Biodegradation of polybrominated diphenyl ethers and strategies for acceleration: A review

Chenghao Zhao[a,c], Ming Yan[a,c,*], Hua Zhong[a,b,c,**], Zhifeng Liu[a,c], Liangsheng Shi[b], Ming Chen[a,c], Guangming Zeng[a,c], Biao Song[a,c], Binbin Shao[a,c], Haopeng Feng[a,c]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] State Key Laboratory of Water Resources and Hydropower Engineering Science, Wuhan University, Wuhan, Hubei 430072, PR China
[c] Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha 410082, PR China

ARTICLE INFO

ABSTRACT

Polybrominated diphenyl ethers (PBDEs), a class of brominated flame retardants (BFRs), are widely used in various commercial products. PBDEs have attracted increasing attention due to their toxicity and bioaccumulation potential. Biodegradation associated technologies are cost-effective and environmentally friendly for possible removal of PBDEs from the environments. In this review, both aerobic and anaerobic biodegradation of PBDEs and the methods for accelerated degradation are discussed. Generally, the degradation of higher PBDEs (higher degree of bromination) is slower than that of lower PBDEs (lower degree of bromination) under both anaerobic and aerobic conditions. The aerobic degradation pathways of PBDEs include cleavage of aromatic ring, debromination, and hydroxylation, while reductive debromination dominates the initial pathway of anaerobic degradation. A number of methods to overcome the chemical inactivity and low bioavailability of PBDEs for degradation enhancement are discussed, such as the addition of external carbon sources, surfactants and vitamin B_{12}. In addition, coupling of chemical degradation and biodegradation is also reviewed.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants, which have been widely used in the production of commercial and household products, such as foams, textiles, and plastics, for over four decades (Stiborova et al., 2015). There are 209 congeners for PBDEs based on different bromine substitutions. The names and molecular structures of PBDEs appearing in this review are shown in Table 1. Three major commercial PBDEs are reported, including deca-BDEs, octa-BDEs, and penta-BDEs (De Wit, 2002). The higher toxicity and bioaccumulation has resulted in the prohibition of production and usage of penta-BDEs and octa-BDEs in Europe and USA in 2003 and 2006, respectively (Stiborova et al., 2015). However, deca-BDEs were excluded in the bans and the contribution of deca-BDEs usually occupied over 75% of the whole PBDEs (Article, 2014). Recent studies reported that deca-PBDEs could be reductively debrominated into lower PBDEs, which are one of the sources of lower PBDEs in the environment detected (Orihel et al., 2016).

Due to the increasing accumulation of PBDEs in the environment, PBDEs contamination has been found in air, water, soil, sediments, and even biota (Wang et al., 2011; Zeng et al., 2013b). For example, high concentration of BDE-209 was detected in male birds in waste management facilities (Gentes et al., 2015), and PBDEs was even detected in the arctic biosphere (Rotander et al., 2012). In China, Guiyu Town, Guangdong Province is one of the largest e-waste recycling centers and PBDEs is detected in all of the environmental samples and even in human bodies (Jiang et al., 2014). PBDEs have attracted great attention due to its biotoxicity, such as endocrine disruption effect to mammalian tissues (Song et al., 2015). PBDEs toxicity is different from that of dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and pesticides. For example, the neurotoxicity and dioxin-like endocrine disruption induced by PBDEs were observed in mice (Jacobson et al., 2016; Tang et al., 2008; Zeng et al., 2013a).

Although the bioaccumulation of PBDEs in the environment is widely studied, the technology for bioremediation of PBDEs contaminated sites has not been sufficiently investigated. Biodegradation is considered as an economical and safe way for PBDEs removal (Chen et al., 2016a, 2017b; Ming et al., 2017). However, owing to high hydrophobicity and low bioavailability of the compounds the efficiency of PBDE biodegradation is relatively low, thus some methods are proposed
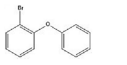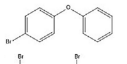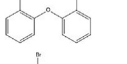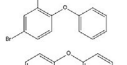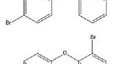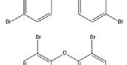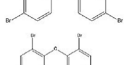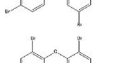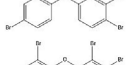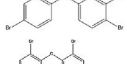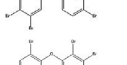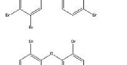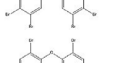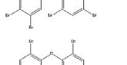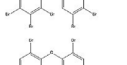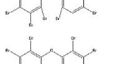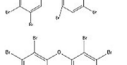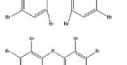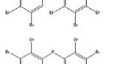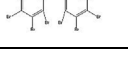
Table 1
Names and molecular structures of the numbered PBDEs in the article.

Classification	Abbreviation	Names	Molecular Structure
Mono-PBDEs	BDE-1	2-monoPBDEs	
	BDE-3	4-monoPBDEs	
Di-PBDEs	BDE-4	2,2′-diPBDEs	
	BDE-7	2,4-diPBDEs	
	BDE-15	4,4′-diPBDEs	
Tri-PBDEs	BDE-17	2,2′,4-triPBDEs	
	BDE-28	2,4,4′-triPBDEs	
Tetra-PBDEs	BDE-47	2,2′,4,4′-tetraPBDEs	
	BDE-49	2,2′,4,5′-tetraPBDEs	
	BDE-66	2,3′,4,4′-tetraPBDEs	
Penta-PBDE	BDE-85	2,2′,4,4′,5-pentaPBDEs	
	BDE-99	2,2′,4,4′,5-pentaPBDEs	
	BDE-100	2,2′,4,4′,6-pentaPBDEs	
Hexa-PBDEs	BDE-138	2,2′,3,4,4′,5′-hexaPBDEs	
	BDE-153	2,2′,4,4′,5,5′-hexaPBDEs	
	BDE-154	2,2′,4,4′,5,6′-hexaPBDEs	
Hepta-PBDE	BDE-183	2,2′,3,4,4′,5′,6-heptaPBDEs	
	BDE-184	2,2′,3,4,4′,6,6′-heptaPBDEs	
Octa-PBDEs	BDE-196	2,2′,3,3′,4,4′,5,6′-octaPBDEs	
	BDE-197	2,2′,3,3′,4,4′,6,6′-octaPBDEs	
Nona-PBDEs	BDE-206	2,2′,3,3′,4,4′,5,5′,6-nocaPBDEs	
	BDE-207	2,2′,3,3′,4,4′,5,6,6′-nocaPBDEs	
	BDE-208	2,2′,3,3′,4,5,5′,6,6′-nocaPBDEs	
Deca-PBDEs	BDE-209	2,2′,3,3′,4,4′,5,5′,6,6′-decaPBDEs	

to enhance the degradation, such as the use of surfactants. In addition, information regarding the detailed degradation mechanisms and limitations in complex systems is still scarce. In this paper the key factors affecting PBDEs biodegradation, such as microbes, kinetics and pathways, are discussed. Furthermore, the methods for enhancing PBDE biodegradation are summarized.

2. Anaerobic biodegradation

2.1. Microbial community

PBDEs affect the structure of microbial community depending on the degree of bromination of PBDEs (Ma et al., 2016). Bacterial community in the river sediments was altered immediately and irreversibly throughout the incubation period owing to amendment with BDE-153 and BDE-154, which were transformed less than 20% after 70 days. Similar results were observed and demonstrated that BDE-154 was one of the most influential factors on the bacterial community compared to lower PBDEs in mangrove microcosms (Wang et al., 2014). However, the bacterial community did not change significantly upon amendment of BDE-47, which was completely transformed after 63 days in the Nan-Kan River sediment. These results show that higher PBDEs have more pronounced impact on the microbial community structure than lower PBDEs.

The concentrations of PBDEs also have influence on microbial community. Low concentration (1 mg/L and 10 mg/L) of BDE-15 and BDE-209 had only small and transitory effect on the bacterial community, which was changed intensely by BDE-15 and BDE-209 at high concentration (100 mg/L) in soils (Liu et al., 2011). The result was consistent with the study of Huang et al. (2014) who also found that the bacterial community changed significantly upon exposure to a higher concentration of BDE-209. The microbial community structure in sediments from Lianjing River was highly related to the concentrations of deca-BDEs and octa-BDEs (Qiu et al., 2012). This is probably due to the increase of the toxicity of PBDEs with increasing concentrations.

2.2. Pathways of debromination

The reductive debromination, which includes *ortho*-, *meta*- and *para*-debromination, dominates the pathways of PBDEs removal under anaerobic conditions. Because BDE-209 is the key source of lower PBDEs in environment and the bioaccumulation of BDE-47 is detected frequently in biota, the debromination pathways of BDE-209 and BDE-47 are used as examples for further discussion below.

It is reported that BDE-209 can be debrominated into three types of nona-BDE and three types of octa-BDEs in sewage sludge amended with inducers (Gerecke et al., 2005), or into three nona-BDEs, five octa-BDEs, one hepta-BDE and one hexa-BDE in enrichment cultures amended with zero-valence iron (ZVI) (Chen et al., 2014). Formation of three nona-BDEs was also observed for debromination of BDE-209 in sediment and biomimetic system amended with vitamin B_{12} (Tokarz Iii et al., 2008). nona-BDEs can be further debrominated into lower PBDEs (tri-BDEs) in sediment with addition of electron donors (Qiu et al., 2012) and in anaerobic microcosms from organic compost (Chang et al., 2016). tri-BDEs resulted from the multi-step debromination of BDE-209 were further debrominated into two di-BDEs and one mono-BDE in PBDEs-adapted sediment (Huang et al., 2014). The primary pathway of BDE-209 debromination in soils under anaerobic conditions is shown in Fig. 1.

The first step of anaerobic debromination of BDE-47 is conversion into tri-BDEs (BDE-17 or 28) under anaerobic conditions. *ortho*-debromination of BDE-47 into BDE-28 took place first, and then BDE-28 was debrominated into BDE-15 (*ortho*-debromination) in a culture consisting of *Dehalococcoides* and *Desulfovibrio* spp. (Lee et al., 2011). Ding et al. (2013) reported that BDE-47 was only debrominated into BDE-17 (*para*-debromination) and BDE-17 was debrominated into BDE-4 (*para*-debromination) in a sediment-free enrichment culture. In the mangrove sediment, more than 90% of BDE-47, however, were debrominated into both BDE-28 and BDE-17 after 7 months of incubation (Zhu et al., 2014a). Metabolism rather than complete debromination of BDE-47 was also observed in sediment microcosms. BDE-47 was decreased over 30% in several of the microcosms without a significant accumulation of by-products except for a slightly increase of BDE-17, indicating that

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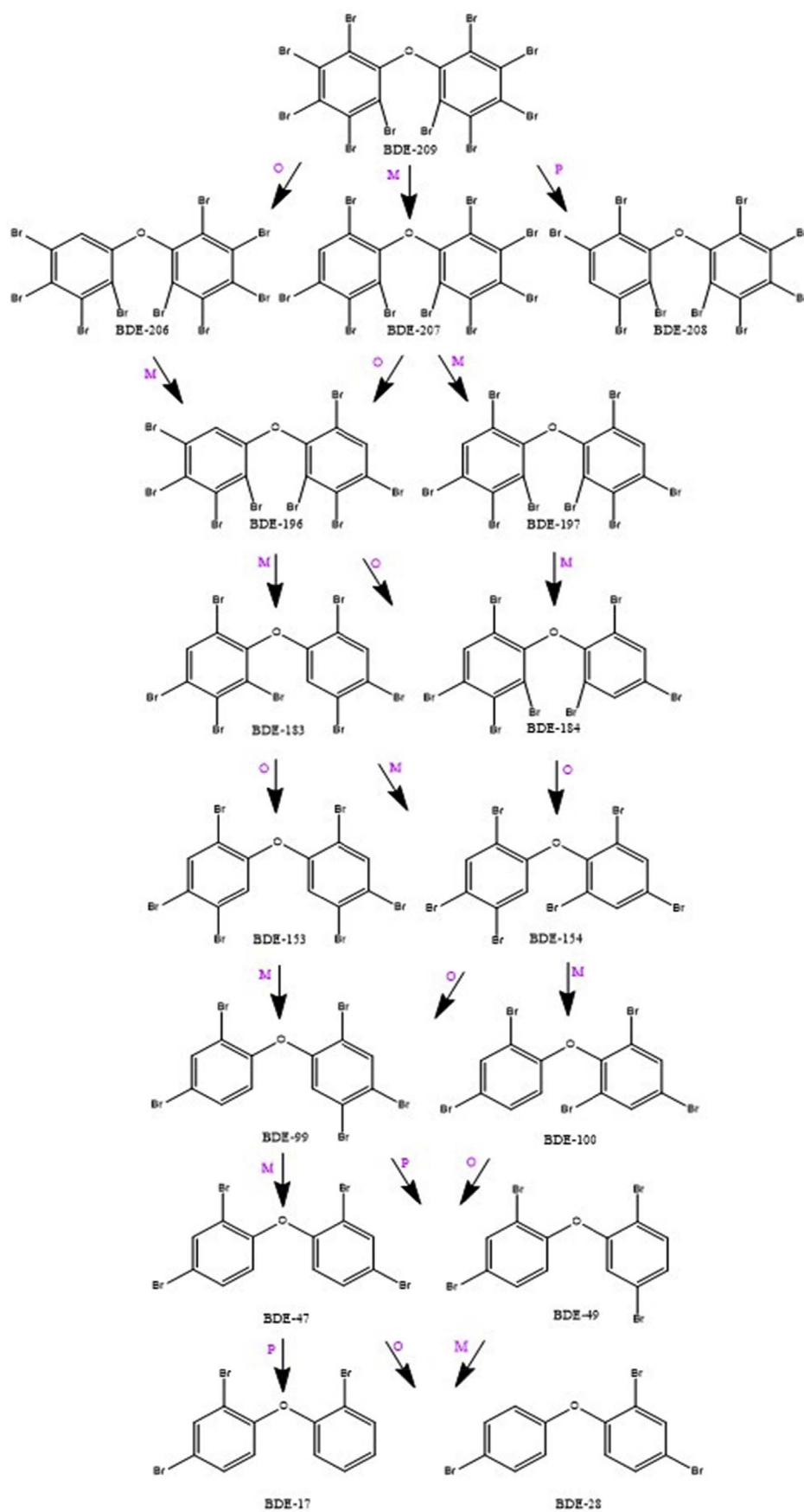
Fig. 1. The pathway of BDE-209 debromination in soils under anaerobic conditions (based on Tokarz Iii et al., 2008). (O, *ortho*-debromination; M, *meta*-debromination; P, *para*-debromination).
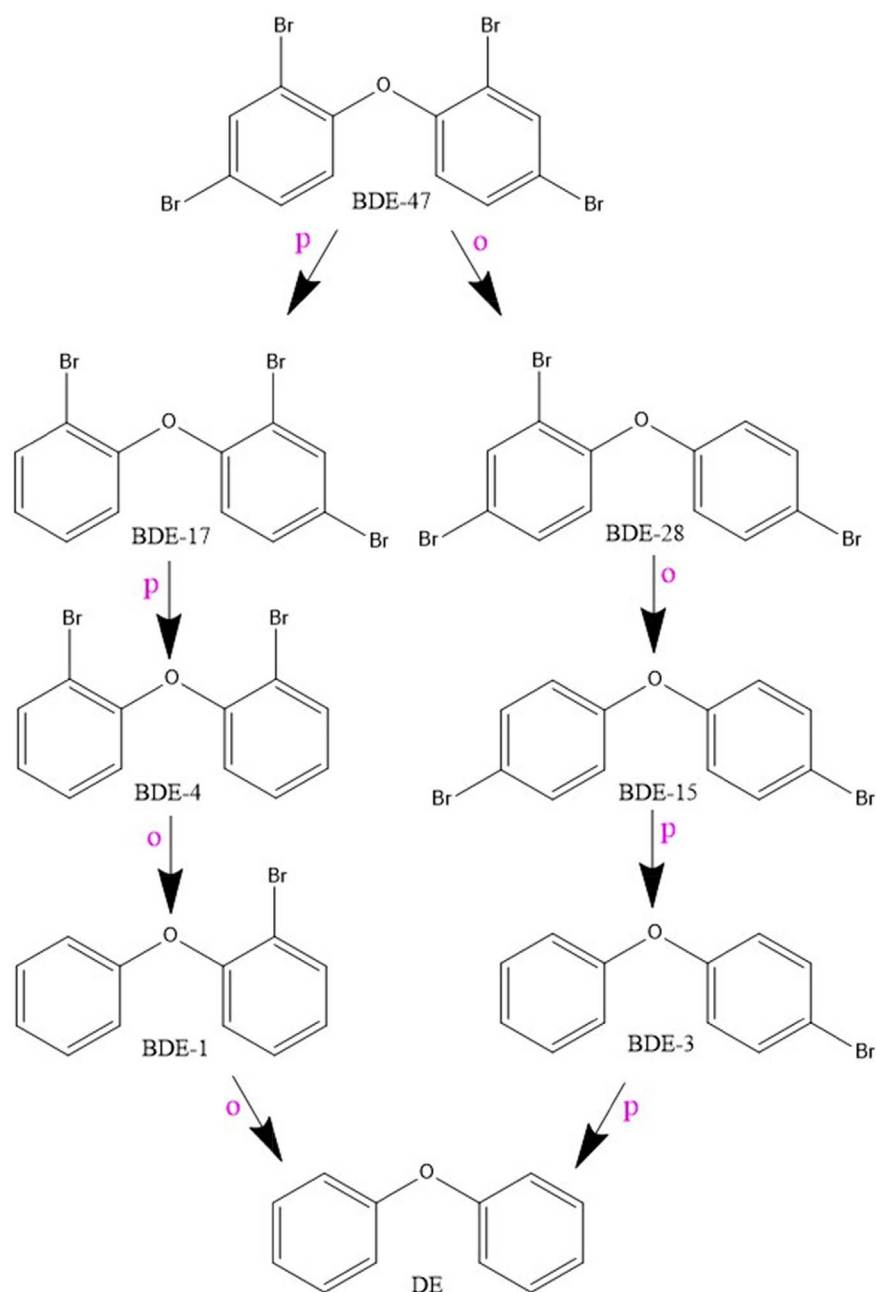
Fig. 2. The pathway of BDE-47 debromination under anaerobic conditions (based on Lee et al., 2011; Ding et al., 2013). (O, *ortho*-debromination; M, *meta*-debromination; P, *para*-debromination).

BDE-47 was likely to be metabolized (Tokarz Iii et al., 2008). The pathway of BDE-47 debromination under anaerobic conditions was shown in Fig. 2.

2.3. First-order kinetics of PBDEs debromination

First-order kinetics is often used to describe PBDEs debromination under anaerobic conditions with half-life and the rate constant (k) as the characteristic parameters of the transformation. The half-lives and rate constants (k) of PBDEs in sediments and sludge under anaerobic conditions are shown in Table 2. The half-lives of PBDEs debromination range from 2.7 d (BDE-3) to more than a decade (BDE-209), indicating that debromination of PBDEs under anaerobic conditions is generally a slow process. Apart from limited microbial population, low bioavailability of PBDEs is another major limiting factor in soil systems since PBDEs had to contact microbial cells or enzymes before debromination can occur. The processes of PBDEs debromination can be enhanced by

some methods, such as the use of micro zero-valence iron (MZVI) and vitamin B_{12}. The half-life (rate constants k) of BDE-209 was 13.4 h (1.24 d^{-1}) in Jhongsing sludge incubated with micro zero-valence iron (mZVI) (Shih et al., 2012b). The half-lives (rate constants k) of BDE-209 and BDE-99 were 18 s (3327 d^{-1}) and 19.9 h (0.836 d^{-1}), respectively, at an initial concentration of 0.3 μg/g in biomimetic system amended with vitamin B_{12} (Tokarz Iii et al., 2008).

2.4. Effect of bromination degree on debromination

Usually, debromination of higher PBDEs is more difficult due to their higher hydrophobicity and lower bioavailability. In a study conducted by Yen et al. (2009), less than 20% of BDE-99, 100, 153 and 154 were transformed in the river sediment but BDE-47 was converted to a negligible level within 70 days. In another study, less than 10% of octa-, hepta- and hexa-BDEs were debrominated in the cultures containing *Dehalococcoides* sp., *Dehalobacter restrictus* and *Desulfitobacterium*

Table 2
Parameters for the First-order kinetics for biodegradation of PBDEs under anaerobic conditions.

PBDEs	Half-lives (d)	K (d^{-1})	Sites	References
BDE-209	18 s	3327	biomimetic system with vitamin B$_{12}$	Tokarz Iii et al., 2008
	> a decade	–	Sediment from Celery Bog Park	Tokarz Iii et al., 2008
	31.5	0.0220	PBDEs-adapted sediment	Huang et al., 2014
	630	0.00110	Jhongsing sludge	Shih et al., 2012b
	578	0.00120	Li-Ming sludge	Shih et al., 2012b
	13.4 h	1.24	in Jhongsing sludge with MZVI	Shih et al., 2012b
BDE-3	2.67	0.260	Li-Ming sludge	Shih et al., 2012a
	3.30	0.210	Jhongsing sludge	
BDE-153	7.6–165	0.0912–0.0042	Eight sediments	Zhu et al., 2014b
BDE-47	76.2	0.00910	Sediment from mangrove	Zhu et al., 2014b
	56.9	0.0122	Sediment from pond	Zhu et al., 2014b
BDE-99	19.9 h	0.836	biomimetic system with vitamin B$_{12}$	Tokarz Iii et al., 2008

hafniense after three months, while it was much faster for BDE-99 and BDE-47, which was debrominated completely in weeks (Robrock et al., 2008). However, under some conditions the chemical property of higher PBDEs can be labile, resulting in readily reaction with nucleophiles and a higher debromination rate. For example, the order of debromination rates in Erren river sediment after 56 days of incubation were BDE-15 < BDE-28 < BDE-47 < BDE-99 < BDE-209 (Huang et al., 2014). In the biomimetic system amended with vitamin B$_{12}$, debromination of BDE-209 was faster than that of BDE-99 and debromination of BDE-99 was faster than that of BDE-47. The results show that the effect of bromination degree on debromination depends highly on the specific incubation conditions.

3. Aerobic biodegradation

Due to extreme hydrophobicity and sorptive binding with organic compounds in the soils, PBDEs are regularly monitored under anaerobic conditions, where anaerobic microbes play the dominant role (Zhu et al., 2014b). Therefore, comparing to anaerobic degradation, only few studies were focused on the aerobic degradation of PBDEs (Robrock et al., 2009). However, aerobic degradation of PBDEs does take place and sometimes is unique with key features different from anaerobic degradation.

3.1. Microorganisms

The specific strains that could aerobically degrade aromatic compounds, such as PCBs and PCCF, were supposed to be able to transform PBDEs due to the similarity of chemical structure of PBDEs to these compounds. The degradation of PBDEs ranging from mono-BDEs to hexa-BDEs by the ether-degrading bacteria and two PCBs-degrading strains under aerobic conditions was reported (2009). Zhou et al. (2007) used white-rot fungi to remove BDE-209 from liquid culture because these fungi could rapidly transform a wide range of aromatic compounds to achieve a removal rate of 42.2% within 10 days. Strains isolated from the media where PBDEs are the sole carbon source can be the aerobic degraders of PBDEs. For example, Vonderheide et al. (2006) showed that degradation of penta-BDEs under aerobic conditions by consortia isolated from penta-BDEs-spiked soils took place. Interestingly, however, they reported a timeframe for a complete removal of only a few minutes. A new strain identified as *Pseudomonas stutzeri* was isolated from a PBDE contaminated site located in Shandong, China to degrade BDE-47 under aerobic conditions, and the degradation rate was 94.7% with BDE-47 as the sole carbon source in the liquid culture within 14 d of incubation (Zhang et al., 2013). Between 62 and 78% of the total amount of 11 PBDEs containing BDE-28, 47, 49, 66, 85, 99, 100, 153, 154, 183 and 209 were transformed by indigenous microbes under aerobic conditions in two industrially contaminated sewage sludge after 11 months (2015).

3.2. Pathways of biodegradation

The processes for PBDEs degradation under aerobic conditions include adsorption on cell surface, assimilation into the cells, breaking down aromatic ring, and then mineralization (Wang et al., 2016b). PBDEs were catalyzed and mineralized by various enzymes, then converted into harmless carbon dioxide and water through tricarboxylic acid cycle (TCA cycle). 4-bromophenol and 4-bromocatechol were detected from the degradation of BDE-3 by *Sphingomonas* sp. SS3 (Schmidt et al., 1992) and *Cupriavidus* sp. (Wang et al., 2015). BDE-3 can even be degraded into 2-hydroxymuconic acid by *Sphingomonas* sp. PH-07 (Kim et al., 2007). 2,4-dibromophenol was identified as the product from the aerobic degradation of BDE-7 and BDE-28 (Kim et al., 2007). BDE-15 was hydroxylated by 2,3-dioxygenase and produce 2′,3′-dihydroxy-4,4′-dibromodiphenyl ether in the presence of *Sphingomonas* sp. PH-07 (Kim et al., 2007), and was debrominated into 4-bromophenol and 4-bromocatechol by *Sphingomonas* sp. SS33 (Schmidt et al., 1993). These intermediates are strong evidences for the ring-cleavage pathway for PBDEs degradation. However, up to date the literatures regarding such a pathway are still very limited and the degradation pathways of diphenyl ether (Kim et al., 2007; Pfeifer et al., 1993; Schmidt et al., 1992; Wang et al., 2015) are often used as the reference for PBDEs degradation. The proposed pathways for the biodegradation of diphenyl ethers are shown in Fig. 3. (Kim et al., 2007; Pfeifer et al., 1993; Schmidt et al., 1992; Wang et al., 2015).

Except for the cleavage of aromatic ring and ether bond, debromination of higher PBDEs also occurs in the aerobic experiments, which compares to reductive debromination of PBDEs under anaerobic conditions. Lower PBDEs of BDE-154, BDE-28 and BDE-15 had been detected in the aerobic degradation of BDE-209 by strain JP12 (Lu et al., 2013). Shi et al. (2013) showed that BDE-209 was aerobically transformed by *Pseudomonas aeruginosa* into lower PBDEs, including two nona-BDEs, four octa-BDEs, one hepta-BDEs. Meanwhile, hydroxylation of PBDEs was frequently detected (Kim et al., 2007; Schmidt et al., 1992; Wang et al., 2015). Mono-PBDEs was transformed to hydroxylated mono-PBDEs by *Burkholderia xenovorans* (Robrock et al., 2009). BDE-209 was converted to OH-PBDEs by crude enzyme extracted from *Pseudomonas aeruginosa* (Liu et al., 2015).

3.3. First-order kinetics of PBDEs biodegradation

The half-life and rate constant k for First-order kinetics of aerobic biodegradation of PBDEs are shown in Table 3. By comparing between Table 2 and Table 3, it is clear that degradation rates of PBDEs under aerobic conditions are generally higher than that under anaerobic conditions. Also, degradation rates of higher PBDEs are lower than that of lower PBDEs under the same conditions, likely due to lower bioavailability and less microbial population for higher PBDEs. Moreover, higher rates with PBDEs-degrading strains in the culture than that in sediments and sewage sludge were observed and the possible reason is
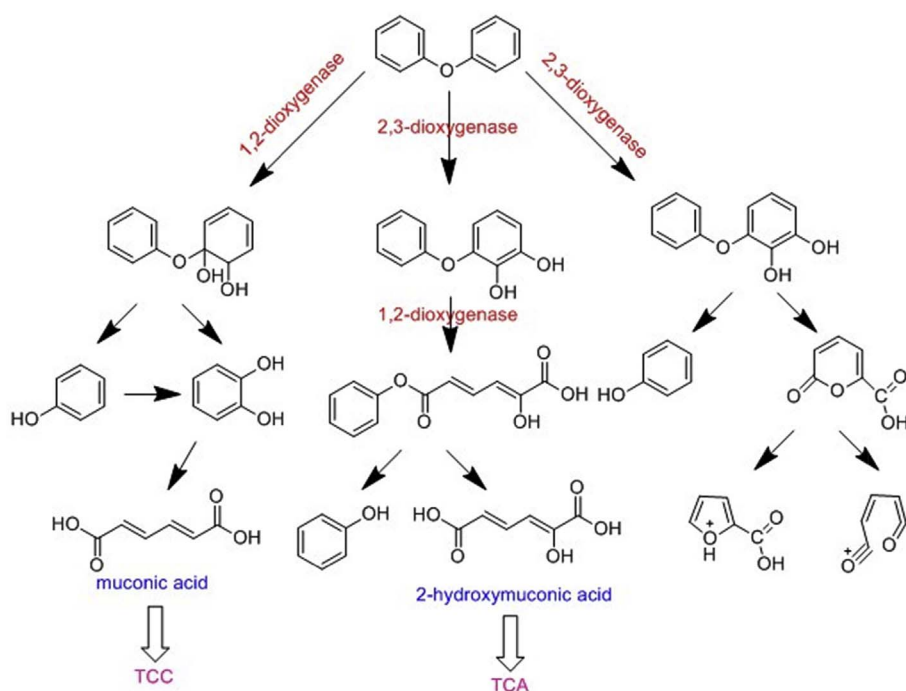
Fig. 3. The pathway for the biodegradation of diphenyl ether by *Sphingomonas* sp. strain SS3, *Sphingomonas* sp., *Pseudomonas cepacia* and *Cupriavidus* sp. under aerobic conditions (based on Pfeifer et al., 1993; Schmidt et al., 1992; Wang et al., 2015; and Kim et al., 2007).

that microbial activity in cultures under controlled conditions is higher than that in sediments and sewage sludge. Another reason is the difference in bioavailability of PBDEs in the two systems, which is more limited in sediments and sewage sludge. Many studies conducted with complex systems did not provide any further insights or substantial information for a better understanding of the degradation process or the mechanisms involved of the target chemicals of choice (Gu, 2016).

3.4. Effect of bromination degree on degradation

Biodegradation of PBDEs is strongly relevant to the degree of bromination under aerobic conditions. BDE-3 was transformed by 23% within 8 days by an isolated *Sphingomonas* sp. in the liquid culture, while only 8% of BDE-15 were transformed by the same strain (Kim et al., 2007). More than 90% of the mono- and di-PBDEs were degraded in 3 days by *Burkholderia xenovorans*, but only 10–45% of penta-PBDEs and 18% of hexa-PBDEs were transformed (Robrock et al., 2009). In sediment, the degradation rates of PBDEs were in the order of BDE-100 < BDE-99 < BDE-47 < BDE-28 < BDE-15 under aerobic conditions (Yang et al., 2015). Therefore, the higher PBDEs were more difficult to degrade than lower PBDEs, likely due to their larger size,

higher hydrophobicity and lower bioavailability to the microbes, which is similar to that under anaerobic condition. Furthermore, large number of bromines on PBDE molecule are unfavorable for hydroxylation and sterically hinder enzymatic reaction and attack (Robrock et al., 2009).

Specific position of bromination substitution exhibits potential impact on PBDEs stability and degradation. BDE-7 and BDE-15 were catabolized by 14% and 8%, respectively, in 8 days by *Sphingomonas* sp. in a culture supplemented with diphenyl ether, where BDE-7 was converted to brominated catechol, which, however, was not detected for BDE-15. BDE-15 was generated from degradation of BDE-28 (tri-BDEs), while no brominated metabolite was observed from degradation of BDE-30 (tri-BDEs) (Kim et al., 2007). The reason was that BDE-30 had a non-substituted phenyl moiety, which resembled the required target site to form the 2, 3-dihydrodiol of diphenyl ether. According to Robrock et al. (2009), *Rhodococcus* sp. was responsible for degradation of BDE-7, but not BDE-4 (di-BDEs). *Burkholderia xenovorans* was capable of transforming BDE-138 (hexa-BDEs), but not BDE-153 (hexa-BDEs) and 149 (hexa-BDEs). The bromine substitution affected the degradation rate either by limiting the accessibility of catabolic enzymes to the target site or by significantly decreasing PBDEs bioavailability (Kim et al., 2007).

Table 3
Parameters for the First-order kinetics for biodegradation of PBDEs under aerobic conditions.

PBDEs	Half-lives (d)	K (d^{-1})	Sites or strains	References
BDE-209	74.5	0.00930	Sediments under Da-An bridge	Chou et al., 2016
	128.4	0.00540	Sediments under Yi-Li bridge	Chou et al., 2016
	105.0	0.00660	Sludge from WWTPs	Chou et al., 2016
	180–240	0.00385–0.00282	Sludge from WWTPs	Stiborova et al., 2015
BDE-99	14.1	0.0492	Sediment from river	Yang et al., 2015
BDE-47	2.2	0.315	*Pseudomonas stutzeri*	Zhang et al., 2013
	9.1	0.0762	*Pseudomonas stutzeri*	Xin et al., 2014
	12.8	0.0542	Sediment from river	Yang et al., 2015
	16.2	0.0428	*Pseudomonas putida*	Lv et al., 2016a
BDE-28	5.8	0.120	Sediment from river	Yang et al., 2015
BDE-15	2.9	0.239	Sediment from river	Yang et al., 2015
	14.9	0.0465	*Pseudomonas putida*	Lv et al., 2016a
BDE-3	10.8	0.0642	*Pseudomonas putida*	Lv et al., 2016a
DE	6.2	0.112	*Pseudomonas putida*	Lv et al., 2016a

4. Methods for degradation enhancement

4.1. Carbon sources

The biomass for PBDEs degradation can be increased after the addition of alternative carbon sources, which subsequently resulted in increasing capability of PBDE degradation. This phenomenon is widely recognized as co-metabolism for many persistent and toxic pollutants (Gu, 2016). PBDE degradation was increased approximately by 10%–15.7% with addition of yeast extract as the co-substrate in a sewage sludge (Stiborova et al., 2015). A slightly enhancement on degradation of BDE-47 by *Pseudomonas stutzer* was observed with ethanol and glucose as carbon and energy sources in 6 days (Zhang et al., 2013). Degradation of BDE-209 was promoted due to the use of phenol, toluene and biphenyl at low concentrations, but the degradation was inhibited at high concentrations of these compounds (Lu et al., 2013). The highest efficiency of BDE-209 degradation was observed when the mass ratio of BDE-209 and glucose was 1:5, while excessive glucose inhibited the degradation (Shi et al., 2013). The explanation was that strains would mainly utilize easily metabolized carbon source when a high concentration of the easily utilizable carbon source existed, which caused inhibition on degradation of the other one. Furthermore, in the presence of mixed culture, not only the biomass of PBDEs-degrading strains is increased, but growth of other strains is also enhanced simultaneously. The other strains may compete for limited nutrients available and thus decrease PBDEs degradation. Therefore, an appropriate concentration of carbon source is important for PBDE degradation.

4.2. Electron acceptors

Lack of appropriate electron acceptor is one of the major limiting factors for biodegradation of refractory compounds under anaerobic conditions. Oxygen was the preferential electron acceptor under aerobic conditions, while electron acceptors were usually absent and the microbial metabolism was suppressed under anaerobic conditions. Relationship between any selective substrate and electron acceptor is governed by thermodynamics in the form of free energy yield. The addition of electron acceptors stimulated anaerobic degradation of PBDEs because they not only stimulate growth of the microbes but also consume the excess electrons to enhance microbial activity (Cunningham et al., 2001). Ferric iron, CO_2, sulfate, and nitrate, can be used as the electron acceptors (Cunningham et al., 2001; Farhadian et al., 2008). The addition of nitrate, sulfate and bicarbonate increased the debromination rate of BDE-209 by 13.6%, 36.4% and 27.3%, respectively (Huang et al., 2014). Zhang et al. (2014) showed that $NaNO_3$ and NH_4NO_3 accelerated PBDEs degradation, resulting in removal rates of 33.4% and 42.3% after 50 days, respectively. The debromination rate of octa-BDEs was increased due to presence of trichloroethene (TCE) as electron acceptor in soils and sediments at 28 locations (Lee and He, 2010). The removal efficiency of BDE-47 was increased from 47.3% to 58.2% in the rhizosphere soils with the addition of NO_3^- (Chen et al., 2015b). Although the addition of electron acceptors was an appropriate method to increase PBDE degradation, only a few studies were reported and the secondary pollution of electron acceptors should be highlighted, for example, carcinogenic nitrite (NO_2^-) can be produced owing to the reduction of nitrate (NO_3^-) under anaerobic conditions.

4.3. Surfactants

Bioavailability of PBDEs was limited partially due to high hydrophobicity of the chemicals. Surfactants can enhance solubility and bioavailability of hydrophobic organic compounds (Yang et al., 2003; Liu et al., 2017), and thus have the potential to enhance biodegradation of PBDEs, but the toxicity and destructive nature of this class of chemicals are limitations for applications. The debromination rates for BDE-209 were enhanced by 50.0% and 31.8%, respectively, with the addition of Brij 30 and Brij 35 in sediments after 56 days of incubation (Huang et al., 2014). Debromination for BDE-209 degradation by white-rot fungi was promoted significantly after 10 days with addition of β-cyclodextrin and low concentrations of Tween 80, while Tween 80 at high concentrations inhibited degradation of BDE-209 because the growth of white-rot fungi was inhibited (Zhou et al., 2007). Lu et al. (2013) showed that Tween 80 slightly enhanced the degradation of BDE-209, but Triton X-100 did not significantly affect the degradation and Tergitol NP-10 slightly decreased the degradation by *Bacillus cereus*. Degradation of PBDEs might be inhibited by surfactants due to the toxicity of them to microbial growth. Such inhibitory effect of surfactants can be mitigated by using biosurfactants, a class of surfactant produced by microbes or plants. The rate of BDE-209 degradation was increased due to the solubilization of tea saponin in mineral salts medium (Tang et al., 2014). The debromination rates of BDE-209 was increased up to 45.5% with surfactin within 56 d in the sediments (Huang et al., 2014). Biosurfactants function not only to solubilize pollutants for assimilation, but also serve as a carbon and energy source. As a result, the claimed degradation is much more complicated to interpret for the detailed mechanisms involved.

4.4. Inducers

The role of inducers was to induce the production of dioxygenases which cleaves the aromatic ring of PBDEs in the process of biodegradation of PBDEs. The chemical structure of inducers was similar to PBDEs and they are easier to be biodegraded by microbes, and then degradation of PBDEs was increased due to the induced production of enzyme. Such a pathway was superior to debromination of PBDEs, which produced more toxic lower PBDEs. Meanwhile, the inducers not only enhance production of the dioxygenase, but also acted as an alternative carbon and energy source for microbial growth. Therefore, the use of inducers was an efficient and environmentally friendly way to increase biodegradation of PBDEs. The removal of mono- and di-BDEs by *Sphingomonas* sp. with 1,2-dioxygenase were described by Schmidt et al. (1992, 1993). Production of dioxygenase was induced by 4-bromobiphenyl as the inducer, which enhanced degradation of PBDEs in sewage sludge from waste water treatment plants (WWTPs) (Stiborova et al., 2015). The degradation of mono-, di- and tri-BDEs was accelerated greatly by *Sphingomonas* sp. with 2,3-dioxygenase induced by diphenyl ether (Kim et al., 2007). Degradation of BDE-47 was enhanced in the presence of diphenyl and PCB-65 by *Pseudomonas stutzeri* within 6 days, and diphenyl and PCB-65 were inducers to produce dioxygenase (Zhang et al., 2013). However, current inducers are not suitable for cleaning up contaminated sites due to the high cost or toxicity, as a result alternative inducers are needed (Stiborova et al., 2015). Moreover, not all of substances with similar chemical structure could act as the inducer. The strain of *Sphingomonas* sp. could grow in the presence of diphenyl ether but it was unable to utilize biphenyl and brominated biphenyl (Kim et al., 2007). The degradation of BDE-209 was suppressed significantly by tetrabromobisphenol A because the competitive effect of the compound is stronger than its enzyme-inducing effect (Lu et al., 2013). Therefore, more information on how to choose the appropriate inducer to enhance PBDE degradation is required.

4.5. Vitamin B12

Coenzyme vitamin B_{12} is well-known to reductively dehalogenate halogenated organic compounds in the biomimetic system (Woods et al., 1999). The debromination rate of BDE-209 was promoted by 36.4% with application of vitamin B_{12} after 56 days of testing (Huang et al., 2014). BDE-209 and BDE-99 were slightly degraded in the anaerobic sediment microcosms over 8 months, but completely debrominated within 5 min and 7 days in the biomimetic system amended with B_{12}, respectively (Tokarz Iii et al., 2008). Similar results was

reported by Gaul et al. (2006), in which penta-PBDEs mixtures were transformed completely in the presence of B_{12} in a few minutes. The considerably high rate of PBDE degradation with B_{12} results in production of lower PBDEs. The hypothesis is that higher PBDEs were reductively debrominated into lower PBDEs with B_{12}, and then the product was degraded and mineralized through TCA cycle.

4.6. Use of organic compost

Aerobic composting is one of the most effective biological methods used to treat persistent organic pollutants (POPs), which consists of heating, thermophilic, cooling and maturing stages (Raj and Antil, 2011; Shao et al., 2017; Wu et al., 2016). PBDEs in natural soils was difficult to remove, while the organic compost was a potential method for PBDE degradation enhancement (Zhang et al., 2014; Barrena et al., 2008). BDE-209 was removed by 66% and 62% during 120 days in the compost materials containing 6-month bagasse/pig manure and 3-month pig manure, respectively (Chang et al., 2016). BDE-47 degradation was enhanced up to 15% in agricultural waste-composting pile compared with the control group after 45 days. In different stages, BDE-47 degradation was correlated to different physicochemical parameters and microbes (Chen et al., 2016b). The compost contains plenty of humus, which can mediate electron transfer and reductive dehalogenation (Zhang and Katayama, 2012). High molecular chemicals including PBDEs can be polymerized into the humus and stabilized. This is particularly favorable for degradation of higher PBDEs.

4.7. Multiple methods

4.7.1. Zero-valence iron (ZVI) reduction and biodegradation

The ZVI-bioremediation technology can be an efficient method to treat higher PBDEs, which are firstly reductively debrominated to lower PBDEs with ZVI, and then the product was metabolized by microbes. Degradation of BDE-209 by *Rhodococcus* sp. was observed to be promoted with co-existing zero-valence iron/activated carbon within 144-h timeframe of the study (Liu et al., 2016). Kim et al. (2012) showed that BDE-209 was reductively debrominated to lower PBDEs with nano-ZVI in 20 days, and the metabolites were biologically transformed to bromophenol and metabolites of lower level in 4 days. BDE-209 debromination can be enhanced through the synergistic effect of ZVI and microbes, and even debromination of lower PBDEs that could not be biodegraded by microbe alone was enhanced (Chen et al., 2014). Stimulation of BDE-209 degradation was reported with synergistic effect of micro ZVI and anaerobic sludge (Shih et al., 2012b). Combination of ZVI and microbes could not only increase the efficiency of PBDEs removal, but also promoted complete mineralization of PBDEs. However, the potential toxicity of nano-ZVI to microbes is a concern since recently it has been shown that microbial growth was inhibited by nano-ZVI and the rate of BDE-209 degradation was decreased (Kim et al., 2012).

4.7.2. Photolysis and biodegradation

Photolysis, such as ultraviolet (UV) light-based photolysis, is one of the important processes for degradation of POPs in various environmental matrix (Chen et al., 2015a, 2017a; Deng et al., 2016). The photo debromination of PBDEs is due to the generation of active free radicals by UV radiation (Wang et al., 2016a,b,c), thus combined microbial degradation with UV light radiation was an economic and efficient treatment method for PBDE contamination (Chou et al., 2013). The removal of PBDEs was detected with positive matrix factorization because of photochemical and microbial degradation in the sediment samples from San Francisco Bay (Rodenburg et al., 2014). Suh et al. (2009) showed that the biodegradation of PBDEs was increased in the presence of UV irradiation. The enhancement of BDE-209 degradation was observed with UV irradiation at 365 nm over 10 months comparing to inoculation in the darkness (Chou et al., 2013). Higher PBDEs were

reductively debrominated to lower PBDEs with the pretreatment of UV, and then lower PBDEs were introduced into TCA cycle and biodegraded (Shih and Wang, 2009).

4.7.3. Hydrogen peroxide oxidation and biodegradation

Hydrogen peroxide (H_2O_2) as the oxidant in chemical remediation or as the donor of oxygen for in situ bioremediation of organic pollutant compounds was reported (Lee and Hosomi, 2001). Combination of H_2O_2 with microbial degradation for the removal of PBDEs had been a popular method in recent years (Xu et al., 2011). The total removal of PBDEs was observed to be 50.8% and 56.5%, respectively, in microcosms with 0.5 and 1 μL of H_2O_2 in microcosms after 50 days (Zhang et al., 2014). The high concentration of BDE-47 was completely mineralized to harmless products in a short time with the combined treatment, in which sequential processes of reductive debromination by nZVI/Pd, fenton-like oxidation, and microbial degradation by *Pseudomonas putida* are involved (Lv et al., 2016b). Li et al. (2016) reported that the degradation of higher PBDEs was enhanced due to combination of fenton-like oxidation and *Phanerochaete chrysosporium*-based biodegradation in soils. Therefore, an appropriate pre-treatment with H_2O_2-based oxidation can be very beneficial for the subsequent biodegradation and mineralization of PBDEs. The drawback of the method is the effect of H_2O_2 on the microbial community structure in soils due to the toxicity of H_2O_2 to the microbial growth (Schrader and Hess, 2004).

4.7.4. Plant uptake and biodegradation

Plant uptake and PBDEs biodegradation in the rhizosphere are two key processes controlling the fate of PBDEs in the contaminated soils under certain circumstances (Zhu et al., 2014a). Chen et al. (2015b) found that BDE-47 degradation in the rhizosphere soils was significantly stronger compared to the non-planted soils due to abundant PBDE-degrading communities in the rhizosphere soils. penta-BDEs mixture consisting of BDE-47, 99 and 100 were taken up by a mixture of plants, including zucchini and radish, and accumulated in roots and shoot tissues (Mueller et al., 2006). In a greenhouse study, Huang et al. (2011) showed that lower PBDEs (mono-BDEs to hexa-BDEs) were taken up in plant roots from soils and the order of PBDEs concentration in plant tissues followed the order of roots > stems > leaves, which agree with the patterns established for different metals and metalloids (Yu and Gu, 2007a,b, 2008a,b; Yu et al., 2007). BDE-209 accumulated in the roots and shoot tissues of radish, alfalfa, summer squash, pumpkin, ryegrass and maize, and the debromination and hydroxylation of BDE-209 were observed in soils and plant samples. Moreover, higher proportion of lower PBDEs in plant tissues compared to soils indicated that lower PBDEs were easier to be taken up by plants (Huang et al., 2009). The combined method of plant uptake and microbial degradation can be an economic and environmentally friendly way to increase PBDEs removal from the contaminated soil, though the degradation is slower compared to other combined methods. The advantages of phytoremediation include low maintenance and natural process operation for years to achieve thorough cleaning up of the soil and sediment matrix economically. In doing so, some chemical can be phyto-extracted from soil and respired into the atmosphere for photo-oxidation, e.g., methyl *tert*-butyl ether (MTBE) (Yu and Gu, 2006).

5. Remark and prospect

Contamination of PBDEs remains an environmental issue because commercial products containing BDE-209 is still in production around the world. They can be debrominated into lower PBDEs under natural conditions, contributing to the new release of PBDEs in the environment. BDE-47 (tetra-PBDEs) and BDE-99 (penta-PBDEs) dominate the concentration in biota, thus the bioaccumulation and toxicity of BDE-47 and BDE-99 to ecosystem and human are new foci of this group of pollutants. The exact pathways of biodegradation of PBDEs are still under exploration and stable isotope-labeling can be an effective tool

for delineation of the information.

The low rates of PBDEs biodegradation shown in this review are owing to chemical stability and low bioavailability of PBDEs, thus a number of methods have been proposed to enhance the removal of PBDEs. The common methods include the addition of carbon sources, electron acceptors, surfactants and inducers. Recently, some novel approaches are applied to PBDEs bioremediation such as use of vitamin B_{12} and organic compost, and vitamin B_{12} can act as super reducing agent for debromination. Combined methods are proposed to enhance the efficiency of degradation and degradation by plants and microbes is the one with the most potential for practical applications on sites due to the environmental friendliness of the method. Application of chemicals, such as electron acceptors, surfactants and inducers, to the rhizosphere soils to enhance the joint degradation of PBDEs by plants and microbe is worth of further research.

Acknowledgments

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