

총 설

하·폐수내 브롬화 디페닐 에테르(Polybrominated Diphenyl Ether, PBDEs)의 분포 및 제거기술 동향

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Treatment Technologies for Removal of Polybrominated Diphenyl Ethers (PBDEs) from Wastewater

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Abstract

Polybrominated diphenyl ethers (PBDEs) are a group of industrial aromatic organobromine chemicals that have been used since the 1970s as flame retardants in a wide range of consumer products and articles, including plastics, computers, textiles and upholstery. Commercial PBDEs were added to Annex A of the Stockholm Convention as persistent organic pollutants in May 2009. PBDEs are still frequently found in sludge and effluent from wastewater treatment plants, even though commercial PBDEs were prohibited or voluntarily phased out several years ago. Conventional wastewater treatment processes are not designed to effectively remove PBDEs. This indicates that there is an urgent need for new developments and improvements to enhance upon the treatment techniques which are currently available. Several studies have suggested the potential removal and degradation technologies for PBDEs in wastewater. In this study, the concentrations and compositional profiles of PBDE congeners in sludge and effluent are investigated by analyzing the relevant literature data in relation to their usage patterns in commercial products in North America and South Korea. The strengths and weaknesses of the current PBDEs removal techniques (i.e., biodegradation, zero-valent iron, photolysis, sorption, etc.) are discussed critically. In addition, future research direction regarding the treatment and removal of PBDEs from wastewater is also suggested, based on the literature review.

Key words : Persistent organic pollutants, Polybrominated diphenyl ethers, Treatment Technologies, Wastewater treatment plant

1. Introduction

PBDEs (Polybrominated diphenyl ethers)는 브롬계 방염제로써 1970년대 이후 매트리스, 가구, 전기/전자기기, 전선, 직물 제조 등에 방염처리 되어왔다(Cincinelli et al., 2012; Daso et al., 2012). PBDEs는 비페닐의 수소가 브롬으로 치환된 구조로써, 치환된 페닐기 브롬원자의 위치와 수에 따라 209종의 동질체(congeners)가 존재하며($C_{12}H_{(10-x)}Br_xO$ ($x=1, 2, \dots, 10$)), 10개의 동족그룹(homologue groups)로

나누어진다(mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-BDE) (Fig. 1). 이들 PBDEs은 상업적 제품으로 c-PentaBDE (commercial pentabromodiphenyl ether), c-OctaBDE (commercial octabromodiphenyl ether), c-DecaBDE (commercial decabromodiphenyl ether)이 사용되어 왔다 (Table 1). 그러나 PBDEs는 발암 및 독성물질로 확인되었고, 생물 축적성 및 환경 내 잔류성이 높아 유엔환경계획(United Nations Environment Programme, UNEP)에서는 2009년 5월 스톡홀름 협약을 통해 상업용 c-PentaBDE와 c-OctaBDE를 잔류성 유기오염물질(persistent organic pollutants)로 선정하였다. 따라서 협약 당사국은 c-PentaBDE와 c-OctaBDE의 제조, 사용, 거래를 금지해야 하며, 2030년까지 모든 제품과 폐기물을 처분해야 할 의무가 있다. c-DecaBDE은 아직까지 규제대상물질로 선정되지 않았지만, c-DecaBDE의 주요 성분인 deca-BDE (>99%)이 자외선이나 미생물에 의

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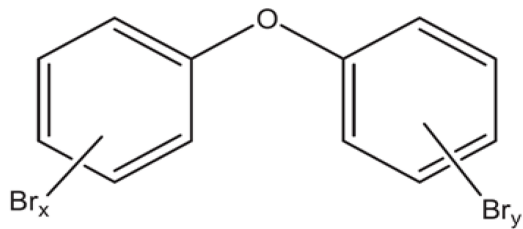
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Table 1. PBDE commercial product profile from various manufacturers.

Commercial Mixture	Products ^a	Homologue group of PBDE congeners (%)							
		tri-BDEs	tetra-BDEs	penta-BDEs	hexa-BDEs	hepta-BDEs	octa-BDEs	nona-BDEs	deca-BDE
c-PentaBDE	DE-71	~ 0.3	~ 39.5	~ 65.0	~ 11.7	~ 0.1			
	DE-71Bb	0 ~ 1	24 ~ 38	50 ~ 62	4 ~ 12				
	Bromkal 70-5DE	~ 0.2	~ 43.4	~ 55.6	~ 9.0	~ 0.3			
c-OctaBDE	DE-79				~ 10.5	~ 45.5	~ 37.9	~ 13.1	~ 1.3
	DE-79Bb			< 0.5	< 12	< 45	< 33	< 10	< 0.7
c-DecaBDE	Saytex 102E							~ 2.49	~ 96.8
	Bromkal 82-ODE						~ 0.6	~ 9.3	~ 91.6
	DE83R / DE83B ^b								> 98

^a La Guardia et al., 2006

^b Environ, 2003



- x + y = 1 mono-BDE
- x + y = 2 di-BDEs
- x + y = 3 tri-BDEs
- x + y = 4 tetra-BDEs
- x + y = 5 penta-BDEs
- x + y = 6 hexa-BDEs
- x + y = 7 hepta-BDEs
- x + y = 8 octa-BDEs
- x + y = 9 nona-BDEs
- x + y = 10 deca-BDE

Fig. 1. Chemical structure and 10 homologue groups of PBDEs.

해 분해될 경우, 유해성이 검증된 octa-BDEs와 penta-BDEs로 생성될 가능성이 있기 때문에 스톡홀름 협약의 잔류성 유기오염물질 후보로써 제안되었다(UNEP, 2007, 2014). 하지만 c-PentaBDE와 c-OctaBDE는 규제 이전 전 세계적으로 100,000 톤이 사용되었고, c-DecaBDE는 1,100,000 톤 이상이 사용되었으며, 현재에도 생산되고 있다. 이들은 대부분 북미지역에서 소비되고 있으며, 전체 사용량의 50%를 차지하고 있는 것으로 나타났다(BSEF, 2003). 국내에서는 또한 2003년 PBDEs 사용량을 조사한 결과, 약 7,800 톤의 c-DecaBDE가 소비된 것으로 파악되었다(ME, 2005). 그러므로, PBDEs 처리 제품은 현재까지 지속적으로 사용되고 있으며, c-DecaBDE는 현재까지 생산되고 있어, 국내의 하폐수 처리시설의 수질에서 고농도의 PBDEs가 검출되고 있는 실정이다. 특히, PBDEs의 사용량이 높았던 북미지역의 하폐수 처리시설 유입수에서는 265 ~ 51,232 ng L⁻¹의 PBDEs가 고농도로 검출되고 있다(Gardner et al., 2012; Ni et al., 2014; Nyholm et al., 2013). 국내 수처리시설의 유입수에서도 0.5 ~ 190 ng L⁻¹의 농도로 검출되고 있는 것으로 조사되었다(Kim et al., 2011; Lee and Kim, 2014). 하지만 PBDEs의 낮은 용해도와 높은 소수성, 난분해성의 특성으로 일반적인 하폐수 처리과정으로는 효율적으로 제거되지 못하고 있으며, 유입되는 PBDEs의 60 ~ 90%는 방류수와 슬러지를 통해 재 배출되고 있는 것으로 나타났다

(Deng et al., 2015; North, 2004; Peng et al., 2009; Song et al., 2006; Xiang et al., 2013).

우리나라는 스톡홀름 협약의 이행 당사국으로서 잔류성 유기오염물질인 PBDEs의 배출저감 관리방안 마련의 의무가 있으며, 이를 위한 중장기적 계획수립에 필요한 제반자료와 저감 및 처리기술방안의 관한 선진적인 연구가 필요하다. 하지만, 국내 하폐수 시설 내 PBDEs의 지속적인 농도 조사와 이를 저감 또는 제거하기 위한 기술 개선 연구는 선진국에 비해 매우 미비한 실정이며, 다각적으로 이루어지고 있지 않은 실정이다. 본 연구에서는 (1) 우리나라와 북미지역인 미국과 캐나다 내 하폐수 처리시설에서 배출되는 방류수와 슬러지 내 PBDEs의 잔류 농도 및 조성을 비교하여, 국내에서 배출되는 PBDEs의 특성을 파악하고자 한다. 또한 (2) 수처리 시설에서 PBDEs의 제거 및 분해를 위한 생물학적, 화학적, 물리학적 처리기술의 연구 현황을 고찰하고, 국내 배출수내 PBDEs의 조성을 고려한 추가적인 연구의 필요성을 제시하고자 한다.

2. Concentration and Composition of PBDEs in Effluent and Sludge from Wastewater Treatment Plant in North America and Korea

우리나라와 북미지역인 미국과 캐나다 내 하폐수 처리시설에서 배출되는 방류수와 슬러지 내 PBDEs의 잔류 농도 및 조성은 현장 모니터링 자료를 기초로 메타분석(meta-analysis)하여, 국가별 방류수와 슬러지 내 잔류 PBDE 농도를 제시하였다(Fig. 2). 특히 방류수와 슬러지 내 PBDEs의 주요 7개의 동질체의 농도와 조성을 파악하고 국가별로 비교 분석하였다(Fig. 3).

국내 하폐수 처리시설에서 배출되는 방류수 내 PBDEs의 농도는 0.03 ~ 5.10 µg L⁻¹의 범위(평균 1.23 µg L⁻¹)이며, 슬러지 내 PBDEs 농도는 17 ~ 6,540 ng g⁻¹인 것으로 나타났다(Hwang et al., 2012; Kim et al., 2011; Kim et al., 2016; Lee et al., 2014; Lee and Kim, 2014; Yoon et al., 2010). 이들 농도는 미국과 캐나다의 수처리 시설에서 배출되는 방류수 내 PBDEs 농도보다 약 25배 낮은 농도이다. 국내에서 배출되는 슬러지 내 평균 PBDEs 농도는 북미지

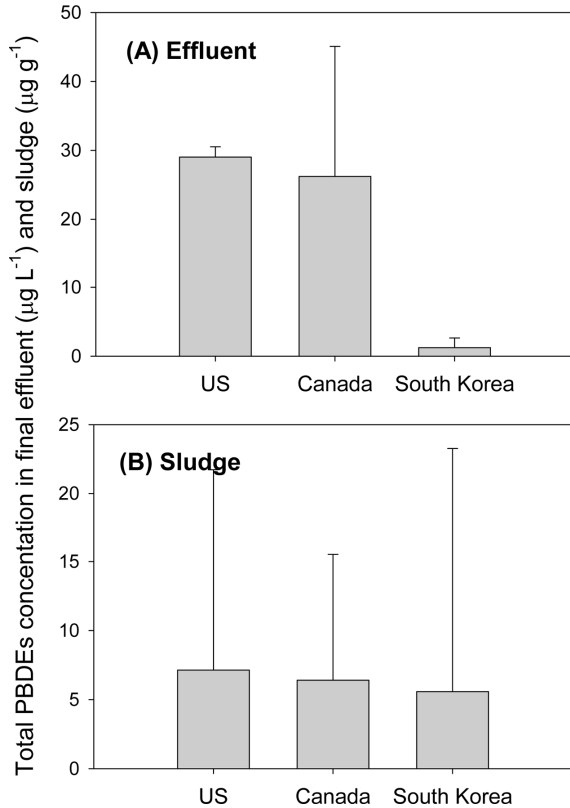


Fig. 2. Total concentration of PBDEs in (A) final effluent and (B) sludge released from wastewater treatment plants in United States (Anderson and MacRae, 2006; Andrade et al., 2010; Arnold et al., 2008; Ciparis and Hale, 2005; Davis et al., 2012; Hale et al., 2002; La Guardia et al., 2006; North, 2004; Reick, 2004; U. S. EPA, 2009; Venkatesan and Halden, 2014; Xia et al., 2010), Canada (Gorgy et al., 2010; Gottschall et al., 2010; Hale et al., 2003; Kim et al., 2013; Rayne and Ikononou, 2005a, b; Song et al., 2006) and South Korea (Hwang et al., 2012; Kim, 2011; Kim et al., 2016; Lee et al., 2014; Lee and Kim, 2014; Yoon et al., 2010).

역의 농도보다 다소 적은 농도로 검출되고 있는 것으로 나타났다. 이와 같이 북미지역 배출농도가 국내 배출농도에 비해 높게 검출되는 것은 PBDEs 사용량의 50% (~33,100 tones)가 북미지역에서 소비되었기 때문인 것으로 판단된다 (BSEF, 2003; Kim et al., 2017).

방류수와 슬러지 내는 잔류 PBDEs 동질체의 조성은 미국과 캐나다의 경우 BDE-209 > BDE-47 ≅ BDE-99 > BDE-100 이 주요 동질체로 나타났으며, 국내에서는 BDE-209 > BDE-207 > BDE-206 이 주요 동질체인 것으로 나타났다(Fig. 3). 특히 미국과 캐나다에서 고농도로 검출된 BDE-47, BDE-99, BDE-100은 국내 방류수와 슬러지 내에서 매우 낮은 농도로 잔류하고 있는 것으로 나타났다. BDE-47, BDE-99, BDE-100은 현재 생산과 사용이 금지된 c-PentaBDE와 c-OctaBDE의 주요 성분이며(Table 1), 이들 제품이 금지되기 전 생산량의 95% (7,100 tonne year⁻¹)는 미국과 캐나다에서 소비

되었기 때문에 국내에서 보다 높은 농도로 검출된 것으로 사료된다(BSEF, 2003). BDE-209는 국내 방류수와 슬러지에서 뿐만 아니라, 북미지역에서도 다른 동질체에 비해 월등히 높은 농도로 잔류하고 있는 것으로 파악되었다. 이는 c-PentaBDE와 c-OctaBDE의 사용 금지와 지속적인 c-DecaBDE 사용에 의한 것으로 판단된다(Kim et al., 2017).

또한 국내의 하폐수 처리시설에서의 슬러지 내 PBDEs의 잔류 농도는 방류수내 농도보다 높게 나타났으며, 특히 BDE-209는 슬러지에서 고농도로 검출되었다. 이는 PBDEs의 209개 동질체 중 BDE-209는 비페닐의 수소가 브롬으로 모두 치환되어 있어 가장 낮은 수용해성(<0.1 µg L⁻¹ at 24 °C)과 가장 높은 소수성(log K_{ow} > 9.97)의 특성을 갖기 때문에 (Breivik et al., 2016), 액상보다는 입자상 물질인 슬러지에 강하게 흡착될 수 있기 때문에 잔류 농도가 높은 것으로 판단된다.

3. Review of Removal Efficiency and Technology of PBDEs in Wastewater

하 폐수시설에서는 유기오염물질의 제거 및 분해를 위해 생물학적, 물리학적, 화학적 처리기술이 적용되고 있다. 생물학적 처리방법은 호기성 박테리아, 균류, 조류, 원생동물 등의 활동을 통해 폐수 내 유기물질을 함유한 폐수를 처리하기 위해 대부분의 수처리 시설에서 적용되고 있는 기술이다. 또한 수질 내 고농도의 난분해성, 독성의 유기화합물질을 효과적으로 처리하기 위해 물리화학적 처리기술이 적용되고 있다. PBDEs 또한 높은 소수성, 독성, 난분해성 특성 때문에 생물학적, 화학적, 물리학적 처리기술에 관한 연구가 활발히 진행되고 있다.

3.1 Biological treatment

He et al. (2006)은 *Sulfurospirillum multivorans*와 *Deharococcoides* 미생물 처리를 통해 고 브롬화 화합물인 저 브롬화 PBDE 동질체로 분해가 될 가능성을 제시하였다. Deplanche et al. (2009)은 황산염 환원박테리아인 *Desulfovibrio desulfuricans* palladized cell(bioPd)을 이용하여 PBDEs의 환원적 탈 브롬화가 90% 이상 인 것으로 확인하였다. 그러나 독성이 큰 저 브롬화 PBDEs(BDE-154, BDE-99, BDE-49, BDE-47)이 분해 산물로써 생성되어 미생물의 분해활동이 저감되고 이에 따라 처리속도가 급하게 감소하는 것으로 나타났다(He et al., 2006; Kim et al., 2012). 뿐만 아니라, 생물학적 탈 브롬화 과정에 필요한 분해시간은 수개월에서 일 년 이상이 요구되어지는 것으로 나타났다(Lee and He, 2010; Robrock et al., 2008). Gereke et al. (2005)은 혐기성 하수슬러지 내 BDE-209이 nona-BDEs와 octa-BDEs로 탈 브롬화 하는데 필요한 분해시간은 238일 이상인 것으로 보고하였다. 그러므로 생물학적 분해를 통한 PBDEs의 제거보다는 물리학적, 화학적 처리 반응을 통한 제거기술이 보다 효과적일 것으로 사료된다.

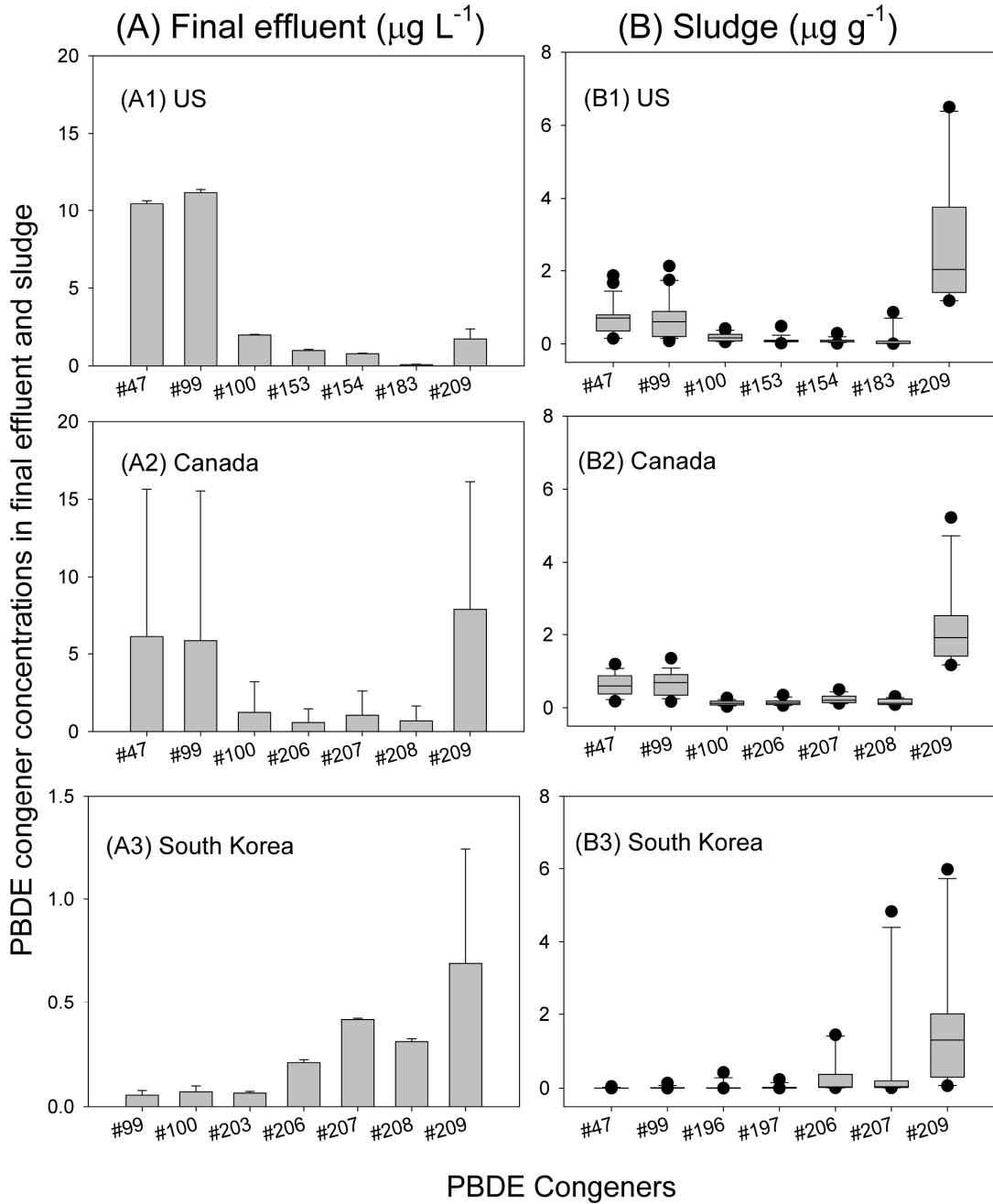


Fig. 3. Average concentration of all reported PBDEs from sewage sludge in North America, Europe, and Asia. Note that ordinate scales differ. The horizontal line, open circle, and closed circle inside the box represent the median, mean, and outliers, respectively.

3.2 Chemical treatment

화학적 처리방법에는 일반적으로 생물학적 처리에 한계가 있을 때, 적용되는 처리방법으로써 중화, 응집/침전, 산화, 환원 등의 반응 원리를 통해 유기화합물을 제거하는 기술이다. 특히 최근 몇 년간, 할로젠 유기 화합물(chlorinated methane, chlorinated benzene 등)을 제거하기 위해 영가 철 (Zero-Valent Iron, ZVI)을 이용한 환원반응이 하폐수의 오염처리 분야에서 성공적인 제거 기술로 평가 받고 있다. 또한 독성이 적고, 경제성이 높아 현장 적용 가능성이 높은 것으로 제시되고 있다. 화학적 처리방법의 또 다른 제

거 기술 중 광화학적 산화 반응 또한 수질 내 미량유기오염물질의 제거 처리시험에서 그 가능성이 제시되고 있다. 따라서 하폐수의 오염처리 분야에서의 할로젠 유기화합물의 분해에 긍정적인 효과를 보이고 있는 ZVI과 광화학적 분해 과정을 통한 PBDEs의 제거 연구 사례와 처리효율에 대해 고찰하고자 한다.

3.2.1 Zero-valent iron (ZVI)

최근 수질 내 존재하는 PBDEs를 제거하기 위해 다양한 형태의 화학적 처리기술이 개발되고 있다(Santos et al.,

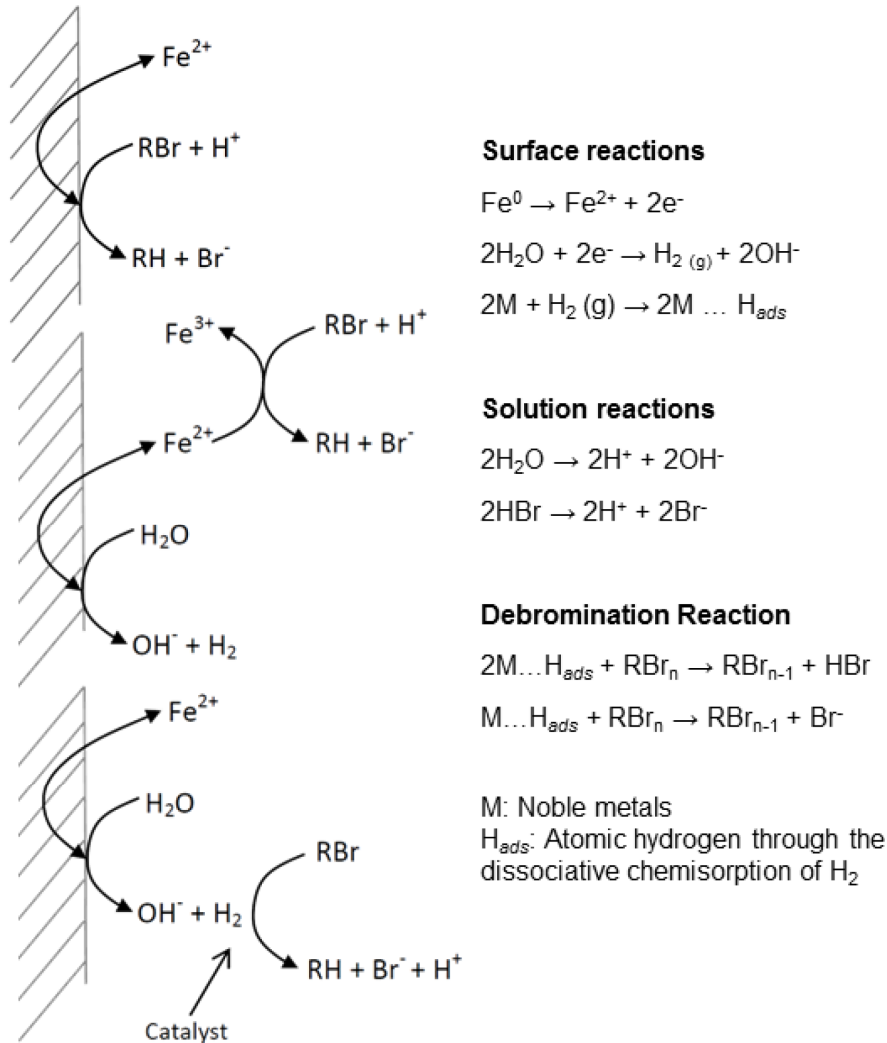


Fig. 4. The proposed pathway by Matheson and Tratnyek (Matheson and Tratnyek, 1994) for reductive debromination (adapted from Ciblak, 2011 and Santos et al., 2016).

2016). 특히 수질 내 할로젠 유기화합물인 PBDEs가 ZVI로부터 전자를 받아서 탈 할로젠 반응으로 제거되어진다. 할로젠 유기화합물인 PBDEs의 탈 브롬화 반응기작은 Fig. 4에 제시하였다.

ZVI에 의한 PBDEs의 탈 브롬화 반응은 일반적으로 유사 1차 반응(pseudo-first order reaction)으로 설명될 수 있지만, 초기 제거 반응속도가 빠르게 일어나고 이후에는 제거속도가 느려지기 때문에 두 단계의 속도 구간으로 나타나기도 한다(Cai et al., 2015; Fang et al., 2011a, b; Keum and Li, 2005; Luo et al., 2012; Peng et al., 2013). 이와 같은 현상은 ZVI가 환원반응을 하는 동안 철산화물 또는 철수산화물이 ZVI 표면에 생성되어 반응표면을 감소시켜 전자 이동을 방해했기 때문인 것으로 추정하였다(Fang et al., 2011a, 2011b; Keum and Li, 2005; Peng et al., 2013). 하지만, 반응 생성물 이외에 다양한 인자 또한 반응속도에 영향을 미치므로 정확한 속도 상수를 예측하기 어려운 실정이다. Habekost and Aristov (2012)는 ZVI에 의한 PBDEs의 환원적 탈 브롬화 반응이 질소조건의 높은 온도(350 ~

600 °C)에서 증가될 가능성을 제시하였고, Hu et al. (2012)은 PBDEs 이성질체(isomers)의 ortho와 meta 위치의 브롬 원자는 순양전하가 para 위치의 브롬보다 크기 때문에, ZVI 표면에서 탈 브롬화의 속도는 meta-Br > ortho-Br > para-Br 순으로 차이가 나는 것으로 제시하였다.

ZVI 반응표면의 감소에 따른 제거효율의 저감을 극복하기 위해, ZVI를 마이크로(mZVI) 또는 나노크기(nZVI)로 비표면적을 증가시켜 탈 브롬화 반응의 속도를 높이고 있다(Fang et al., 2011a; Shih and Tai, 2010). Fang et al. (2011b)은 nZVI에서의 BDE-209 탈분해 반응속도는 철 분말에서 보다 약 5배 높은 것으로 측정하였다. 또한 Shih and Tai (2010)과 Zhuang et al. (2010)은 표면적이 넓은 nZVI에서의 PBDEs의 탈 브롬화 반응 속도가 mZVI보다 큰 것으로 측정하였다. 그 외 탈 브롬화 효율을 증가시킬 수 있는 방법으로써 촉매 금속을 코팅시킨 이중금속 나노 영가철(bimetallic nZVI)이 제시되고 있다. Fang et al. (2011b)은 Ni를 촉매 금속으로 한 nZVI(iron-nickel nanoparticles, nZVI/Ni)를 이용하여 BDE-209의 탈 브롬화 반응 속도를 측정하였

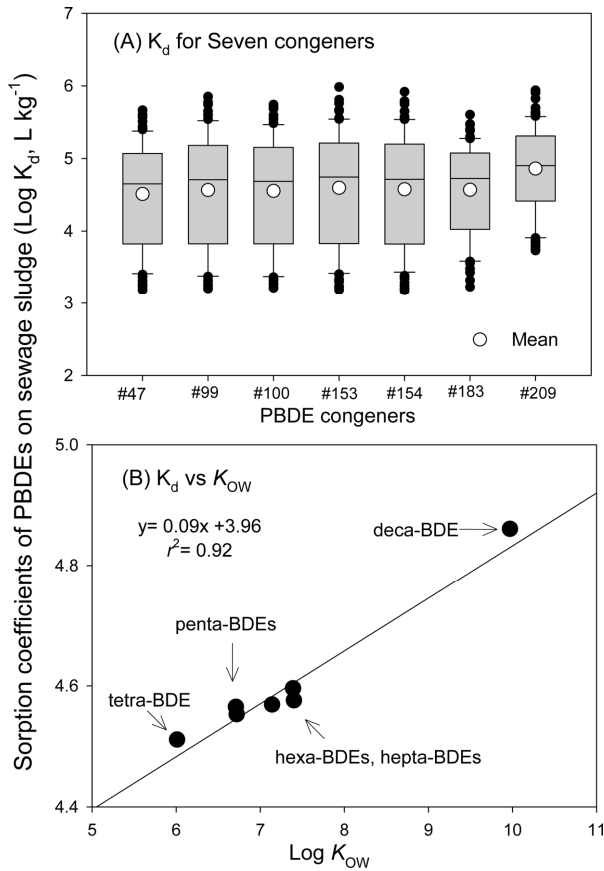


Fig. 5. (A) Sorption coefficient (K_d) values for seven PBDE congeners in sewage sludge in wastewater treatment plants (Data: Kim et al., 2013). The horizontal line, open circle, and closed circle inside the box represent the median, mean, and outliers, respectively. (B) Relationship between sorption coefficients (K_d) of PBDE congeners and partition coefficient (K_{ow}) of octanol and water (adapted from Kim et al., 2017).

고, 그 결과, 1차 속도 상수는 1.662 h^{-1} 으로 기존의 nZVI에 의한 반응 속도보다 약 52배 증가되었음을 보여주었다. Zhuang et al. (2010)와 Zhuang et al. (2011) 또한 촉매금속 Pb이 포함된 nZVI(iron-palladium nanoparticles, nZVI/Pd)은 nZVI에 비해 tri-, di-, mono-BDEs의 반응속도가 각각 2, 3, 4배 증가되고 있음을 제시하였다.

mZVI, nZVI, bimetallic ZVI를 이용한 수질 내 존재하는 PBDEs의 탈 브롬화 제거효율은 약 59~86%로써 효과적인 기술로 제시되고 있지만(Santos et al., 2016), 탈 브롬화에 의한 분해산물(저 브롬화 화합물)에 대한 잠재적인 독성과 잔류성에 대한 연구가 미흡하므로 제거 효율만으로 처리기술의 적절성을 평가하기 어렵다. 또한 다음에 열거하는 바와 같이, PBDEs 제거 효율 감소 원인 규명에 대한 연구 필요성이 제시되고 있다. i) Zhuang et al. (2012)는 금속 촉매의 과도한 코팅이 탈 할로젠 반응을 감소시키는 원인으로 지적하였고, 0.3 Pd/Fe wt. % 이상일 경우 탈 할로젠 반응이 급격히 감소될 것으로 제시하였다. ii) 또한 nZVI은

쉽게 응집되어 큰 입자를 형성하기 때문에 제거반응에 참여하는 표면적이 감소하여 탈 브롬화 반응 또한 감소될 것으로 제시되었다(Wang, Ni et al., 2013). iii) 뿐만 아니라, 수질 내 PBDEs의 농도가 높을 경우 제한된 반응표면에서 PBDE 동질체 사이의 경쟁효과에 의해 제거효율이 감소될 수 있을 것이다(Fang et al., 2011a, 2011b). iv) 그리고 하 폐수에 존재하는 유기물(예, 휴믹물질 등) 또한 PBDEs와 ZVI의 탈 브롬화 반응을 감소시키는 원인으로 제시되고 있다. 즉, 휴믹 물질에 존재하는 카르복시기와 페놀성 수산기는 우선적으로 ZVI 표면에 화학적 흡착결합 반응을 하기 때문에 PBDEs의 탈 브롬화 반응을 방해하게 된다(Cai et al., 2015; Tan et al., 2014). 따라서 ZVI을 통한 PBDEs의 제거 효율성을 증가시키기 위해서는 추가적인 연구를 기초로 적용 가능성을 고찰해야 할 것이다.

3.2.2 Photolysis

수용액상에서 PBDEs은 광화학적 분해반응으로 환원적 탈 브롬화를 통해 저 브롬화 화합물로 분해된다(Bezares-Cruz et al., 2004; Eriksson et al., 2004; Fang et al., 2008; Rayne et al., 2006; Sanchez-Prado et al., 2012; Sun et al., 2013; Wei et al., 2013). PBDEs의 광분해 반응은 대부분 유사 1차 속도 모델로 설명되지만, 속도상수와 양자효율(quantum yields)은 유기용매의 종류와 radiation의 종류/강도, PBDE 이성질체에 따라 다르게 나타난다. Eriksson et al. (2004)은 PBDEs의 광분해 반응속도가 메탄올에서보다 메탄올/물 혼합용액에서 약 1.7배 느리며, 메탄올과 물보다 수소공여체의 능력이 큰 tetrahydrofuran(THF)에서는 약 2~4배 느린 것으로 측정하였다. Xie et al. (2009) 또한 THF에서 BDE-209의 반응속도와 양자효율이 메탄올에서 보다 각 2배, 1.3배 감소하는 것으로 제시하였다. 그러나 유기용매의 수소 공여체의 증가만으로 광분해 속도와 양자효율의 저감 현상을 충분히 설명하기 어렵다. THF > 톨루엔 > 메탄올의 순으로 수소 공여체의 능력이 감소하지만, nona-BDEs의 광분해는 오히려 메탄올 또는 THF에서 보다 톨루엔에서 반응속도가 증가하였다(Davis and Stapleton, 2009). 이와 같은 결과는 톨루엔이 발색단용매(chromophore solvent)로서 방향족 고리가 빛을 흡수하는 화학구조의 용매이기 때문에 간접적으로 PBDEs의 광화학적 분해가 발생했기 때문인 것이다(Schwarzenbach et al., 2005). 따라서 톨루엔에서 저 브롬화 화합물의 광화학적 분해 효율은 약 30%로 메탄올에서의 효율(7~12%)보다 높게 나타난 것으로 확인하였다(Davis and Stapleton, 2009; Sanchez-Prado et al., 2012).

하지만, 수용액상에서 PBDEs의 광분해 반응은 유기용매에서와 달리 거의 일어나지 않으며, 유기용매를 통한 외삽법을 통한 예측도 어려운 실정이다(Wang et al., 2015). 따라서 하폐수 시설 유입수내 PBDEs의 광화학적 분해 기술을 현실적으로 적용하기 위해서는 개선된 연구가 필요하다. 뿐만 아니라 PBDEs의 광화학적 분해는 다양한 원인으로 인해 분해 효율이 저감될 가능성이 제기되었다. Wei et al.

(2013)은 핵산에서 UV를 통한 저 브롬화 이성질체(≤ 8 Br)의 탈 브롬화반응은 meta \geq ortho $>$ para 순으로 일어나는 것 제시하였다. 이와 같은 현상은 PBDE 이성질체의 para 위치의 브롬과 탄소와의 결합안정성이 ortho와 meta 위치의 브롬과의 결합보다 높기 때문인 것으로 추정하고 있다 (Davis and Stapleton, 2009; Wang, Hou et al., 2013; Wei et al., 2013; Xie et al., 2009; Zeng et al., 2008). 그러나 고 브롬화 화합물의 경우, 많은 브롬이 치환되어 구조적인 복잡성과 브롬의 치환 형태의 관련성 때문에 이성질체 간의 탈 브롬화 반응의 차이는 없는 것으로 제시되었다(Fang et al., 2008).

PBDEs의 탈 브롬화 반응은 조사되는 광선의 세기와 파장에 따라 다르게 나타난다. Shih and Wang (2009)는 UV 파장의 길이에 따라 BDE-209의 탈 브롬화 반응을 측정하였고, 긴 파장(350~400 nm)보다 비교적 짧은 파장(300~330 nm)으로 조사하였을 때 분해속도가 빠른 것으로 나타났다. 이는 BDE-209는 300~330 nm 영역의 파장에서 흡수가 가장 잘 이루어져 탄소와 브롬의 결합을 쉽게 깨뜨려 저 브롬화 화합물로 분해되는 속도가 가장 빠른 것으로 추정되었다. 뿐만 아니라, 광선의 세기 또한 PBDEs의 탈 브롬화 반응에 영향을 미치는 중요한 인자이다. Bezares-cruz et al. (2004)는 BDE-209를 계절별 태양광 조사를 통해 탈 브롬화 반응상수를 제시하였고, 광세기가 가장 큰 7월의 탈 브롬화 반응상수($1.86 \times 10^{-3} \text{ S}^{-1}$)가 10월의 반응상수($1.11 \times 10^{-3} \text{ S}^{-1}$)보다 커 광세기의 증가에 따른 광화학적 분해반응이 증가하는 것으로 나타났다.

그 외에 하폐수 내 존재하는 유기물질 또한 PBDEs의 광화학적 분해반응의 영향 인자로 제시되고 있다. Leal et al. (2013)은 수질 내 휴믹산과 풀빅산이 조사되는 빛을 차단하여 탈 브롬화 반응을 감소시키는 것으로 보고하였다. 하지만 휴믹물질이 광분해에 미치는 영향에 대한 자세한 메카니즘 및 구체적인 영향에 관한 연구는 미비한 실정이다.

3.3 Physical treatment

하폐수 시설에서 이용되는 물리학적 처리는 스크리닝, 침사, 응결, 침강분리, 부상분리, 흡착 등이 적용되고 있다. 이 중 흡착 제거 방법은 소수성이 크며, 난분해성이 큰 유기오염물질을 제거하는데 효과적인 것으로 알려져 있다. 특히 활성탄소를 이용한 흡착제거는 미량의 유기오염물질이라도 효과적으로 제거되는 것으로 나타났다. 뿐만 아니라, 하폐수 처리 과정 시 발생하는 활성 슬러지 또한 수질 내 존재하는 유기오염물질을 제거하는 흡착제로써의 역할을 하고 있다(Rashed, 2013).

Song et al. (2006)은 하폐수 처리시설 내 활성슬러지를 통한 PBDEs의 흡착제거 효율이 80% 이상인 것으로 제시하였고, Lyman (1990)은 수용액상 내 유기탄소에서 PBDE 동질체의 흡착상수($\log K_d$)는 di-BDEs (4.11) < tri-BDEs (4.35~4.41) < tetra-BDEs (4.57~4.73) < penta-BDEs (4.89~5.17) < hexa-BDEs (5.11~5.69) < octa-BDEs (5.92~6.22) < deca-BDE (6.80) 순이며, 고 브롬화 화합물일수록 흡착제

거 효율이 증가하는 것으로 제시하였다. 이와 같은 흡착경향은 Kim et al. (2017)의 북미지역, 유럽, 아시아 지역 하폐수 시설에서 배출되는 슬러지와 방류수에 잔류하는 PBDEs 농도를 통한 메타분석 결과에서도 나타났다. PBDE 동족그룹의 흡착은 deca-BDE > hepta-BDEs \cong hexa-BDEs > penta-BDEs > tetra-BDEs 순으로 감소하였으며(Fig. 5A), PBDE 동질체의 K_{OW} 와 유의한 양의 상관관계($y = 0.09x + 3.96$, $r^2 = 0.92$) (Fig. 5B)를 나타냈다. 그러므로 저 과불화 화합물에 비해 소수성이 강한 deca-BDE는 슬러지 표면에 강하게 partitioning되어 슬러지에 고농도로 잔류하는 것으로 판단하였다. Ni et al. (2014)은 PBDEs의 제거를 위해 표면적이 넓고, 높은 공극률을 갖는 호기성 입자를 통해 폐수 내 질소, 인, 유기물, 중금속 등을 제거하는 호기성 슬러지 입자 기술(aerobic granulation technologies)을 적용하였다. 그 결과, 호기성 입자슬러지 표면에서 PBDE의 흡착은 변형된 유사 1차 속도 반응으로, BDE-209는 저 브롬화 화합물에 비해 높은 흡착반응을 나타냈다.

하지만 PBDEs의 흡착제거는 온도와 접촉시간, 슬러지양이 증가할수록, pH가 낮아질수록 효율이 증가하지만, 이온강도의 증가는 PBDEs의 흡착을 저감시킨다(Ni et al., 2014). 이는 이온 농도의 증가에 따라 PBDEs의 용액 내 활동도가 증가되어, 고상 표면에 PBDE의 partitioning이 감소되었기 때문이다. Ter Laak et al. (2009)은 수질 내 용존 유기탄소 또한 PBDEs의 흡착제거에 영향을 미치는 것으로 제시하였다. Li (2015)은 용존 유기탄소의 PBDEs 흡착상수를 $10^{3.97} \sim 10^{5.16} \text{ L kg}^{-1}$ 범위로 측정하였고, 고 브롬화 화합물의 동질체일수록 흡착이 증가하는 것으로 보고하였다. 그러므로 낮은 용해도와 높은 소수성의 PBDE 동질체는 폐수 내 용존성 유기물질과 강하게 흡착되어 방류될 가능성이 있을 것으로 판단된다. 하지만 이에 대한 자세한 흡착 메카니즘은 여전히 불확실한 실정이다(EU, 2003; Kim et al., 2011; Kim and Osako, 2004).

4. Results and Discussions

우리나라에서는 2004년 c-PentaBDE 사용이 금지되었으나 c-DecaBDE는 현재에도 상업적으로 사용되고 있다(ME, 2010). 이로 인해 하폐수 처리시설 유입수에는 c-DecaBDE의 주요 성분인 BDE-209가 검출되고 있으며, 수처리 후 배출되는 슬러지와 방류수에서 또한 BDE-209가 고농도로 잔류하고 있는 것으로 나타났다. 따라서 효과적인 PBDEs 제거를 위해 생물학적, 화학적, 물리학적 처리기술의 개선을 위한 연구는 활발히 진행되고 있다. 하지만 제한된 처리기술을 국내에 적용하기 위해서는 다각적인 고찰과 추가 연구가 필요하다. 생물학적 처리의 경우, 독성이 강한 저 브롬화 화합물이 분해산물로 생성되어 미생물의 분해효율을 저감시키고, 긴 분해시간이 요구되는 것으로 나타났다. 따라서 국내 수처리 시설에 고농도로 잔류하는 고 브롬화 화합물인 BDE-209를 제거하기 위해서는 박테리아, 균류, 조류 등을 포함한 미생물학적 추가 연구가 필요하다. 뿐만

아니라 생물학적 처리기술의 효율적 처리를 위해 화학적/물리학적 처리기술과 연계된 복합기술에 관한 연구가 필요할 것이다. 이를 위해 각 처리기술의 공정 방법과, 중간처리 후 생산될 수 있는 분해산물의 대사체 패턴의 예측에 관한 연구가 요구된다. 화학적 처리기술에서 영가철을 이용한 탈 브롬화 기술과 광화학적 분해 기술은 다양한 인자를 고려하여 연구가 진행되고 있지만, 수처리시설 내로 유입되는 다량의 하폐수를 처리하기에는 한계가 있으며, 경제적인 비용 또한 문제로 제시되고 있다. 따라서 복합적이며 융합적인 기술 조합으로 처리효율과 비용을 해결해야 할 것이다. 물리학적 흡착제거 기술은 보다 경제적으로 PBDEs를 효율적으로 제거할 수 있는 기법으로 평가될 수 있지만, 제거에 사용된 흡착제(활성탄소, 슬러지 등)가 2차 오염원이 될 수 있으므로 이에 대한 사후처리방안에 대한 모색도 필요한 시점이다. 뿐만 아니라 폐수 내 존재하는 용존 유기물질, 이온강도 등의 복합적 수질인자는 PBDEs를 흡착제거를 저감시키는 원인이 될 수 있어 방류수와 함께 수계로 유출될 수 있다. 그러므로 PBDEs의 흡착제거 반응을 저감시키는 수질조건과 시설 운영인자를 면밀히 검토하고, 이에 관여하는 반응 기작에 대한 후속 연구가 필요하다.

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[Supplementary Information]

Table S1. Summary of study on treatment technologies (biological process, zero-valent iron, photolysis, and sorption) for removal of PBDEs from wastewater

	Summary	Ref.
Biological process	Debromination of deca- and octa-BDE mixture is demonstrated with anaerobic bacteria including <i>Sulfurospirillum multivorans</i> and <i>Dehalococcoides</i> species. Hepta- and octa-BDEs were produced by the <i>S. multivorans</i> culture when it was exposed to deca-BDE, although no debromination was observed with the octa-BDE mixture. A variety of hepta- through di-BDEs were produced by <i>Dehalococcoides</i> -containing cultures exposed to an octa-BDE mixture, despite the fact that none of these cultures could debrominate deca-BDE. The more toxic hexa-154, penta-99, tetra-49, and tetra-47 were identified among the debromination products.	He et al., 2006
	The ability of palladized cells to promote the reductive debromination of a BDE-47 is demonstrate. BioPd was five times more effective than using commercial Pd(0) catalyst	Deplanche et al., 2009
	Microcosms (<i>Dehalococcoides</i> etc) were investigated to determine their debromination potential with an octa-BDEs consisting of hexa- to nona-BDEs. Debromination products ranging from hexa- to mono-BDEs were generated within 2 months. Tetra-BDEs accounted for 50 % of the total product.	Lee and He, 2010
	Bacteria representing three different dehalogenating genera, <i>Dehalococcoides</i> , <i>Dehalobacter</i> , and <i>Desulfitobacterium</i> , were evaluated to provide a broad understanding of anaerobic PBDE debromination. Debromination of the highly brominated congeners was extremely slow, with usually less than 10 % of nM concentrations of PBDEs transformed after three months.	Robrock et al., 2008
	Degradation of BDE-209 and the formation of octa- and nona-BDEs were experimented under anaerobic conditions. Sewage sludge was used as the inoculum and incubated up to 238 days with and without a set of five primers. concentrations of BDE-209 decreased by 30 % within 238 days. This corresponds to a pseudo-first-order degradation rate constant of $1 \times 10^{-3} \text{ d}^{-1}$. Without primers, the degradation rate constant was 50 % lower.	Gereke et al., 2005
Zero-Valent iron	Using steel pickling waste liquor as a raw material to prepare nZVM can overcome this deficiency. nZVM and nZVI both can effectively remove BDE-209 with little difference in their removal efficiencies, and humic acid inhibited the removal efficiency, whereas metal ions promoted it. Both nZVM and nZVI removed BDE-209 with similar removal efficiencies. The effects and cumulative effects of humic acid and metal ions on nZVM and nZVI were very similar in terms of the efficiency of the BDE-209 removal.	Cai et al., 2015
	Ni/Fe bimetallic nanoparticles used to degrade BDE-209. Ni/Fe bimetallic nanoparticles with diameters in the order of 20-50 nm could effectively degrade BDE-209 in THF/water. Ni/Fe bimetallic nanoparticles with diameters in the order of 20-50 nm could effectively degrade BDE-209 in THF/water.	Fang et al., 2011a
	Nanoscale zero-valent metallic particles (S-nZVI) were prepared from steel pickling waste liquor by chemical deposition and used to remove BDE-209 in a water/THF (4/6, v/v) solution. nZVI and Ni/Fe particles were also prepared. The degradation rate of BDE-209 by S-nZVI followed a pseudo-first order kinetics. The removal efficiency increased with increasing metal dosage but decreased with increasing initial BDE-209 concentration. High reaction rate was observed at more water content solvent, indicating that hydrogen ion was the driving force of reaction. Comparing different nanoscale Fe-based materials, the removal of BDE-209 by S-nZVI was found more effective than nZVI.	Fang et al., 2011 b
	Within 40 days 92 % of BDE-209 was transformed into lower bromo congeners. During the initial reaction period of BDE-209 (<5 days), hexa- to hepta-BDEs were the most abundant products, but tetra- to penta-BDE were dominant after 2 weeks. The amount of mono- to tri-BDEs was steadily increased during the experiments. The reaction rate constants of lower BDEs decreased as the number of bromines decreased. The initial reductive debromination rate constants were positively correlated with the heats of formation of BDEs.	Keum and Li, 2005
	Debromination of BDE-209 and -47 by Fe-Ag nano-particles were investigated under microwave radiation (Fe-Ag/MW). Approximately 97 % of BDE-209 or 78 % of BDE-47 were rapidly transformed to its degradation products within 8 min in the Fe-Ag/MW. The dehalogenation efficiency was enhanced apparently by microwave radiation. di- to nona-BDEs were formed during BDE-209 reduction, while diphenyl ether to tri-BDEs were observed during BDE-47 degradation.	Luo et al., 2012
	Removal processes of BDE-209 and -3 with mZVI were investigated to get better understandings for the removal mechanism based upon adsorption and degradation. The removal kinetics revealed two-step kinetics: a fast removal step at the beginning of the reaction and a follow-up slow removal step. About 10-20 % of BDE-209 and 15-30 % of BDE-3 were adsorbed on mZVI. 70 % of BDE-209 and 60 % of BDE-3 was degraded by mZVI within about one month.	Peng et al., 2013
	Reductive PBDEs occurs efficiently at moderately elevated temperatures (350-600°C) with zero valent iron (iron powder) in a nitrogen atmosphere.	Habekost and Aristov, 2012
	To better understand the mechanism of this reaction, seven selected BDE congeners and their anions were investigated at the density functional theory level. The debromination preference is theoretically evaluated as meta-Br > ortho-Br > para-Br. In addition, both the calculated frontier orbital energies and adiabatic electronic affinities were found to be highly related to their experimental reductive debromination rate constants.	Hu et al., 2012

Table S1. Summary of study on treatment technologies (biological process, zero-valent iron, photolysis, and sorption) for removal of PBDEs from wastewater (continued)

	Summary	Ref.
Zero-Valent Iron	Within 40 min 90 % of BDE-209 was rapidly removed by nZVI as compared to around 40 d needed for 24-fold weight of microscale ZVI. The removal by nZVI is much faster than that by microscale ZVI due to its high surface area and reactivity. At a different pH, the pseudo-first-order removal rate constants of BDE-209 linearly increased from 0.016 to 0.024 min ⁻¹ with the decreasing of aqueous initial pH values from 10 to 5. The degradation of BDE-209 with nZVI is favorable in an acid condition. The debromination pathways of BDE-209 with NZVI were proposed on the basis of the identified reaction intermediates ranging from nona- to mono-BDEs for an acid condition and from nona- to penta-BDEs for an alkaline condition. The debromination of PBDEs from para positions is more difficult than that from meta or ortho positions.	Shih and Tai, 2010
	nZVI could effectively debrominate the PBDEs into lower brominated compounds and diphenyl ether. The reaction rate constants were estimated by assuming the reaction between PBDEs and nZVI was a pseudo-first-order reaction and the rates decreased with fewer bromine substituents.	Zhuang et al., 2010
	Palladization of nZVI promoted the dehalogenation kinetics for mono- to tri-BDEs. Compared to nZVI, the iron-normalized rate constants for nZVI/Pd were about 2-, 3-, and 4-orders of magnitude greater for tri-, di-, and mono-BDEs, respectively, with diphenyl ether as a main reaction product.	Zhuang et al., 2011
	Two kinds of commercially available nanoscale Fe(0) slurries, a freeze-dried laboratory-synthesized Fe(0) nZVI, and their palladized forms were used to investigate the effect of particle properties and catalyst on PBDE debromination kinetics and pathways. The activity of nZVI/Pd was optimized at 0.3 Pd/Fe wt %. commercially available nanoscale Fe(0) slurries. debrominate selected environmentally-abundant PBDEs, including BDE 209, 183, 153, 99, and 47, to end products di-BDEs, mono-BDEs and DE in one week, while nZVI/Pd (0.3 Pd/Fe wt %) mainly resulted in DE as a final product.	Zhuang et al., 2012
	To minimize the aggregation and size effects of nZVI, nZVI/boron nitride nanosheets composites (BNNSs) were fabricated via a one pot "autoclave route" on a gram-scale. The BNNSs matrixes benefit the retention of the activity for nZVI. The high specific surface area (182 m ² g ⁻¹) and density of structural defects allows enrichment of the pollutants, leading to a relatively high conversion by the nearby supported nZVI. Meanwhile, the gram-scale bifunctional nZVI/BNNSs have both reductive and magnetic properties, which make them highly reactive towards the test PBDEs.	Wang, Ni et al., 2013
	Influence of humic acid (HA) and transition metals on the removal of PBDEs by nZVI were investigated. The specific surface area and average size of the nZVI particles were 35 m ² g ⁻¹ and 50-80 nm, respectively. HA inhibited the removal of PBDEs; as the concentration of HA increased, its inhibitory effect intensified and the first-order kinetic constants decreased. Cu ²⁺ , Co ²⁺ , and Ni ²⁺ enhanced the removal of PBDEs (Ni ²⁺ > Cu ²⁺ > Co ²⁺). The values of the first-order kinetic constants under the combined effect were between the values of the rate constants under the individual components.	Tan et al., 2014
Photolysis	Photochemical degradation of 15 individual PBDEs substituted with 4–10 bromine atoms was studied in methanol/water (8:2), pure methanol and THF by UV light in the sunlight region. The photochemical reaction rate decreased with decreasing number of bromine substituents in the molecule but also in some cases influenced by the PBDE substitution pattern. The reaction rate was dependent on the solvent in such a way that the reaction rate in a methanol/water solution was consistently around 1.7 times lower than in pure methanol and 2–3 times lower than in THF. The UV degradation half-life of deca-BDE (T _{1/2} = 0.5 h) was more than 500 times shorter than the environmentally abundant congener 2,2',4,4'-tetraBDE (T _{1/2} = 12 d) in methanol/water.	Eriksson et al., 2004
	Photolysis of BDE-209 was investigated in THF, dichloromethane, isopropanol, acetone, ethanol, methanol, acetonitrile and dimethylsulfoxide. Hydrogen donating efficiency and electron donating efficiency of solvents were not the decisive factors for the photolytic rate, which was proved by the fast photolysis of BDE-209 in CCl ₄ , a solvent without hydrogen and difficult to donate electrons. Besides hydrogen addition process, intermolecular polymerization might occur during the photolysis.	Xie et al., 2009
	Photodegradation of BDE-206, -207, and -208 was examined individually in different solvents (toluene, methanol, and THF) exposed to natural sunlight and then analyzed to identify the primary degradation products. Rapid degradation of nona-BDEs (half-lives ranging from 4.25 to 12.78 min) was observed coincident with formation of octa- and hepta-BDEs. BDE-207 photodegraded most rapidly while BDE-206 photodegraded the slowest. Mass balances were found to vary with the type of solvent (recovery ranging from 76 to 95 %).	Davis and Stapleton, 2009
	Photochemical degradation of BDE-100 was examined using an artificial UV light. Photoproducts detected during ice photolysis of BDE-100 which were: two tetra-BDEs (BDE-3 and -47), two tri-BDEs, two di-BDEs. BDE-100 photolysis proceeded fast and a 75 % degradation was recorded to the UV irradiation for 10 min.	Sanchez-Prado et al., 2012
	Photolytic kinetics of BDE-47 and -28 were observed in natural waters. The rate constants for BDE-47 and -28 (9.01 and 17.52 × 10 ⁻³ min ⁻¹), added to isopropyl alcohol, were very close to those (9.65 and 18.4 × 10 ⁻³ min ⁻¹) in water, proving the less indirect photolytic contribution of ·OH in water.	Wang et al., 2015

Table S1. Summary of study on treatment technologies (biological process, zero-valent iron, photolysis, and sorption) for removal of PBDEs from wastewater (continued)

	Summary	Ref.
Photolysis	BDE-209, -208, -207, -206, -196, -183, -154, -153, -100, -99, -85, -47 and -28 in hexane were individually exposed to sunlight for up to 64 h. The disappearance rate constant increased exponentially with increasing number of bromines. While no evident difference in debromination preference among ortho, meta and para bromines was found for heavier congeners, the vulnerability rank order was meta ≥ ortho > para for the lighter congeners (≤8 Br). The total molar mass of PBDEs continuously decreased during sunlight exposure.	Wei et al., 2013
	BDE-47 has been used to investigate the degradation and transformation of PBDEs in gas and liquid phases under UV with 30 mW cm ⁻² . BDE-47 can be transformed to less-brominated BDE analogs. A total of six compounds that are less-brominated BDEs and two brominated phenols were observed as transformation products in the reaction mixtures. Different degradation rates of BDE-47 in n-nonane and in isooctane in the same chamber system were observed. Degradation rate of BDE-47 in n-nonane was faster than in isooctane. Under UV irradiation, the bromine on the ortho positions of the phenyl rings was lost first to form BDE-28, which then progressively lead to BDE-15 or -8.	Wang, Huo et al., 2013
	To better understand PBDE photodegradation and validate the photodegradation model, experiments were conducted on the photodegradation of BDE-209, BDE-184, BDE-100, and BDE-99 under UV light (254 nm, 2.7×10 ⁻⁸ mol/s/cm ³) in isooctane. photodegradation of PBDEs is a first-order reaction and, further, that the rate-determining step is the stepwise loss of bromine. BDE-99 will remain the most abundant penta-BDE, while BDE-49 and BDE-66 will increase greatly and will be comparable in abundance to BDE-47.	Zeng et al., 2008
	Photodegradation of BDE-28, 47, 99, 100, 153, 183 in hexane was investigated under UV light in the sunlight region. All photodegradation reactions followed the pseudo-first-order kinetics, with the half-lives ranging from 0.26h for BDE-183 to 6.46h for BDE-100. The photochemical reaction rates decreased with decreasing number of bromine substituents in the molecule. Principal photoproducts detected were less brominated PBDEs, and no PBDE-solvent adducts were found. For less brominated diphenyl ethers, the photoreactivity of bromines at various positions of phenyl rings decreased in the order: ortho>para; while for higher brominated diphenyl ethers, the difference became not significant.	Fang et al., 2008
	A linear increase of the photodegradation rate constant for BDE-209 was observed with the solar light intensity and irradiation ranges of wavelength, 300-330 nm, 350-400 nm, and 300-400 nm. The degradation reactions follow the pseudo-first-order kinetics. The photodegradation of BDE-209 produced other less brominated diphenyl ethers under ultraviolet light exposure. BDE-209 underwent rapid reductive debromination in these photodecomposition experiments. The formation rate constants of three nonabromodiphenyl ethers increase with the order of BDE-206, -207 and -208, indicating debromination mainly occurred at para>meta>ortho positions.	Shih and Wang, 2009
	BDE-209 dissolved in hexane, reacts in minutes via direct solar irradiation, at midlatitude in afternoon July and October sunlight. Observed first-order reaction rate constants at the different exposure times were 1.86×10 ⁻³ s ⁻¹ (July) and 1.11×10 ⁻³ s ⁻¹ (October). The range of wavelengths where both the molar absorptivity of BDE-209 and the solar irradiance flux are significant occurs between 300 and 350 nm.	Bezares-cruz et al., 2004
	Kinetics of BDE-209 photodegradation in water was studied and the influence of different fractions of aquatic humic substances was evaluated. The photodegradation of BDE-209 in aqueous solution followed pseudo-first-order kinetics. The average quantum yield obtained of 0.010 (about 20-fold lower than the quantum yield determined in ethanol) allow to predict an outdoor half-life time of 3.5h. The photodegradation percentage of BDE-209 decreased substantially in the presence of humic and fulvic acids.	Leal et al., 2013
Physical process	Detailed characterization of the distribution of BDE-28, 47, 99, 100, 138, 153, 154, and 183 was carried out at five sites along the treatment process at an activated sludge-type secondary treatment municipal facility. Presence of dissolved organic matter affected the mobility of PBDEs during the initial stages of the treatment process. About 9% of the influent mass of PBDE to the facility is estimated to be discharged into the final effluent.	Song et al., 2006
	Concentrations of BDE-47, -99, -100, -153, -154, -183, and -209 in sewage sludge have been investigated in North America, Europe, and Asia. Hydrophobic interactions mainly contribute to PBDE retention in the sewage sludge; more hydrophobic congeners are sorbed to a greater extent than less hydrophobic ones, with deca-BDE > hepta-BDEs ≈ hexa-BDEs > penta-BDEs > tetra-BDEs.	Kim et al., 2017
	Removal of BDE-209 from wastewater is mainly via biosorption onto aerobic granular sludge. The uptake capacity increased when temperature, contact time, and sludge dosage increased or solution pH dropped. Ionic strength had a negative influence on BDE-209 adsorption. The modified pseudo first-order kinetic model was appropriate to describe the adsorption kinetics. Microbial debromination of BDE-209 did not occur during the first 30 days of operation.	Ni et al., 2014

Table S1. Summary of study on treatment technologies (biological process, zero-valent iron, photolysis, and sorption) for removal of PBDEs from wastewater (continued)

	Summary	Ref.
Physical process	Desorption of BDE -47, -99, -153, -183 from a polymer phase to an aqueous medium was monitored at humic acid concentrations (0, 2.4, 11.8, 47.1, and 118 mg L ⁻¹). The lot DOC-water sorption coefficients (L Kg ⁻¹) of BDE-47, -99, -153, -183 were 5.96, 6.35, 6.71, 6.63, respectively. The rate of release of the chemical by the polymer phase demonstrates that the chemical sorbed to dissolved humic acid contributed significantly to the total mass transfer when the affinity for the humic acid was sufficiently high.	Ter Laak et al., 2009
	Influence of DOM in the binding (DOM-water partition coefficients, K_{DOC}) and abiotic photodegradation rates, mechanisms, and product formation of PBDEs was quantified. PBDEs strongly bind to DOM, whereby the measured K_{DOC} were nearly an order of magnitude lower than previously reported values for the same PBDE congeners in soil or commercially available organic matter. The K_{DOC} values range from 103.97 to 105.16 L kg ⁻¹ of organic carbon, which increase with congener hydrophobicity. This association with DOM facilitates PBDE photodegradation, resulting in at least a factor of 2 increase in rate constants for the indirect relative to direct photolysis of BDE-47. Photodegradation rates are strongly positively associated with DOM aromaticity and negatively correlated to dissolved oxygen.	Li, 2015