Reductive transformation of hexabromocyclododecane (HBCD) by FeS

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ABSTRACT

Both iron monosulfide (FeS) and brominated flame retardants (BFRs) are widely found at relatively high levels in anoxic sediments, but little is known about the reactions of FeS with BFRs. Prior studies showed that FeS was variously reactive with chlorinated organic pollutants in many anoxic environments. It is intuitive that FeS is also reactive with BFRs under anoxic conditions. This study was initiated to test such a hypothesis by quantifying the rates of reductive transformation of tetrabromobisphenol A (TBBPA), decabrominated diphenyl ether (decaBDE) and hexabromocyclododecane (HBCD) using synthetic FeS as the reactive agent. The results showed that over 90% of HBCD was transformed by FeS within 24 h, whereas both TBBPA and decaBDE were found nonreactive within 2 days. The transformation of HBCD followed a pseudo-first-order rate kinetic and the observed rate constants were dependent on the initial concentrations of FeS and HBCD. The transformation rates of β- and γ-HBCD were significantly faster than that of α-HBCD. Analysis of bromine ion and other transformation products suggested that sequential dibromoelimination to form 1,5,9-cyclododecatriene was likely to be a dominant pathway for the reductive transformation of HBCD by FeS. Surface characterization of FeS by XPS indicated that both Fe(II) and S(-II) on the FeS surface might have contributed considerably to the transformation of HBCD. These findings imply that FeS may play an important role in natural attenuation of HBCD and that it may be used as a reactive agent for treating HBCD-contaminated sediments.

1. Introduction

Tetrabromobisphenol A (TBBPA), decabromodiphenyl ether (decaBDE) and hexabromocyclododecane (HBCD) are high production volume brominated flame retardants (BFRs). The global demands of these three typical BFRs in 2001 were 119 700, 56 100 and 16 700 tons, respectively (Hale et al., 2006). Due to their extensive use and improper disposal, the widespread occurrence of these BFRs in various environmental compartments has been well documented (Kefeni et al., 2011; Law et al., 2014). Moreover, there is increasing evidence for the endocrine, reproductive and behavioral effects of these BFRs on biota (Lyche et al., 2015), which has led to HBCD being included in Annex A of the Stockholm Convention on Persistent Organic Pollutants in 2013 (Stubbings and Harrad, 2014). Therefore, an urgent need is to improve our understanding of the environmental fates of these BFRs and to

develop effective approaches for dealing with the relevant environmental contamination.

Due to their low aqueous solubility (<0.8 mg L^{-1}) and high log K_{ow} (>4.5), TBBPA, decaBDE and HBCD are expected to undergo adsorption on solid particles of various environmental matrices (de Wit, 2002). As a major and final sink of BFRs, anoxic sediments may have retained a large quantity of TBBPA, decaBDE and HBCD (Bogdal et al., 2008; Chen et al., 2007; Yang et al., 2012). Indeed, high levels of these BFRs have been detected in various sediments from different countries around the world (see Table A1 in Supplementary Data for some examples), with the highest concentrations of TBBPA, decaBDE and HBCD exceeding 9.8, 44 and 27 mg kg^{-1} dry weight, respectively (La Guardia et al., 2013; Morris et al., 2004). Therefore, understanding of the fates of these BFRs in anoxic sediments is critical to quantifying their ultimate fates in the aquatic environment.

Reductive dehalogenation mediated by anaerobic microbes is an important route for transformation of many persistent halogenated compounds in anoxic sediments (Zanaroli et al., 2015). Growing

evidence indicates that TBBPA and HBCD can be biodegraded via reductive dehalogenation in anoxic sediments (Davis et al., 2005, 2006; Ronen and Abeliovich, 2000; Voordeckers et al., 2002). For examples, Voordeckers et al. (2002) observed microbial dehalogenation of TBBPA to bisphenol A in anoxic sediments, and Davis et al. (2006) reported sequential debromination of HBCD by microbes in anoxic sediments via a series of dihaloelimination steps. However, several studies showed that biodegradation of decaBDE could be very slow (La Guardia et al., 2007; Tokarz et al., 2008; Zhu et al., 2014). It should be noted that the growth and activity of indigenous dehalorespiring microbes are usually prone to shifts of various environmental factors, which can considerably affect the effectiveness of these microbes (Zanaroli et al., 2015).

Another important route for transformation of many BFRs in anoxic sediments is abiotic reductive dehalogenation. Recent studies showed that zero-valent iron (ZVI) could reductively transform TBBPA, decaBDE and HBCD, and that the reduction rates tended to increase with increasing surface area of ZVI (Keum and Li, 2005; Lin et al., 2012; Tso and Shih, 2014; Yu et al., 2012; Zhuang et al., 2012). Bimetallic nanoparticles (such as Ni/Fe, Pd/Fe and Ag/Fe) were also reported to be able to rapidly debrominate either TBBPA or decaBDE (Fang et al., 2011; Huang et al., 2013; Luo et al., 2010). However, the abilities of naturally occurring solid reductants in sediments to transform BFRs are poorly studied.

Reduced sulfur species are the natural reductants in anoxic environments that can mediate the reductive dehalogenation of BFRs. Lo et al. (2012) reported that polysulfides (S_n^{2-}) and bisulfide (HS^-) were able to reductively dehalogenate HBCD. Keum and Li (2005) found that 33% of decaBDE was degraded in sodium sulfide solution within 14 days, having the degradation product profile similar to that of ZVI treatment. The sulfur species demonstrated to function as reductants in these studies are dissolved sulfuric ions, having high affinity for many heavy metals to form metallic sulfides in the natural anoxic environments (Richard and Luther, 2007). To date, however, very little is known about the effects of low water soluble metallic sulfide minerals, such as iron monosulfide (FeS), on the environmental fates of BFRs. The only one study involved in this topic was performed by Keum and Li who reported that 2% of decaBDE was transformed by a commercial FeS over a reaction time period of 14 days (Keum and Li, 2005).

FeS is a reductive mineral that occurs naturally in many anoxic environments (Richard and Luther, 2007). Although FeS is generally considered to be metastable and can be transformed to pyrite (FeS_2), anomalous enrichment of this mineral under anoxic conditions likely occurs when the pyrite formation is retarded by various geochemical factors (Hurtgen et al., 1999; Kraal et al., 2013). In fact, FeS accumulation at a level greater than 10 μmol g^{-1} dry weight has been reported in a variety of anoxic sediments (see Table A2 for some examples), with the highest FeS content exceeding 0.37 wt% dry weight (Hurtgen et al., 1999). More importantly, prior studies have reported the capacity of FeS to reductively dehalogenate a range of chlorinated organic pollutants such as γ-hexachlorocyclohexane, carbon tetrachloride, hexachloroethane, and trichloroethylene (Butler and Hayes, 1998; He et al., 2010; Liu et al., 2003). It is intuitive that FeS may play an important role in abiotic reductive dehalogenation of many BFRs in anoxic sediments.

To test such a possibility, we synthesized FeS and further estimated its reactivity with three typical BFRs (i.e., TBBPA, decaBDE and HBCD) under anoxic conditions, with an emphasis on the reaction rate and mechanism. Our results can help to improve our understanding of the environmental fates of BFRs in reducing environments (especially anoxic sediments) and facilitate the development of a remedial option that can be employed in anoxic environments contaminated by BFRs.

2. Materials and methods

2.1. Synthesis and characterization of FeS

Chemicals used in this study were HPLC grade where available and otherwise were analytical grade (see Text A1 in Supplementary Data for more details). FeS was synthesized by mixing $FeCl_2$ and Na_2S in a glovebox (Super 1220/750, Mikrouna Co. Ltd., Shanghai, China) filled with high purity N_2 (99.999%) according to the method described in Liu et al. (2003) with minor adjustments. In brief, 250 mL of 0.2 M Na_2S was slowly added into 250 mL of 0.2 M $FeCl_2$ in a container on a magnetic stir plate. After aging for 3 days, the FeS precipitate was centrifuged, washed with fresh deoxygenated water, dried under N_2, and stored in the glovebox until used in subsequent experiments. The N_2-gas BET analysis showed that the obtained FeS had a specific surface area of 33.6 m^2 g^{-1}, which was comparable to that (36.5 m^2 g^{-1}) of the FeS synthesized by Rickard (1997) with a similar method. XRD analysis indicated that the FeS solid might be poorly crystalline mackinawite (Fig. A1 in Supplementary Data), being consistent with the finding of Jeong et al. (2008). More details on the surface characterization of FeS are provided in Text A2 and Fig. A1.

2.2. Batch rate experiments

Batch experiments were conducted to quantify the transformation rate for each of the three typical BFRs in the presence of FeS and under room temperature (about 25 °C) conditions. To ensure anoxic condition, the reactors (4 mL screw-capped vials) were prepared and mixed within the glovebox. All experiments were initiated by mixing a small amount of stock solution of a given individual BFR (prepared in ethanol) with 2 mL of FeS slurry (prepared in water). The initial concentrations of FeS ranged from 0.6 to 13.7 mg L^{-1}, a range that may be found in anoxic sediments (Table A2). The initial concentrations of TBBPA, decaBDE, and HBCD ranged from 0.5 to 4 mg L^{-1}, which were well within the concentration ranges of these BFRs detected in contaminated sediments (Table A1). In order to examine the effect of ethanol as a co-solvent on the reaction between HBCD and FeS, a series of ethanol-water mixtures were used to dissolve HBCD, with ethanol content varying from 2% to 80% (v/v). The initial solution pH (prepared in Mini-Q water) was 6.8, which was chosen to simulate natural aquatic environments normally having the neutral pH range 6—8. More details on the compositions of the reaction solutions are given in Table 1. After mixing of FeS with a given BFR solution, the reactors

Table 1
The fitted parameters (i.e., k_{obs}, R^2 and the estimated half-lives) for the pseudo-first-order reactions between the three typical BFRs and FeS under different experimental conditions.

	$[BFRs]_0$	$[FeS]_0$	Ethanol content	k_{obs}	$t_{1/2}$	R^2
TBBPA	2	5.5	2	—	—	—
decaBDE	1	5.5	2	—	—	—
HBCD	0.5	5.5	2	36.7 ± 3.3	18.9	0.98
	1	5.5	2	53.9 ± 3.0	12.9	0.98
	2	0.6	2	3.0 ± 0.3	230	0.97
	2	2.7	2	38.2 ± 3.8	18.1	0.96
	2	5.5	2	85.5 ± 5.2	8.1	0.98
	2	5.5	40	39.9 ± 5.2	17.4	0.92
	2	5.5	80	1.7 ± 0.4	408	0.82
	2	9.1	2	77.3 ± 7.4	9.0	0.94
	2	13.7	2	68.4 ± 4.2	10.1	0.97
	3	5.5	2	44.4 ± 5.7	22.6	0.82
	4	5.5	2	4.8 ± 0.8	147	0.87

$[BFRs]_0$ and $[FeS]_0$: mg L^{-1}; Ethanol content, % (v/v); k_{obs}, ($\times 10^{-3}$ h^{-1}); $t_{1/2}$, h; —, Not calculated.

were capped and placed on an end-over-end rotator in the glove-box. Three vials were taken from the glovebox at each pre-determined sampling time for analysis of each of the three BFRs. Control reactors without FeS addition were run concurrently.

A preliminary experiment was conducted to compare the extraction recoveries of the three BFRs by common organic solvents (i.e. methanol, hexane, or toluene) using different extraction methods (see SI Tables A3 and A4 for more details). The results showed that methanol, hexane, and a mixture of methanol and toluene (v/v, 1/1) gave the best extraction recoveries for TBBPA (100.3%), decaBDE (100.8%), and HBCD (98.7%), respectively (see SI Tables A3 and A4). Therefore, the three different solvents (or sol-vent mixture) and their associated extraction procedures were employed to extract BFRs residues in the reaction solutions. Some details on the extraction methods were described below. The method for TBBPA was largely adapted from that of Lin et al. (2012). Briefly, 20 μL of concentrated HCl (12 M) was used to facilitate the release of TBBPA from FeS into the reaction solutions and the resulting supernatants were extracted twice with 1 mL of methanol for 10 min. TBBPA in the two extracts was combined and subse-quently analyzed by a HPLC (LC-20AB, Shimazu, Kyoto, Japan). A similar method was used to extract decaBDE residues from its re-action solutions, except that hexane rather than methanol was used as the extractant. The decaBDE extracted was analyzed by a GC-ECD (GC-2010, Shimazu, Kyoto, Japan). In the extraction procedure of HBCD, concentrated HCl could not be used because the H_2S or HS^- formed by the reaction between concentrated HCl and FeS might influence the transformation of HBCD (Lo et al., 2012). Instead, 20 μL of 5 M NaCl was added into the reaction solutions to enhance the aggregation of FeS particles (Rickard, 2006); and then, the so-lutions were centrifuged at 10 000 rpm for 10 min to separate FeS solids from the solutions. After centrifugation, the supernatants were extracted twice with 1 mL of hexane for 10 min and the FeS solids were extracted twice with 1 mL of a methanol/toluene (1/1, v/v) mixture for 10 min. The resulting extracts were combined and used for HBCD analysis by the GC-ECD. While the total concentra-tions of HBCD were determined by the GC-ECD, α-, β- and γ-HBCD were analyzed by a HPLC (Agilent 1100, Agilent Technologies, CA, USA) equipped with a TQMS (Sciex API 4000, Applied Biosystems, CA, USA). More details on instrumental analysis of TBBPA, decaBCE, HBCD and its isomers were described in SI Text A3.

To validate the extraction and analysis procedures, reagent blank, FeS blank, BFR control, and spiked control samples were used. Specifically, reagent blank, FeS blank and BFR control referred to the reaction solution (water/ethanol mixture; v/v, 98/2), the reaction solution with FeS addition and the reaction solution with addition of individual BFRs, respectively. Spiked control samples were prepared by spiking individual BFRs into FeS blank. Addi-tionally, the internal standards (tetrachlorobisphenol A for TBBPA, and hexabromobenzene for decaBDE and HBCD) were added to the spiked control samples before extraction. While no BFRs were detectable in the blank samples, the recoveries of the three BFRs (and the internal standards) from the control samples were greater than 98.5% with a standard deviation less than 1.5% (see SI Table A5 for more details).

2.3. Identification of HBCD transformation products

A separate experiment was performed to identify HBCD trans-formation products as the batch experiment results showed rapid transformation of HBCD in the presence of FeS. To obtain sufficient mass of the products, a larger reaction system (50 mL of reaction solution in a 100 mL glass bottle) and an elevated initial concen-tration of reactants (20 mg L^{-1} HBCD and 137 mg L^{-1} FeS) were used. The other experimental conditions were kept the same as

those of batch rate experiments. At predetermined time intervals, three bottles were taken from the glovebox for the analysis of transformation products. The reaction solution (solid-liquid mixture) in each of the bottles was divided into two fractions: 2 mL for determination of Br^- and the remaining solution for the analysis of the transformation products.

The aliquots used for quantifying Br^- were centrifuged at 10 000 rpm for 10 min. After centrifugation, the FeS solids were washed three times with 10 mL of 1 mM HCl solution to desorb Br^-. The HCl eluents were combined with the supernatants from centrifugation and the mixtures were used for analyzing Br^- on an ICP-MS (Agilent 7700×). For the analysis of the transformation products, the larger aliquots were centrifuged at 10 000 rpm for 10 min. The supernatants were extracted twice with 10 mL of hexane and the FeS solids were extracted three times with 5 mL of methanol/toluene mixture (1/1, v/v). The resulting extracts were combined, dried under N_2, redissolved in hexane, and then analyzed with a GC-MS (QP2010Plus, Shimazu, Kyoto, Japan). We converted the solvent matrix from polar methanol/toluene mixture to nonpolar hexane matrix before GC-MS analysis to avoid the damages of polar solvents to the weakly polar capillary chro-matographic column used in this study.

The FeS solids after reaction with HBCD in the water/ethanol (v/v, 98/2) solution for 2 days (referred to as HBCD-reacted FeS) were obtained by centrifugation, given that HBCD in the reaction solu-tions was transformed completely. The wet FeS solids were dried under N_2, and used for analysis of the chemical composition and oxidation states of Fe, S and O species on FeS surface by a XPS (see Text A2 for details). The other two types of FeS samples (i.e. FeS before reaction and FeS after reaction with the water/ethanol so-lution for 2 days, referred as to Blank FeS and Control FeS, respec-tively) were also obtained and subjected to XPS analysis. The method described by Jeong et al. (2010) was used to fit our XPS data. Detailed information on the instrumental analysis conditions of this study is provided in Text A3.

3. Results and discussion

3.1. Contrasting transformation patterns of TBBPA, decaBDE and HBCD

Due to the frequent co-occurrence of TBBPA, decaBDE and HBCD in various anoxic sediments (Chen et al., 2013; Feng et al., 2012; Lee et al., 2015; Verslycke et al., 2005), studying their transformation patterns under the same conditions is important not only for a better understanding of their environmental fates, but also for the development of suitable remediation approaches for sediments co-contaminated by these BFRs. Surprisingly, little such empirical research has been done. This study was among the first to study the abiotic transformation patterns of these BFRs under the same conditions, although their biodegradation patterns under anaerobic conditions in the same sewage sludge were investigated by Gerecke et al. (2006) who found that the biodegradation rates were in the decreasing order of TBBPA > HBCD ≫ decaBDE. As indicated in Fig. 1, no remarkable transformation was observed for both TBBPA and decaBDE by the synthetic FeS in a water/ethanol (98/2, v/v) solution within the time period of this study (48 h). This was consistent with the observation of Keum and Li (2005) who re-ported that only 2% of decaBDE was transformed by a commercial FeS within 14 days. Contrarily, it was found that over 90% of HBCD was transformed within 48 h by the synthetic FeS in a water/ ethanol (98/2, v/v) solution (Fig. 1). The rapidly abiotic trans-formation of HBCD by FeS observed in this study indicated that FeS may have a pronounced impact on the persistence of HBCD in anoxic sediments even in a relatively short period of time. However,
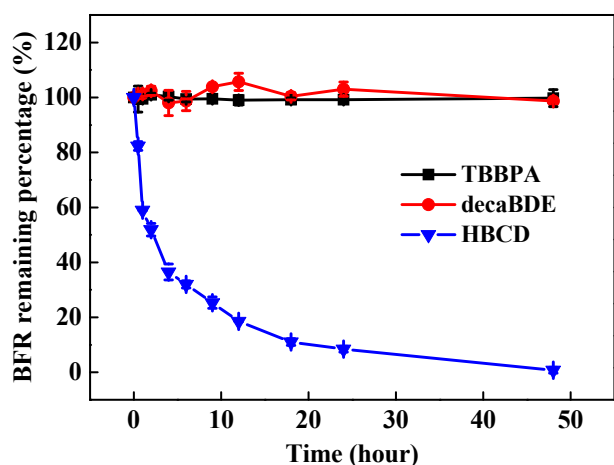
Fig. 1. Transformation of TBBPA, decaBDE and HBCD by FeS within 48 h. The $[FeS]_0$, $[TBBPA]_0$, $[decaBDE]_0$ and $[HBCD]_0$ were 5.5, 2, 1 and 2 mg L^{-1}, respectively.

whether TBBPA and decaBDE are persistent in anoxic FeS-rich environments over longer periods of time (e.g. weeks to months) is required to be studied in the future.

3.2. Diastereomer-specific transformation of HBCD

Within the time period of this study, HBCD transformations by the synthetic FeS could be approximated as pseudo-first-order kinetics (Fig. 2A). As indicated by the R^2 values, the data of total HBCD, α- and γ-HBCD showed a better fit for a pseudo-first-order kinetic model than that of β-HBCD (Fig. 2A). Nonetheless, it is remarkable that the three major HBCD diastereomers appeared to

have been transformed at different rates. The observed rate constant value was the highest for β-HBCD (131×10^{-3} h^{-1}), followed in descending order by γ-HBCD (107×10^{-3} h^{-1}) and α-HBCD (41.4×10^{-3} h^{-1}). A similar phenomenon was reported by Lo et al. (2012) who studied the abiotic transformation of HBCD by dissolved S_n^{2-} and HS^- (prepared as Na_2S). In addition, Gerecke et al. (2006) observed that the biodegradation rates of β- and γ-HBCD in digested sewage sludge under anaerobic conditions were 1.6–1.8 times faster than that of α-HBCD. The preferred transformation of β- and γ-HBCD suggested less resistance of these two isomers under environmental conditions, being consistent with the common finding that α-HBCD is the dominant HBCD isomer found in many anoxic environmental matrices (Kefeni et al., 2011; Law et al., 2014). Note that isomers-specific biotic and abiotic transformation were also observed for hexachlorocyclohexane (HCH, with similar stereochemistry to HBCD), which was attributed at least partly to the fact that HCH isomers differed in the numbers of vicinal and antiparallel chlorine atoms (Beurskens et al., 1991). Such a mechanism, however, seems inapplicable to our results, given that α-, β- and γ-HBCD have identical vicinal and antiparallel dibromides (Heeb et al., 2007). Instead, it was reported that α-HBCD has a square-like and highly symmetrical conformation, which is not observed in the other HBCD isomers (Heeb et al., 2008). This special conformation is thought to display increased stability (Heeb et al., 2008), providing one possible explanation for the observed recalcitrance of α-HBCD. Despite this, further study is needed to get a better understanding of the mechanisms underlying the diastereomer-specific transformation of HBCD.

3.3. Effect of cosolvent on transformation of HBCD

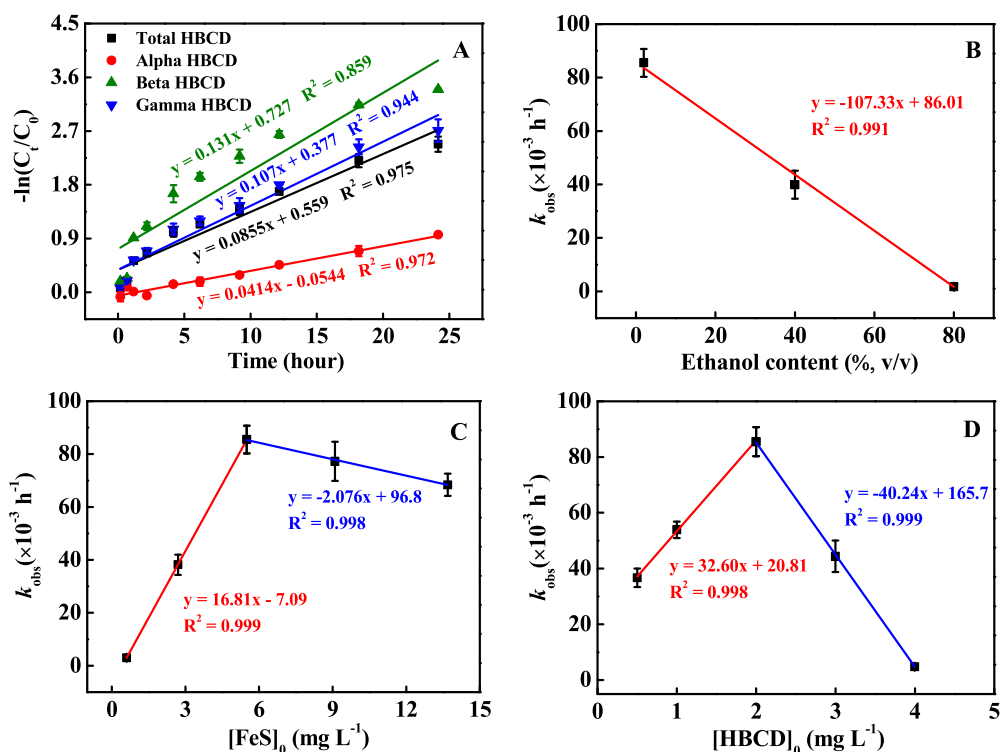Due to the hydrophobicity of BFRs, water/cosolvent mixtures

Fig. 2. Pseudo-first-order kinetics for HBCD transformation by FeS and the effects of three major factors on kinetic rate constant (k_{obs}). (A) the transformation kinetics of total HBCD and the three major isomers; (B) the effect of ethanol content; (C) the effect of $[FeS]_0$; and (D) the effect of $[HBCD]_0$. When the effect of a given factor was examined, the other two factors were kept constant: $[FeS]_0$, $[HBCD]_0$, and ethanol content were kept at 5.5, 2 mg L^{-1} and 2%, when necessary. See Table 1 for details on the experimental conditions. The correlations shown were statistically significant ($P < 0.05$).

having a cosolvent content $\geq$50% (v/v) were frequently used in the literature to prepare reaction solutions for studying their abiotic transformation (Lin et al., 2012; Lo et al., 2012; Tso and Shih, 2014). However, the absence of such mixtures in environmental matrices raises a question concerning the environmental relevance of these previous studies. In an attempt to address this issue, the effect of cosolvent (ethanol) on the rate of HBCD transformation by the synthetic FeS was examined in this study. It was found that the HBCD transformation rates (k_{obs}) in the water/ethanol mixtures decreased linearly as the ethanol content increased from 2% to 80% (Fig. 2B and Table 1). This result was clearly consistent with the notion that an increase in the content of cosolvent in water/cosolvent mixtures can decrease the absorption of organic contaminants (such as BFRs) on surface of solid reductants/oxidants and thereby decreases their transformation rates (Tso and Shih, 2014; Yu et al., 2012). It also indicated that the HBCD transformation by the synthetic FeS was largely a surface-mediated reaction in which the close attachment of HBCD to FeS surface enabled the electron transfer (as discussed further in another section below). Moreover, by extrapolating the best-fit linear relationship between ethanol content and the k_{obs} value (Fig. 2B) to a more realistic situation where the ethanol content is equal to zero, we found that the theoretical k_{obs} (0.0860 h^{-1}) for this situation was very similar to the k_{obs} (0.0855 h^{-1}) for the water/ethanol (98/2, v/v) mixture that was chosen as a reaction solution in other experiments of this study. This similarity was important since it could be considered as a plausible reflection of the environmental relevance of our results.

3.4. Effects of initial concentrations of FeS and HBCD on transformation of HBCD

It is interesting to note that initial concentrations of FeS and HBCD had significant effects on HBCD transformation. As shown in Fig. 2C and Table 1, the transformation rate of HBCD (k_{obs}) increased linearly when the initial concentration of FeS ([FeS]$_0$) increased from 0.6 to 5.5 mg L^{-1}, which could be attributed to the increased reactive sites (FeS surfaces) due to the elevated amount of FeS in the reaction mixtures. However, the k_{obs} decreased gradually as the [FeS]$_0$ increased from 5.5 to 13.7 mg L^{-1}. It was likely that further increase of [FeS]$_0$ might have increased aggregation tendency and hence reduction of effective surface areas as the FeS concentration increased beyond 5.5 mg L^{-1} (Michel et al., 2005; Yu et al., 2012). The increased aggregation tendency of FeS might also have slowed the diffusion of HBCD to the reactive FeS surfaces (Michel et al., 2005; Yu et al., 2012), even if it had not decreased the amount of reactive FeS surface area. To test these two hypotheses, we further examined the effect of initial concentration of HBCD ([HBCD]$_0$) on the k_{obs} by setting out a batch experiment with constant [FeS]$_0$ at 5.5 mg L^{-1}. If the second hypothesis was valid, the k_{obs} would increase (or at least level off) as [HBCD]$_0$ increased from 2 mg L^{-1} to a higher concentration. It was found, however, that the k_{obs} of HBCD increased linearly in the range of 0–2 mg L^{-1} and decreased in the range of 2–4 mg L^{-1} (Fig. 2D). A similar pattern was also reported by Luo et al. (2010) in an effort to explore the effect of initial concentration of Fe–Ag bimetallic nanoparticles on the transformation rate of TBBPA. Our results suggested that the HBCD transformation capacity of the synthetic FeS reached its maximum near the concentration ratio of [FeS]$_0$/[HBCD]$_0$ = 2.25, indicating FeS could have a reinforcing effect on the environmental fate or remediation efficiency of HBCD when FeS and HBCD were present in a concentration ratio around 2.3.

3.5. Transformation products and pathway of HBCD

No definitive evidence is currently available on the ability of abiotic reductants to transform HBCD in reaction mixtures into the completely debrominated product 1,5,9-cyclododecatriene (CDT), although it was reported that HBCD could be transformed biotically into CDT (Davis et al., 2006). To our knowledge, only two attempts have been made in recent years to identify the products of HBCD transformation by abiotic reductants in reaction mixtures. Lo et al. (2012) reported two unknown products for the transformation of HBCD by reduced sulfur species, whereas Tso and Shih (2014) found two 'known' products [dibromocyclododecadiene (DBCDi) and CDT] for the transformation of HBCD by nanoscale ZVI. However, these proposed products were not confirmed since no authentic standards were used to identify products in these two studies. In this study, three isomers of CDT (including t,t,t-1,5,9,-CDT and t,t,c-1,5,9-CDT) were identified by comparing their mass spectra with those of the corresponding authentic standards (Fig. 3A; see Text A4 and Table A6 for more details on the identification). This finding provided definitive evidence for the ability of the synthetic FeS to completely debrominate HBCD. Yet, our results on additional transformation products indicated that only a fraction of the HBCD in the reaction mixtures was debrominated completely by the synthetic FeS into CDT within the time frame of this study. On the one hand, two tetrabromocyclododecene (TBCDe) isomers and five DBCDi isomers were identified as less brominated BCD intermediate products (see Text A4 and Table A6 for more details on the identification) by comparing their mass spectra with those of the corresponding transformation products reported in the literature (Barontini et al., 2001; Davis et al., 2006). Moreover, most of these intermediate products were still observed at the end of the experiment (48 h, Fig. 3B). On the other hand, the molar ratio of the Br^- generated to the HBCD removed increased with time and finally reached a value of approximately three (48 h, Fig. 4), which was apparently lower than the expected value (six) for the assumed complete debromination of HBCD into CDT.

Based on the transformation products identified in this study, a tentative pathway for the complete debromination of HBCD by FeS was proposed (Fig. 3C). In short, the pathway comprised three reaction steps, wherein HBCD might be sequentially debrominated via dibromoelimination to form TBCDe, DBCDi and CDT, respectively. During each step, two Br atoms could be removed from two vicinal carbons and a double bond was subsequently formed between the two adjacent carbon atoms. Such a pathway was believed to be also operative in the microbially mediated debromination of HBCD (Davis et al., 2006), whilst part of this pathway has been proposed recently for the reductive debromination of HBCD by nanoscale ZVI (Tso and Shih, 2014). The scenario that abiotic and biotic reductive debromination of HBCD may share some common reaction steps deserves further investigation, since it likely has important implications for the remediation of anoxic sediments contaminated by HBCD.

3.6. Mechanisms of surface-mediated transformation of HBCD

Surface-mediated reductive transformation of certain chlorinated organic pollutants (e.g. hexachloroethane and γ-hexachlorocyclohexane) and inorganic pollutants (e.g. selenium) by FeS have been reported extensively (Butler and Hayes, 1998; Han et al., 2013; Liu et al., 2003). It can, therefore, be expected that the efficient HBCD transformation observed in this study is largely a surface-mediated process. In an attempt to test this expectation, we conducted additional experiments of HBCD debromination without FeS solid surfaces. The results showed that no significant HBCD transformation (<5%) occurred 48 h after the addition of HBCD (2 mg L^{-1}) into a 0.2 M FeCl$_2$ solution (Fig. A2; see also Text A5) or the solution obtained by removing solid phase through centrifugation from a FeS slurry (5.5 mg L^{-1}, approximately equal to
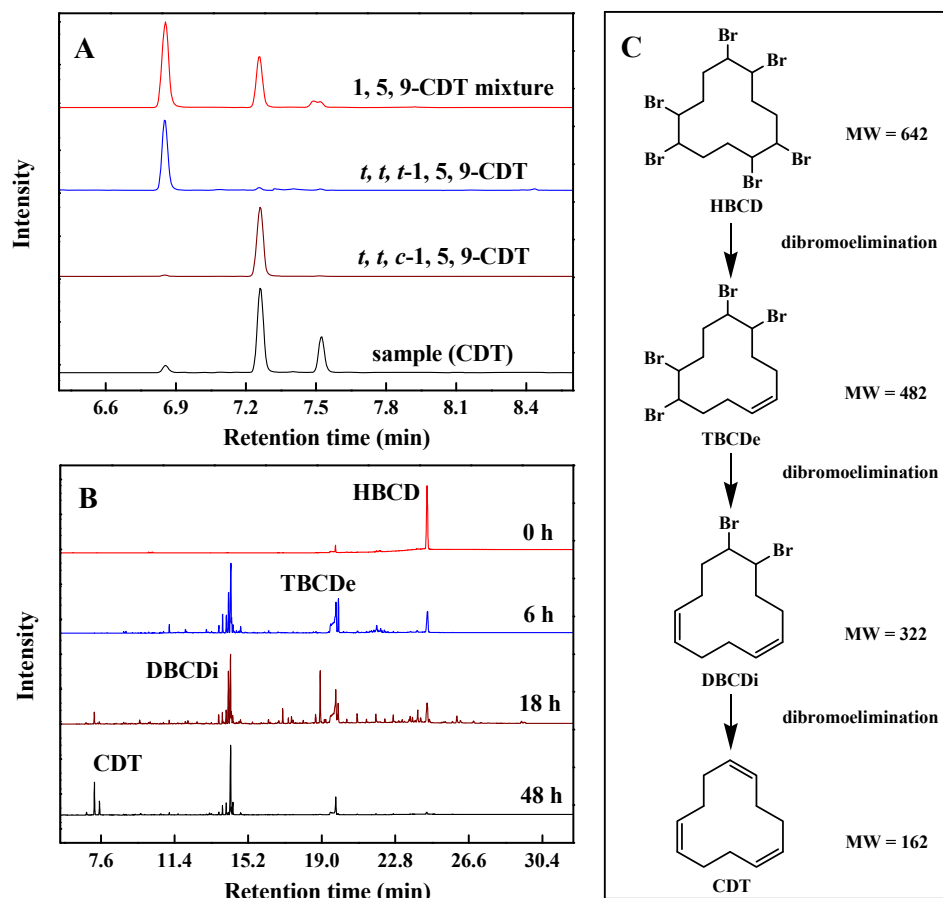
Fig. 3. GC-EI/MS chromatograms of the products and proposed pathway of HBCD transformation by FeS. (A) GC-EI/MS chromatograms of the authentic standards of 1,5,9-CDT mixture, *t,t,t,*-1,5,9-CDT and *t,t,c,*-1,5,9-CDT and those of CDT isomers in the samples; (B) GC-EI/MS chromatograms of the products of HBCD transformation at different sampling time points; and (C) proposed transformation pathway.
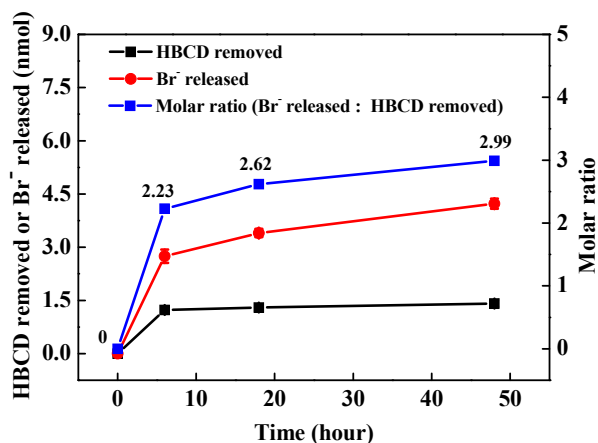

Fig. 4. The amounts of HBCD removed by FeS, the amounts of Br^- released, and their corresponding molar ratios. Values at different sampling time points within 48 h of the reaction are shown. $[HBCD]_0$ and $[FeS]_0$ were 20 and 137 mg L^{-1}, respectively.

0.063 mM). Additionally, it was found that the proportion of HBCD transformed (approximately 50%, Fig. A2) within 48 h observed in a 0.2 M Na_2S solution (whose S level being at least 3200 times higher than that of 5.5 mg L^{-1} FeS) was remarkably lower than that recorded in the presence of 5.5 mg L^{-1} FeS (95%, Fig. 1). These results were consistent with our expectation as to the dominant role of the FeS surface in HBCD transformation.

Our XPS analyses of the surfaces of blank, control and HBCD-reacted FeS provided insights into the mechanisms of the surface-mediated transformation of HBCD. As shown in Table 2, the relative area of the peaks associated with Fe(II)−S on the surface of HBCD-reacted FeS was apparently lower than those for blank and control FeS (also see Fig. A3), whereas an opposite pattern was observed for Fe(III)−S. A similar phenomenon was reported by Scheinost et al. (2008) who employed XPS to investigate the changes of the surface Fe species on FeS after the mineral was used to reduce selenium(IV). Note that a slight increase in the relative area of the peaks associated with Fe(III)−O was recorded in HBCD-reacted FeS (Table 2), indicating the concurrence of Fe(III) (oxyhydr) oxide formation and HBCD transformation. These results presented evidence that Fe(II) on the FeS surface was oxidized into Fe(III) during the reduction of the adsorbed HBCD. According to the $S(2p_{3/2})$ spectra, the relative area of the peak associated with bulk S^{2-} on surface of HBCD-reacted FeS was markedly lower than those for blank and control FeS, although only a minor increase in surface S^{2-} was observed in HBCD-reacted FeS (Table 2). The remarkable decrease in bulk S^{2-} could be considered as evidence for an increase in surface defects resulted from the oxidation of surface-bound S^{2-} (Scheinost et al., 2008). Indeed, an increase in the relative area of the peaks associated with S_2^{2-} (disulfide) and S_n^{2-} (polysulfide) was observed in surface of HBCD-reacted FeS (Table 2), providing further evidence that the S^{2-} at surface defects might have been oxidized (Scheinost et al., 2008; Jeong et al., 2010). As to the O(1s) spectra, the relative area of the peak associated with H_2O on surface of HBCD-reacted FeS was considerably lower than

Table 2
XPS binding energies (BE) of Fe(2p$_{3/2}$), S(2p), and O(1s) and the relative abundances of Fe, S and O species on the surfaces of different FeS samples.

Species	BE (eV)[a]	Relative abundance (area, %)		
		Blank FeS[c]	Control FeS	HBCD-reacted FeS
Fe(2p$_{3/2}$)				
Fe(II)—S	706.7	62	56	47
	707.7			
	708.7			
	709.7			
Fe(III)—S	708.2	27	34	40
	709.2			
	710.2			
	711.2			
Fe(III)—O	711.1	11	10	13
	712.1			
	713.1			
	714.1			
S(2p$_{3/2}$)[b]				
Surface S^{2-}	160.9	19	19	21
Bulk S^{2-}	161.6	53	52	41
S$_2^{2-}$	162.3	15	16	21
S$_n^{2-}$	163.3	13	13	17
O(1s)				
O^{2-}	530.3	16	24	33
OH$^-$	531.4	38	41	47
H$_2$O	532.8	46	35	20

[a] The binding energies are correct within ±0.2 eV.

[b] The S(2p) spectra was fitted using the doublets of S(2p$_{3/2}$) and S(2p$_{1/2}$) separated by 1.18 eV with their peak area ratio being 2:1. Although only the S(2p$_{3/2}$) peak position was indicated, the area for S(2p) included those for S(2p$_{3/2}$) and S(2p$_{1/2}$).

[c] Blank, Control, and HBCD-reacted FeS referred to FeS before reaction, FeS after reaction with the water/ethanol solution (v/v, 98/2) for 2 days, and FeS after reaction with HBCD in the water/ethanol solution for 2 days, respectively.

those for blank and control FeS, whereas the opposite was true for OH$^-$ (Table 2). This observation was consistent with the finding of Han et al. (2013) who proposed that a major source of surficial OH$^-$ is H$_2$O sorbed on the FeS surface. Additionally, an elevated relative area of the peak associated with O^{2-} was recorded for HBCD-reacted FeS, indicating that more Fe(III)-containing (oxyhydr)oxide precipitates would be formed on the FeS surface if the reaction time is extended (Jeong et al., 2010). In fact, an increase in relative area of the peak associated with Fe(III)—O was recorded by Han et al. (2013) when they compared the Fe(2p$_{3/2}$) spectra of FeS reacted with selenium(IV) for one day to that for 30 days. Collectively, our XPS data provided direct evidence that both Fe(II) and S(-II) on the surface of the synthetic FeS were oxidized during the debromination of HBCD by FeS, indicating their involvement in the process. It should be noted that Scheinost et al. (2008) proposed a similar mechanism for surface-mediated selenium(IV) reduction by FeS and Sivavec et al. (1995) attributed trichloroethylene reduction by FeS to the surface-bound Fe(II) but not S(-II) species. Additional research is needed for distinguishing the relative importance of the two surface-bound functional groups in facilitating reduction of various pollutants by FeS.

4. Conclusions

The most important finding of this study is that the synthetic FeS was able to rapidly transform HBCD with a half-life of about 8 h. Moreover, this finding was obtained under the experimental conditions mimicking situations in real environments. For instance, both [FeS]$_0$ and [HBCD]$_0$ used in this study cover a range of concentrations that may occur in naturally anoxic sediments. Therefore, this study not only provides the clue that the reductive transformation by FeS may significantly impact the environmental fates of HBCD in anoxic sediments, but also suggests the possibility that FeS may be used for remediation of various anoxic

environments contaminated by HBCD. Yet, given the complexity of real environments, further studies are needed to examine the potential variations of HBCD transformation by FeS under varying environmental conditions, before FeS can be applied in practice for HBCD remediation.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.05.066.

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