concluded as (1) at aqueous TX-100 concentration below CMC, HCB desorption from soils to solution was unchanged or slightly inhibited, HCB transport from solution to Cu/Fe reactive sites was facilitated via the preferentially adsorbed TX-100 on Cu/Fe nonreactive sites; (2) at aqueous TX-100 concentration above its CMC, HCB desorption from soils to solution was elevated, HCB transport from solution to Cu/Fe reactive sites was lowered because of its increased solubility in solution, and Cu/Fe reactive sites were further covered by TX-100. Thus, increased dechlorination can be achieved at aqueous TX-100 concentration below CMC, while increased or decreased dechlorination at aqueous TX-100 concentration above CMC was determined by the two converse influences. Regarding the influence of surfactant on soil remediation by ZVI, only Park et al. investigated the influence of didycyl on HMX destruction in slurry and proposed that didycyl at low concentration adsorbed on ZVI increased HMX concentration near the reactive surface⁶.

Table 1 Dechlorination rate constants with different TX-100 concentrations

TX-100 concentration	Rate constants (h^{-1})	Coefficient (R^2)
0 mM	0.0045	0.9824
1 mM	0.0332	0.9546
4 mM	0.0124	0.9029
6 mM	0.0047	0.9677

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