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MINI-REVIEW

Phthalates biodegradation in the environment

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Abstract Phthalates are synthesized in massive amounts to produce various plastics and have become widespread in environments following their release as a result of extensive usage and production. This has been of an environmental concern because phthalates are hepatotoxic, teratogenic, and carcinogenic by nature. Numerous studies indicated that phthalates can be degraded by bacteria and fungi under aerobic, anoxic, and anaerobic conditions. This paper gives a review on the biodegradation of phthalates and includes the following aspects: (1) the relationship between the chemical structure of phthalates and their biodegradability, (2) the biodegradation of phthalates by pure/mixed cultures, (3) the biodegradation of phthalates under various environments, and (4) the biodegradation pathways of phthalates.

Keywords Phthalates · Biodegradation · Environment · Pathway

Introduction

Phthalate esters (PEs) or phthalates are the dialkyl or alkyl aryl esters of 1,2-benzendicarboxylic acid (phthalic acid). The name *phthalate* derives from phthalic acid, which refers to three isomers, i.e., the *ortho*-isomer or phthalic acid (PA), *para*-isomer or terephthalic acid (TA), and *meta*-isomer isophthalic acid (IA). Phthalates are synthesized in substantial amounts mainly to produce various forms of plastics. PA esters are mainly used as plasticizer in polyvinyl chloride production, while TA esters are used to make polyester fibers and polyethylene terephthalate (the material used to produce bottles for carbonated drinks). IA esters, which are produced in relatively smaller amounts than the other two esters, are used to make dope, resin, etc. On the global scale, an increase from 2 to 5.5 million tons in the production of phthalates has been recorded from 1980 to 2000.

Phthalates have been liberated and detected in various environments including air (Wensing et al. 2005), soils, sediments, landfill leachates (Schwarzbauer et al. 2002; Zheng et al. 2007), and natural waters as a result of the production, usage, and disposal of plastics (Staples et al. 1997). When used as plasticizers, phthalates are not chemically bonded to the plastics polymer and can therefore eventually migrate from the plastics into the environment. Phthalates and their metabolites have been found to be potentially harmful for human and environment due to their hepatotoxic, teratogenic, and carcinogenic characteristics (Matsumoto et al. 2008).

Numerous studies have demonstrated that microorganisms play the major roles in the phthalates degradation in the environment under various conditions, which has been reviewed by Staples et al. (1997). This paper is focused on summarizing the studies on phthalates (including PA and its isomers) biodegradation, mainly in the last decade, in the following aspects: the relationship between the chemical structure of phthalates and their biodegradability, the biodegradation of phthalates by pure/mixed cultures, the biodegradation of phthalates under various environments, and the phthalate biodegradation pathway.

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Table 1 Aerobic phthalate-degrading bacteria species

Species	Isolated from	Phthalates	Concentration (mg/L)	Performance	References
(1) α-*Proteobacteria*					
Methylobacterium mesophilicum Sr	Mangrove sediment	Monomethyl phthalate (MMP)	100	Completely degradation in 8 days	Li and Gu 2007
Sphingomonas paucimobilis	Soil	MMP	4	Shaking flask, 30°C, completely degraded in 5 h	Vega and Bastide 2003
Sphingomonas paucimobilis Sy	Mangrove sediment	DMT	100	Complete degradation in 100 h	Li et al. 2005b
Sphigomonas sp. DK4	Activated sludge (Petrochemical wastewater) or river sediment	DEP, DPrP, DBP, DHP, BBP, DCP, DPP, DEHP	5 for each	Batch mode, 30°C, pH 7, DEP, DPrP, DBP, DHP, BBP, DCP and DPP were completely degradation in 2, 2, 2, 4, 2, 4, and 2 days; DEHP was 90% degraded in 5 days	Chang et al. 2004
Sphingomonas sp. DEP-AD1	Activated sludge	DEP	610	100% degraded in 150 h, with maximum degradation rate of 13.5 mg-DEP/(L h)	Fang et al. 2007
Sphingomonas yanoikuyae DOS01	Deep ocean sediment	DMT	30	Complete degradation to MMT in 170 h	Wang and Gu 2006a
Sphingomonas chungbukensis KCTC 2955	Sediment	DPP	90	Complete degradation within 60 h, at pH 7.0 and 30°C	Kim et al. 2008
(2) β-*Proteobacteria*					
Comamonas acidovorans Fy-1	Activated sludge	PA	2,600	100% degradation in 48 h	Wang et al. 2003
Comamonas testosteroni YZW-D	Sediment	IA and TA	Unknown	Unknown	Wang et al. 1995
Burkholderia cepacia DB01[a]	Unknown	PA, IA and TA	1,000	Grow in all three medium	Chang and Zylstra 1998
Delftia tsuruhatensis TBKNP-05	Activated sludge	DBP	2,780	Complete degradation in 5 days	Patil et al. 2006
Viarovorax paradoxus T4	Deep ocean sediment	(1) DMT, MMT, and TA	(1) DMT 23.5, MMT 152, TA 155;	(1) Complete degradation of DMT, MMT and TA in 22.5, 100, and 75 h	Wang and Gu 2006a;
		(2) DMI, MMI, and IA	(2) DMI 143, MMI 218, IA 202	(2) Complete degradation of DMI, MMI and IA in 100, 120, and 50 h	Wang and Gu 2006b
(3) γ-*Proteobacteria*					
Shihouhao Klebsiella oxytoca Sc	Mangrove sediment	DMI	108	Completely degraded into MMI in 36 h	Li et al. 2005b
Pasteurella multocida Sa	Mangrove sediment	DMT	98	Complete degradation in 60 h	Li et al. 2005b
Pseudomonas aeruginosa PP4	Soil (contaminated with oil and plastics)	PA, IA, and TA	1,000	Degradation rate: $t_{1/2}$=7.91 h (IA); $t_{1/2}$=3.45 h (TA); $t_{1/2}$=5.43 h (PA)	Vamsee-Krishna et al. 2006

Table 1 (continued)

Species	Isolated from	Phthalates	Concentration (mg/L)	Performance	References
Pseudomonas aeruginosa P1	Bioaugmented slurry reactor	DBP	Unknown	Show DBP degrading ability	Shailaja et al. 2007
Pseudomonas sp. PPD	Soil (contaminated with oil and plastics)	PA, IA and TA	1,000	Degradation rate: $t_{1/2}$=4.46 h (IA); $t_{1/2}$=2.73 h (TA); $t_{1/2}$=4.52 h (PA)	Vamsee-Krishna et al. 2006
Pseudomonas fluorescens B-1	Mangrove sediment	(1) DBP (2) BBP	(1) 2.5 and 10.0 (2) 2.4–20.8	Complete degradation, first-order parameters: (1) k_1=0.028–0.048 h^{-1}, $t_{1/2}$=14.38–24.15 h; (2) k_2=0.74 day^{-1}, $t_{1/2}$=22.35 h	Xu et al. 2005 Xu et al. 2007
Pseudomonas fluorescens FS-1	Activated sludge	DMP, DEP, DnBP, DiBP, DnOP, and DEHP	50–400 (for each)	In 100 mg/L, more than 99% of DMP, DEP, DnBP, and DiBP, less than 30% of DnOP, and 20% of DEHP were removed in 3 days	Feng et al. 2004
Moraxella sp. VG45	Oil-field soil	PA	330	Degradation was plasmid mediated by a 60-kb plasmid in the culture	Rani et al. 1996
Acinetobacter lwoffii	River water	DBP and DEHP	20	Complete degradation of DBP and 20% degradation of DEHP in 5 days	Hashizume et al. 2002
(3) γ-*Proteobacteria*					
Acinetobacter lwoffii ISP4	Soil	IA	1,000	Degradation rate: $t_{1/2}$=0.92 h	Vamsee-Krishna et al. 2006
Xanthomonas maltophila B-14846	Soil	Diethyl terephthalate (DETP)	4,840	25% degradation in 48 h	Jackson et al. 1996
(4) *Actinobacteria* (High G+C)					
Mycobacterium sp. NK301	Garden soil	DEHP	1,000	30°C, pH 6.8 98% was degraded in 21 h	Nakamiya et al. 2005
Corynebacterium sp.O18	Activated sludge (Petrochemical wastewater) or river sediment	DEP, DPrP, DBP, DHP, BBP, DCP, DPP, DEHP	5 (for each)	Batch mode, 30°C, pH 7, DEP, DPrP, DBP, DHP, BBP, and DPP were completely degraded in 2, 2, 4, 7, 3, and 4 days; DCP was 69% degraded in 5 days DEHP was 57% degraded in 5 days	Chang et al. 2004
Corynebacterium nitrilophius G11	Soil	DBP	100	20% degradation in 3 days	Chao et al. 2006
Aureobacterium saperdae B-14840	Soil	(1) DEP (2) DETP	5,550	(1) 100% degradation in 30 h (2) 25% degradation in 48 h	Jackson et al. 1996
Gordonia sp. MTCC 4818	Creosote-contaminated soil	BBP	24	100% degradation in 4 days, 28°C by using shaking flask	Chatterjee and Dutta 2003
Gordonia polyisoprenivorans G1	Soil	DEHP	(1) 100 (2) 243 mg/kg in soil	(1) 91.8% was degraded in 2 days (2) 50% degradation in 3 days	Chao and Cheng 2007
Brevibacterium iodinum	Soil	DEHP	Unknown	Enriched to inoculate a SBR treating DEHP, together with other two bacteria *Bacillus brevis* and *R. luteus*	Juneson et al. 2001

Table 1 (continued)

Species	Isolated from	Phthalates	Concentration (mg/L)	Performance	References
Micrococcus kristinae B-14845	Soil	(1) DEP (2) DETP	5,550	(1) 100% and (2) 25% degradation in 48 h	Jackson et al. 1996
Microbacterium sp. CQ0110	Activated sludge (DEHP exposed)	DEHP	1,350	Complete degradation in 10 days, $t_{1/2}$=1.59 days	Chen et al. 2007
Arthrobacter keyseri 12B (also as *Micrococcus* sp.)	compost	(1) DMP, DEP and DBP; (2) DBP and PA;	(1) Unknown (2) Unknown	(1) Degradation happened (2) DBP can be degraded through PA to protocatechuate by novel pathway	Eaton 2001
Arthrobacter sp.	Soil	DMP	52.4	Complete degradation in 20 h to MMP	Vega and Bastide 2003
Arthrobacter sp. WY[b]	Municipal waste-contaminated soil	BBP	1,000	Shaking flask, 28°C, 50% and 95% degradation after 16 and 39 days	Chatterjee and Dutta 2008
Rhodococcus rubropertinctus	–	TA	830	TA could be degraded through benzoate, protocatechuate, and to cycle *ortho*-cleavage	Naumova et al. 1986
Rhodococcus sp. DK17	Soil	PA and TA	830	PA and TA can be degraded into protocatechuate	Choi et al. 2005
Rhodococcus sp. RHA1	Lindane-contaminated soil	PA	Unknown	PA is catabolized by a branched β-ketoadipate pathway	Patrauchan et al. 2005
R. rhodochrous G2, G7	Soil	DBP	100	Complete degradation in 2–3 days	Chao et al. 2006
R. rhodochrous G2, G7	Soil	DEHP	100	98.4% degradation in 3 days by G2; 91.7% degradation in 5 days by G7	Chao and Cheng 2007
R. rhodochrous B-16898, B-16899, B-16902, B-16909	Soil	DETP	5,550	97–99% degradation in 48 h	Jackson et al. 1996
R. rhodochrous ATCC 21766		(1) DOP (2) DEHP	(1) 1,000 (2) 9,360	(1) About 50% degradation (2) 67% degradation in 200 h	Nalli et al. 2002 Nalli et al. 2006
R. coprophilus G5, G9	Soil	DBP	100	Complete degradation in 2–3 days	Chao et al. 2006
R. ruber G17	Soil	DBP	100	Complete degradation in 2 days	Chao et al. 2006
R. ruber Sa	Mangrove sediment	DMI, DMP, and DMT	40–80	Complete degradation of DMI, DMT, and DMP (80 mg/L for each) in 1, 5, and 9 days	Li et al. 2005a
R. ruber CQ0301	Landfill soil	DBP	50 mg/kg	Degradation kinetics parameters: k=0.133, $t_{1/2}$=5.2 days	Li et al. 2006
R. erytropolis S1 (or *Nocardia erythropolis*)	Activated sludge	(1) DEHP (2) DBP	1,500–3,000	(1) Complete degradation in 3–5 days (2) Complete degradation in 1–3 days	Kurane 1997
R. luteus	Soil	DEHP	1,000	Enriched to inoculate a SBR treating DEHP, together with other two bacteria *Bacillus brevis* and *Brevibacterium iodinum*	Juneson et al. 2001
(5) *Firmicutes* (Low G+C)					
Enterococcus sp. OM1	Activated sludge	DEHP	1,000	Degradation constant: k=0.133 $days^{-1}$, $t_{1/2}$=5.2 days	Chang et al. 2007

Table 1 (continued)

Species	Isolated from	Phthalates	Concentration (mg/L)	Performance	References
				DEP, DBP, BBP can be also degraded	
Bacillus sp. S4	Sludge	DEHP	1,000	Degradation constant k=0.081, $t_{1/2}$=8.6; DEP, DBP, BBP can also be degraded.	Chang et al. 2007
Bacillus sp. NCIM 5220	Activated sludge	(1) DMP	(1) 5,820–7,760	(1) Immobilized in alginate and polyurethane foam; Complete degradation in 12–15 days	Niazi and Karegoudar 2001
		(2) DBP	(2) 2,780–8,340	(2) Immobilized in alginate, complete degradation in 3 days	Patil and Karegoudar 2005
Bacillus subtilis No.66	Soil	DEHP	3,900	81.6% degradation in 5 days	Quan et al. 2005
Bacillus brevis	Soil	DEHP	1,000	Enriched to inoculate a SBR treating DEHP, together with other two bacteria *Brevibacterium iodinum* and *R. luteus*	Juneson et al. 2001
(6) *Bacteroids/Chlorobi*					
Flavobacterium aquatile B-14842	Soil	(1) DEP (2) DETP	5,550	(1) 100% degradation in 48 h (2) 23% degradation in 48 h	Jackson et al. 1996
Flavobacterium sp. no. A-9	Soil	DMP	1,000	Complete degradation in 2 days	Kido et al. 2007
Flavobacterium sp. no. A-1	Soil	PA	10	Complete degradation can be achieved in less than 2 days	Tanaka et al. 2006

[a] Originally as *Pseudomonas fluorescens* PHK, known as *Pseudomonas putida* and was later classified as *Pseudomonas cepacia*
[b] Mixed culture, completely degradation

Table 2 Anoxic and anaerobic phthalates-degrading bacteria species

Division	Species	Isolated from	Phthalates	Concentration (mg/L)	Performance	References
Anoxic						
γ-*Proteobacteria*	*Pseudomonas pseodoalcaligenes* B20b1	Sewage effluent	DBP	2000	20 days, 30 ºC, nitrate as electron acceptor. DBP was degraded to MBP and PA	Benckiser and Ohow 1982
α-*Proteobacteria*	*Agrobacterium* sp. DMT	Sediment—sulfate-reducing microcosm	DMT	50	72% degradation in 2 months, MMT was the end product	Cheung et al. 2007
β-*Proteobacteria*	*Thauera* sp. DMP	Sediment—sulfate-reducing microcosm	DMP	232	22% degradation in 2 months, MMP was the only by product	Ditto
γ-*Proteobacteria*	*Xanthobacter* sp. DMI	Sediment—sulfate-reducing microcosm	DMI	98	65% degradation in 60 days, MMI was the end product	Ditto
Actinobacteria	*Rhodococcus* sp. YZ2	Digested sludge	DMP	70–600	Biodegradation under denitrifying condition. Half-life was 0.89–2.22 days	Wu et al. 2007
Anaerobic						
Firmicutes	*Clostridium* sp. NO9	River sediment	DEP, DBP, DEHP	Unknown	Complete degradation of DEP and DBP in 28 days; remaining DEHP were 0.8% and 8.3%	Chang et al. 2005a
	Bacillus sp. NO11 and NO14	River sediment	DEP, DBP, DEHP	Unknown	Complete degradation of DEP and DBP in 28 days; remaining DEHP were 0.8% and 8.3%	Chang et al. 2005a
	Pelotomaculum terephthalicum (JT^T) *Pelotomaculum isophthalicum* (JI^T)	anaerobic TA-degrading and IA-degrading enrichment	TA, IA and PA	TA: 166 IA: 332 PA: 498	Cocultured with *Methanospirillum hungatei*, JT^T can utilize TA as sole carbon and other PA isomers with crotonate as cosubstrate; JI^T can completely degrade IA, PA, and TA within 30 days	Qiu et al. 2006

The chemical structure and biodegradability of phthalates

The basic chemical structure of phthalates is benzene dicarboxylic acid with two side chains, which can be alkyl, benzyl, phenyl, cycloalkyl, or alkoxy groups. Studies have demonstrated that phthalates with shorter ester chains like dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), diphenyl phthalate (DPP), dipropyl phthalate (DPrP), and butyl-benzyl phthalate (BBP) can be readily biodegraded and mineralized. On the other hand, phthalates with longer ester chains, such as dicyclohexyl phthalate, dihexyl phthalate (DHP), dioctyl phthalate (DOP), and di-2-ethylhexyl phthalate (DEHP) are less susceptible to biodegradation (Wang et al. 2000; Chang et al. 2004).

The biodegradability difference of phthalates is likely due to the steric effect of phthalates side ester chains, which hinders the hydrolytic enzymes from binding to the phthalates and thereby inhibits their hydrolysis. This has been supported by Xia et al. (2004) in a study of quantitative structure–activity relationship analysis of phthalates and their aerobic biodegradabilities. On the other hand, the branched ester chain is not a significant factor limiting the degradation of phthalates (Ejlertsson et al. 1997). The author reported that, when inoculated with DBP under a methanogenic condition, butyl 2-ethyl-hexyl phthalate was readily degraded in 60 days, whereas DEHP showed little or no degradation, although both have the same branched side chain (2-ethylhexyl).

Different phthalates isomers show different biodegradation rates, and phthalate-hydrolyzing enzymes are structurally specific. Gu et al. (2005) reported that a dimethyl isophthalate (DMI)-hydrolyzing enzyme purified from *Rhodococcus erythopolis* readily hydrolyzed DMI and DMP while hardly hydrolyzed dimethyl terephthalate (DMT). Based on laboratory tests using different sludges from anaerobic reactors, the lag phases for three phthalate isomers' biodegradation were in the following order: PA<TA<IA. This order appears to be related to the environmental abundances of the organisms with the specific ability to degrade one of the isomers and therefore be directly related to the phthalate isomers amounts released into the environments (Kleerebezem et al. 1999b).

Biodegradation of phthalates by pure culture

Most phthalate-degrading isolates are either aerobes or facultative anaerobes. Tables 1 and 2 list the known pure cultures capable of degrading phthalates. It shows that the phthalate-degrading bacteria are mainly from four divisions in *Bacteria*, i.e., *Proteobacteria*, *Actinobacteria* (or high G+C), *Firmicutes* (or low G+C), and *Bacteroids/Chlorobi*. Among them, the commonly found genera are *Sphingomonas* (α-*Proteobacteria*), *Comamonas* (β-*Proteobacteria*), *Pseudomonas* (γ-*Proteobacteria*), as well as *Arthrobacter* and *Rhodococcus*. A microbial community analysis revealed that community change was associated with the genera *Sphingomonas*, *Pseudomonas*, and *Actinomycetes*, in an enriched compost medium with a high concentration of DEP (10–100g kg^{-1}) (Kapanen et al. 2007).

Table 3 Phthalates biodegradation in sludge

Sludge	Phthalates	Concentration	Condition	Kinetic parameters		Reference
				constant (K_h) ($\times 10^{-2}$ day^{-1})	half life ($t_{1/2}$) (day)	
Digested sludge	DMP	10 mg/L	Anaerobic, mesophilic (37°C)	69.6	1.0	Wang et al. 2000
	DBP			51.8	1.4	
	DOP			3.36	19.4	
Digested sludge (primary sludge)	DEP	5 mg/L	Anaerobic, mesophilic	8.0	8.6	Gavala et al. 2003
	DBP	7 mg/L		13.7	5.1	
	DEHP	7 mg/L		0.35-3.6	19-198	
Activated sludge	DEHP	6.3 mg/kg	Composting	2.4	28.9	Amir et al. 2005
Lagooning sludge	DEHP	28.7 mg/kg	Composting	1.5	45.4	Amir et al. 2005
Sewage sludge	DBP/ DEHP	2 mg/kg	(1) Inoculated control	(1) 58.1/11.1	(1) 1.2/6.2	Chang et al. 2005b
			(2) Nitrate reducing	(2) 12.1/5.3	(2) 5.7/13.1	
			(3) Sulfate reducing	(3) 17.0/5.7	(3) 4.1/12.2	
			(4) Methanogenic	(4) 9.8/4.6	(4) 7.1/15.1	
Secondary sludge	DEP	50 mg/kg	Aerobic, 30°C, pH 7	25.7	2.7	Chang et al. 2007
	DBP			37.9	1.8	
	BBP			33.2	2.1	
	DEHP			18.2	3.8	

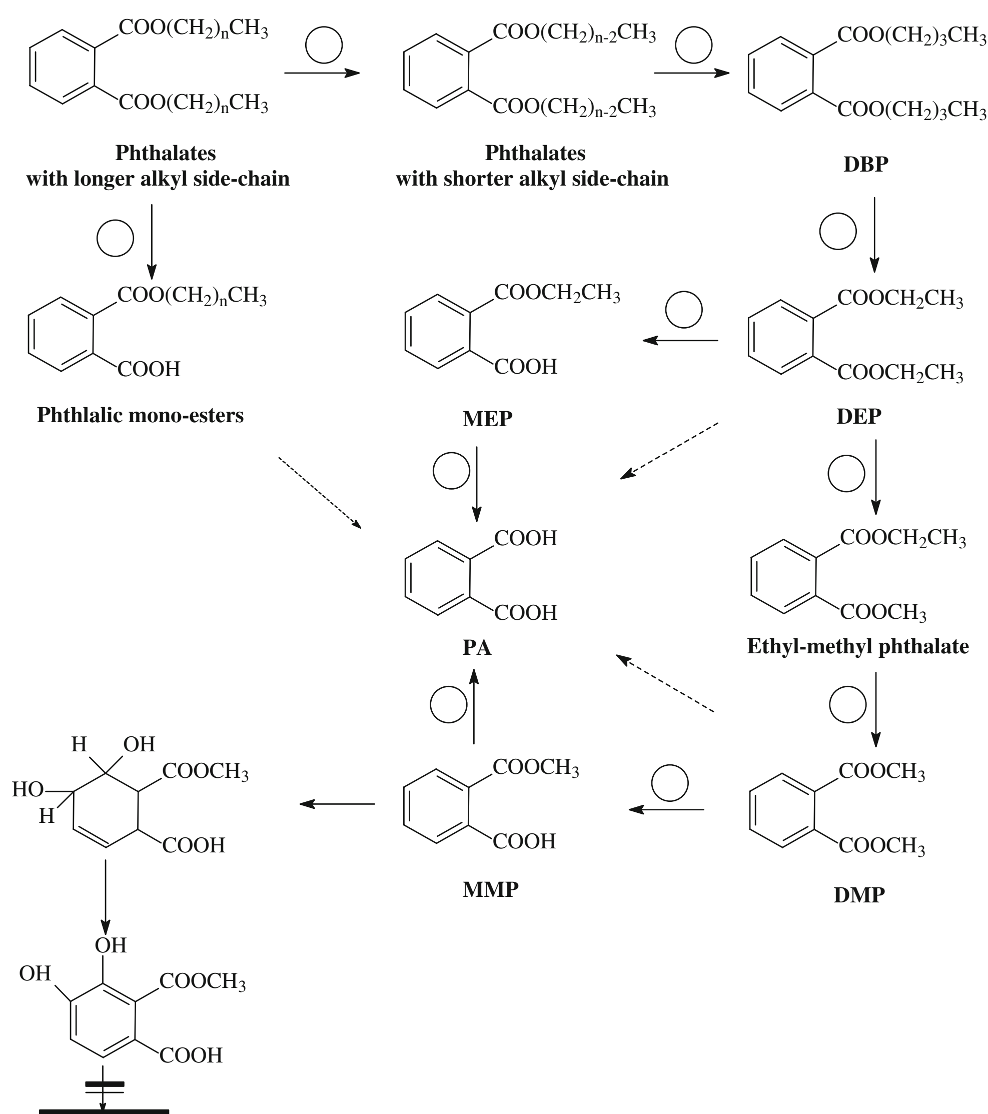

Fig. 1 Phthalates degradation pathways and the enzymes involved. *E1* DAP esterase, *E2* MAP esterase

However, anaerobic phthalate-degrading isolates were little known because of the lack of syntrophic conditions, as shown in Table 2. So far, only three isolates, one *Clostridium* sp. and two *Bacillus* sp. strains, were found to be solely capable of degrading phthalates anaerobically (Chang et al. 2005a). When cocultured with methanogens, two phthalate isomer-degrading strains, i.e., *Pelotomaculum terephthalaicum* JT^T (previously known as subcluster Ih of "*Desulfotomaculum* lineage I") and *Pelotomaculum isophthalicum* JI^T, were successfully isolated from an anaerobic TA and IA enrichment culture (Qiu et al. 2006).

In addition to *Bacteria*, a few fungi species, including *Aspergillus niger* AG-1 (Ganji et al. 1995), *Sclerotium rolfsii* (Sivamurthy et al. 1991), *Penicillium lilacinum* (Engelhardt et al. 1977), *Fusarium oxysporum* (Kim and Lee 2005), *Phanerochaete chryososporium*, *Trametes versicolor*, *Daldinia concentrica* (Lee et al. 2004), and *Polyporus brumalis* (Lee et al. 2007), as well as green microalga *Closterium lunula* (Yan and Pan 2004) and *Chlorella pyrenoidosa* (Yan et al. 2002), can also degrade phthalates. The broad-range degradation ability of fungi is attributed to the strong extracellular ligninolytic enzymes, such as lignin peroxidase, manganese-dependent peroxidase, and laccase. For instance, the cutinase-producing *F. oxysporum* showed high enzymatic activities and was able to degrade BBP (Kim et al. 2002), DEHP (Kim et al. 2003), DBP (Kim and Lee 2005), DPrP (Kim et al. 2005), dipentyl phthalate (Ahn et al. 2006), and DHP (Kim et al. 2007) within several hours.

Biodegradation of phthalates by mixed culture

In natural environments, complete degradation of complex organics, like phthalates, is always carried out syntrophically by several members of microorganisms (Gu et al. 2005). The biodegradation of phthalates primarily involves the sequential hydrolysis of ester linkage, which results in monoesters and, subsequently, PA, while forming alcohols simultaneous-

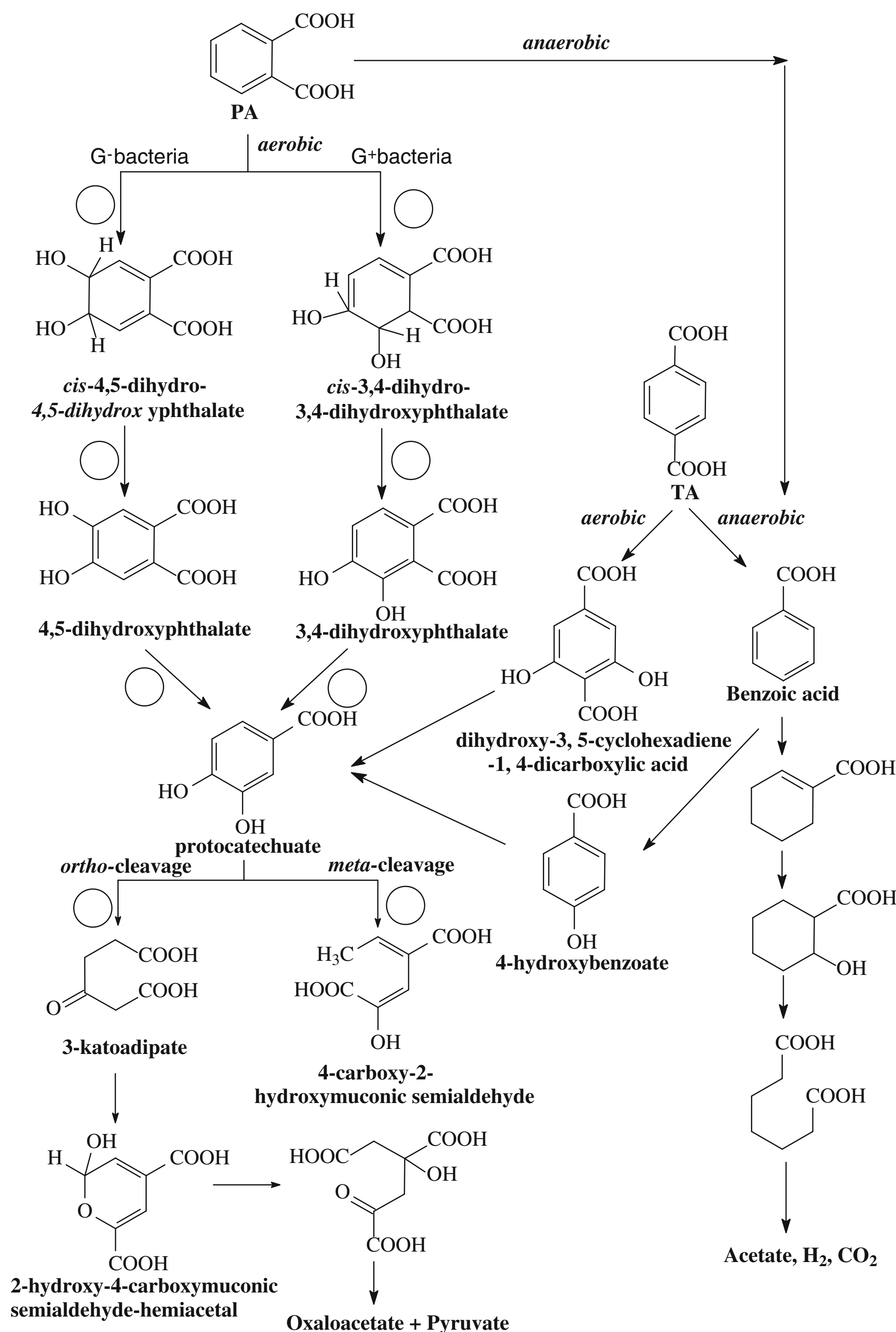

Fig. 2 PA and TA biodegradation pathway and enzymes involved. *E3* PA 4.5-dioxygenase (E.C.1.14.12.7), *E4* PA 3,4-dioxygenase, *E5 cis*-4, 5-dihydroxy-4,5-dihydrophthalate dehydrogenase, *E6 cis*-3, 4-dihydroxy-3,4-dihydrophthalate dehydrogenase, *E7* 4,5-dihydroxyphthalate decarboxylase (E.C. 4.1.1.55), *E8* 3,4-dihydroxyphthalate decarboxylase (E.C. 4.1.1.69), *E9* 4,5-protocatechuate dioxygenase (EC1.13.11.8), *E10* 3,4-protocatechuate dioxygenase (EC1.13.11.3)

ly. Thus, the microbial assimilation of phthalates requires diverse metabolic genes and enzymes, indicating a single organism is unlikely able to completely mineralize phthalates (Staples et al. 1997). As examples, in the degradation of DMP isomers by *Rhodococcus ruber* Sa, their corresponding intermediates, monomethyl phthalate (MMP) isomers, were not further degraded (Li et al. 2005a); BBP metabolites, monobutyl phthalate (MBP) and monobenzyl phthalate, could not be further degraded by the BBP-degrading bacteria Gordonia sp. MTCC 4818 (Chatterjee and Dutta 2003) while Engelhardt and Wallnofer (1978) also reported that a DBP-degrading bacterium could not degrade MBP.

So far, mixed culture consortia have been shown to completely mineralize phthalates. Wang et al. (2004c) reported that DMP was completely mineralized by two consortia of microorganisms; one comprised of *Pseudomo-*

nas fluorescens, *P. aureofaciens*, and *Sphingomonas paucimobilis*, whereas the other comprised of *Xanthomonas maltophilia* and *S. paucimobilis*. DMP was also found to be serially degraded by a coculture of an *Arthrobacter* sp. and *S. paucimobilis*. The former species was responsible for transforming DMP into MMP, which was utilized by the latter species (Vega and Bastide 2003). BBP was completely mineralized by a mixed culture consortium, in which *Arthrobacter* sp. WY was able to metabolize BBP into MbuP, MBzP, and PA, while *Acineobacter* sp. FW was capable of degrading de-esterified alcohol and thus completed BBP mineralization (Chatterjee and Dutta 2008). Anaerobically, coculturing is also required for the degradation of phthalates. When cocultured with *Methanospirillum hungatei*, *P. terephthalaicum* JT^T and *P. isophthalicum* JI^T can completely degrade TA and IA, respectively (Qiu et al. 2006).

In addition, mixed cultures can also increase phthalates degradation rates. In the presence of both *Sphingomonas* sp. DK4 and *Corynebacterium* sp. O18, the degradation rates of the eight phthalates examined were enhanced (Chang et al. 2004).

Biodegradation of phthalates under various environmental conditions

Phthalates biodegradation under various environmental conditions, such as in wastewater treatment processes, sludge, freshwater and sediment, soils, and landfill sites, have been extensively studied. Generally, phthalates biodegradation shares the following common characteristics in different environments: (1) a decrease in biodegradability with the increase in phthalates side chain length; (2) anaerobic degradation of phthalates is generally much slower than aerobic degradation (Staples et al. 1997; Yuan et al. 2002); (3) the primary biodegradation of phthalates is always expressed in the first-order kinetics (Wang et al. 1997b; Gavala et al. 2003); (4) high concentration of phthalates and/or their metabolites inhibit their biodegradation.

Wastewater treatment processes

Discharge from sewage works is a major source of phthalates into the environment. In comparison to other phthalates, DEP and DEHP, in the ranges of 1–74 and 28–122 μg/L, respectively, have been found in higher concentrations in raw sewage (Marttinen et al. 2003a). Generally, phthalates is not readily mineralized in the wastewater treatment processes since high hydrophobicity and low solubility allow phthalates to be adsorbed to suspended organic matter and subsequently transferred to settled sludges (Gavala et al. 2003).

The fate of phthalates in wastewater treatment plant (WWTP)- and laboratory-scaled reactors, such as sequencing batch reactor, packed-bed reactor, and upflow anaerobic sludge blanket (UASB) reactor, has also been studied broadly. Although adsorption is found to be dominant, biodegradation also contributes to the removal of phthalates. Marttinen et al. (2003a) studied the DEHP degradation in a WWTP using mass balance analysis and found that DEHP removal efficiency from the water phase was approximately 94%, 29% of which was attributed to biodegradation. A similar result was found in a trickle filter WWTP, where the biodegradation efficiency of DEHP was found to be in the range of 1% to 44% (Oliver et al. 2005). Fauser et al. (2003) studied the fate of phthalates in WWTP, and the results showed that with the mean inlet of 240 g-DEHP/day, 70% DEHP was biodegraded, and 28% was in the sludge (Fauser et al. 2003). Roslev et al. (2007) reported a pronounced biodegradation of different phthalates in WWTP where the overall microbial degradation of DMP, DBP, BBP, and DEHP was estimated to be 93%, 91%, 90%, and 81%, respectively. First-order coefficiencies for DEHP degradation ranged in $19.2–31.2\times10^{-2}$ day^{-1} under various conditions. However, the physicochemical sewage treatment plant cannot efficiently remove DEHP. Only 20% of DEHP (150 μg/L in influent) was removed from sewage in an urban physicochemical WWTP, and it is unlikely that the DEHP removal was primarily due to biodegradation (Barnabé et al. 2008).

Phthalate biodegradation in reactors is greatly dependent upon the reactor design and the seed sludge. For instance, compared to the continuous flow mode, the recirculating flow mode of a trickling filter microcosm improved the DEP and DEHP removal efficiency to 99% in 48 h and 88% in 96 h, respectively (Oliver et al. 2007). Complete removal of DMP in wastewater was accomplished using a packed-bed reactor with an acclimated mixed bacterial culture (Juneson et al. 2002). Marttinen et al. (2004b) reported that the sequencing batch reactor could efficiently remove 95% of DEHP, together with NH_4-N, from reject water originating from sewage sludge. The total removal of DEHP attributed to biodegradation was about 36–42% based on mass balance analysis. The reduced removal of DEHP was a result of prolonged sorption on wastewater solids, and the fraction with a slow desorption rate reduced the DEHP bioavailability (Marttinen et al. 2004b). In another study, DEHP was degraded with the half-life of 2–5 days in a sequencing batch reactor. However, the type of inoculum used may play a very important role for this quick degradation, since the reactor was inoculated with an acclimated mixed culture composed of *Brevibacterium iodinum*, *Rhodococcus luteus*, and *Bacillus brevis*, which can utilize DEHP as a sole source (Juneson et al. 2001).

Anaerobic reactors were successful in the degradation of DMP (Liang et al. 2007) and phthalate isomers, such as PA (Tur and Huang 1997) and TA (Kleerebezem et al. 1997, 1999a; Wu et al. 2001; Kleerebezem et al. 2005), in wastewater. Liang et al. (2007) reported that more than 99% of DMP (600 mg/L) and 93% of chemical oxygen demand (COD) were effectively removed in a UASB reactor at an 8-h hydraulic retention time. A full-scale TA wastewater treatment plant was able to remove 90% of COD and 85–90% of TA, with an organic loading rate of 3 g-COD/(L day) and 1 day of hydraulic retention time (Qiu et al. 2004). In a two-stage UASB, TA was degraded at the rate of 15 g-COD/(Lday) after 125 days of activation (Kleerebezem et al. 2005). By introducing a bio-filter or reticulated polyurethane foam particles into a UASB, anaerobic hybrid reactors exhibited high removal capabilities in PA and TA. The specific PA removal rate reached 0.8–0.85 g-COD/(g-volatile suspended solid day) in the loading of 26 g-COD/(Lday) (Tur and Huang 1997); the specific TA removal rate was 10–17 g-COD/(Lday) with 5–8 h of hydraulic retention time (Kleerebezem et al. 1999a). However, both reactors needed almost 3 months of acclimation before effective degradation take place.

Sludge

Sewage sludge contains relatively high concentrations of phthalates as a result of accumulation from the urban runoff, drainage, and domestic and industrial discharges. Most of the phthalates are biodegradable in sludge, and first-order kinetics is frequently used to describe their biodegradation, as summarized in Table 3. As mentioned above, phthalate biodegradation under anaerobic conditions is much slower than under aerobic conditions, and the degradation rate is dependent on the inoculum. Kleerebezem et al. (1999b) reported that all three phthalate isomers and their corresponding dimethyl-esters could be completely mineralized anaerobically by all seed sludge studied, such as digested sludge and granular anaerobic sludge. However, the lag phases required for 50% of degradation of these compounds are usually quite long and may range from 17 to 156 days.

DEHP is a major pollutant identified at high concentrations in digested sludge, and its concentrations range from several to hundreds of mg kg^{-1} in dry weight (Cheng et al. 2000). Although slow, DEHP removal in sludge under composting aerobic and anaerobic conditions has been verified. Marttinen et al. (2004a) reported that composting removed 58% and 34% of DEHP from raw sludge and digested sludge during 85 days stabilization. In another study, DEHP in sewage sludge was removed 94% by composting or by mixing with thermally dried soil within 9 months (Bago et al. 2005). Under the aerobic condition, the biodegradation of DEHP was 33–41% and 50–62% in 7 and 28 days in sludge, respectively (Marttinen et al. 2004a). Anaerobically, DEHP degradation was in the range of 23–61% under thermophilic and mesophilic conditions (El-Hadj et al. 2006).

High concentrations of DEHP (more than 60 mg/L) in digested sludge are likely to have a negative effect on degradation of other phthalates, such as DBP, DEP, and DMP, as well as the biogas production in sludge digesters (O'Connor et al. 1989; Alatriste-Mondragon et al. 2003; Gavala et al. 2003). Battersby and Wilson (1989) reported that increasing concentrations of DEHP (25, 50, 100, and 200 mg/l) decreased biogas from 48% to 6% of the theoretical gas production over a period of 60 days. This is probably caused by the partial metabolism of DEHP and the production of the intermediate 2-ethyl hexanol, which has been reported to be toxic to the methanogenic process (Ejlertsson and Svensson 1997). On the other hand, DEHP in sludge was found to degrade under good ventilation, sufficient sunlight, and proper moisture conditions (Cheng et al. 2000). The half-lives of DEHP have been reported to be 45.4 and 28.9 days in composting lagoon sludge and activated sludge under aerobic conditions, respectively (Amir et al. 2005).

Freshwater and sediment

Phthalates are ubiquitously detected in freshwater and tend to adsorb on sediment (Chang et al. 2005a). Among eight phthalates found in Taiwan's rivers, DEHP was in the highest concentration ranging from less than 0.1 to 18.5 μg/L in river water and 0.5 to 23.9 μg/g in sediment (Yuan et al. 2002), which is in the same range with many other places in the world (Turner and Rawling 2000). These eight phthalates could be biodegraded in the river sediment with the average half lives of 2.5–14.8 (aerobically) and 14.4–34.7 days (anaerobically). Generally, the biodegradation half-lives are ranged from less than 1 day to 2 weeks (Amir et al. 2005). The biodegradation of DEHP (52 μg/L) was almost complete in 2 days in water, and the biodegradation half-life in the sediment was about 14 days (Yuwatini et al. 2006).

Aerobic microorganisms, such as *Acinetobacter lwoffii* (Hashizume et al. 2002) and *Sphigomonas* sp.(Chang et al. 2004; Kim et al. 2008), and anaerobes, such as *Clostruium* sp. and *Bacillus* sp. (Chang et al. 2005a), that can degrade phthalates have been isolated from river sediment recently. Although phthalate-degrading isolates are not as many as those from activated sludge and soil, these bacteria can potentially degrade phthalates in the freshwater environment. Additionally, the phytoplankton in the aquatic environment can also efficiently degrade phthalates under proper nitrogen and phosphorous nutrient and illumination conditions (Li et al. 2007).

Soil and slurry

Phthalates biodegradation in soil or soil slurry has been widely studied in the last decade and were mostly conducted using sludge-amended soil or the soils inoculated with phthalate-biodegrading enrichment (Wang et al. 1997a; Roslev et al. 1998; Madsen et al. 1999; Cartwright et al. 2000; Juneson et al. 2001; Wang et al. 2004a,b; Di Gennaro et al. 2005; Zhou et al. 2005; Chao et al. 2006; Mohan et al. 2006; Chao and Cheng 2007; Shailaja et al. 2007).

In a shaking flask test of phthalate biodegradation in sludge-amended soil, all of the 14 commercial phthalates as tested by Sugatt et al. (1984) were readily biodegraded, based on both primary and ultimate degradation criteria. Microorganisms in the sewage sludge were demonstrated to dominate DEHP degradation in sludge-amended soil (Roslev et al. 1998; Madsen et al. 1999). Similarly, DBP (100 μg/g) biodegradation in soil was reported to be enhanced by inoculation with DBP-degrading bacteria, although the indigenous microbial population in soil was capable of degrading DBP (Wang et al. 1997a). The DEHP mineralization rate increased fourfold after inoculating the soil with DEHP-degrading bacteria SDE-2 (Roslev et al. 1998). Additionally, three predominant strains, *B. iodinum*, *R. luteus*, and *B. brevis*, were isolated from DEHP-degrading contaminated soil. Inoculated with the DEHP-degrading bacteria enrichment into a soil-slurry sequential batch reactor (SBR), DEHP degradation half-time was only 2–5 days at ambient temperature (20–22°C; Juneson et al. 2001).

Mohan et al. (2006) and Shailaja et al. (2007) studied DEP and DBP biodegradation in soil, respectively, by using a slurry-phase reactor bioaugmented with the outlet from an effluent treatment plant. The degradation of DEP and DBP were almost completed within 48 and 72 h and well fitted in the zero-order degradation kinetics. The half-life for DEP in soil and aqueous phase were 1.19 and 2.52 days, respectively (Mohan et al. 2006); the DBP degradation rate could reach 10.60 mg/(L days) with a half-life of 0.75 day (Shailaja et al. 2007). All these studies indicate that inoculating phthalate-degrading pure or mixed cultures enrichment into soil is a promising strategy for removing these hazardous compounds, which is also the basic idea of bioaugmentation. On the other hand, the treatment of contaminated soil in the slurry phase seems a good way for bioremediation, since slurry can improve the contact between microorganisms and contaminants by increasing the distribution of nutrients, terminal electron acceptors, and substrates.

Landfill sites

The degradation intermediates of phthalates were detected in the majority of the landfill leachate (Jonsson et al. 2003a,c), indicating phthalates were degraded in the landfill sites. Tests on BBP and DEHP in landfill reactors confirmed the phthalates degradation (Jonsson et al. 2003b). In an anaerobic digester for municipal solid waste, DEP and PA (50–250 mg/L) could be completely degraded into methane and CO_2 (Ejlertsson et al. 1996a). However, microorganisms in landfill environments have a substantially lower phthalate-degrading potential than those in the anaerobic reactors. Thus, adding waste sludge in the landfill site was suggested to enhance phthalates degradation (Ejlertsson et al. 1996a).

Phthalates degradability was increased along with the aging process of the landfills (Ejlertsson et al. 1996b). Phthalate diesters (PDEs) and the degradation products phthalate monoesters (PMEs) were below the detection limit in the acidogenic leachate from a full-scale young landfill site. During the transformation from acidic to initial methanogenic conditions, PDEs and PMEs concentrations decreased simultaneously (Ejlertsson et al. 1996b; Jonsson et al. 2003b). Sometimes, PMEs were present in concentrations several orders of magnitude higher than those of the PDEs (Jonsson et al. 2003c). After the establishment of stable methanogenic conditions, PMEs further decreased. However, based on the studies of the nonenzymatic base-catalyzed hydrolysis of phthalates, Wolfe et al. (1980) found that PMEs are more persistent than their corresponding PDEs. One hypothesis is that the carboxylate anion near the ester bond makes PMEs hard to hydrolyze, possibly due to the electrostatic repulsion toward the catalytic nucleophile attacking the ester bond (Maruyama et al. 2005). To bind this anion and neutralized its negative charge, the PME esterase is proposed to have a positively charged amino acid, resulting the narrow substrate specificity of PME esterase.

Biodegradation pathways

Exploring the degradation pathways of phthalates may help to understand their mineralization process and the toxicological behavior of their metabolites (Nozawa and Maruyama 1988; Horn et al. 2004). Generally, the phthalates biodegradation pathways consist of two processes: primary biodegradation from PDEs to PMEs and then to PA and ultimate biodegradation from PA to CO_2 and/or CH_4 (Staples et al. 1997).

Primary degradation pathway

Primary degradation consists of different type of pathways, including de-esterification or dealkylation, β-oxidation and *trans*-esterification, as shown in Fig. 1. (1) De-esterification: the most common one is the de-esterification of PDEs serially to form PMEs and PA. This degradation pathway is

the same under both aerobic and anaerobic conditions (Shelton et al. 1984) and by at least 20 bacterial genera (Eaton and Ribbons 1982). (2) β-oxidation: Phthalates with longer side chains than DEP are occasionally converted to those with shorter chains by β-oxidation, which removes one ethyl group each time (Amir et al. 2005). Then, DEP is further converted to PA by two pathways, de-esterification and an alternative *trans*-esterification pathway. (3) *Trans*-esterification (or demethylation): DEP can be degraded by replacing a ethyl group with a methyl group in each step, producing ethyl-methyl phthalate and DMP, the process of which is termed as *trans*-esterification (Cartwright et al. 2000).

There are a few exceptions to the general pathways during phthalates biodegradation, as shown in the dotted arrow in Fig. 1. For instance, in the degradation of DMP by *Arthrobacter* sp., one pathway was the hydrolysis of DMP directly into PA. In addition, DEP may also be directly degraded into PA without intermediates MEP by *Aureobacterium saperdae* NRRL B-14840 (Jackson et al. 1996).

Ultimate degradation pathway

PA is a central intermediate in the biodegradation of phthalates and polycyclic aromatic hydrocarbons, including phenanthrene (Kiyohara and Nagao 1978), fluorene (Grifoll et al. 1994) and fluoranthene (Eaton 2001). The pathways of ring cleavage of PA are different under aerobic and anaerobic conditions (Cartwright et al. 2000).

Under the aerobic condition, PA is degraded by two dioxygenase-catalyzed pathways, forming the common intermediate protocatechuate (3, 4-dihydroxy benzoate; Eaton and Ribbons 1982; Nomura et al. 1992), shown in Fig. 2.

For Gram-negative bacteria, a dioxygenase catalyzes the formation of *cis*-4,5-dihydro-4,5-dihydroxyphthalate, which is oxidized by an NAD-dependent dehydrogenase to form 4,5-dihydroxyphthalate. Protocatechuate is then formed by decarboxylation of 4,5-dihydroxyphthalate under the catalyzation of decarboxylases. For the Gram-positive bacterium *Arthrobacter keyseri* (formerly *Micrococcus* sp.) 12B, PA is converted to protocatechuate through *cis*-3,4-dihydro-3,4-dihydroxyphthalate and 3,4-dihydroxyphthalate (Eaton and Ribbons 1982).

Protocatechuate is metabolized further through either *ortho*- or *meta*-cleavage pathway by ring cleavage enzymes (Eaton and Ribbons 1982). By the *meta*-cleavage pathway, protocatechuate is converted to 4-carboxy-2-hydroxymuconic semialdehyde, 2-hydroxy-4-carboxymuconic semialdehyde-hemiacetal, 4-oxalocitramalate, and then pyruvate and oxaloacetate. By the *ortho*-cleavage pathway, also known as the ketoadipate pathway, protocatechuate degrades into 3-ketoadipate. *P. fluorescens* and *P. putida* use the *ortho*-cleavage pathway (Dennis et al. 1973), while *P. acidovorans* and *P. testosterone* use the *meta*-cleavage (Nakazawa and Hayashi 1977). *A. keyseri* 12B used the *meta*-cleavage pathway (Keyser et al. 1976), but its mutant strain 12C had the *ortho*-cleavage pathway (Eaton and Ribbons 1982).

TA is readily used as a carbon source by aerobic bacteria (Keyser et al. 1976). The pathway of TA under the aerobic condition is different from that of PA. TA is converted via benzoic acid, 4-hydroxybenzoate to protocatechuate (Naumova et al. 1986), or via dihydroxy-3,5-cyclohexadiene-1,4-dicarboxylic acid to protocatechuate (Schlafli et al. 1994).

Anaerobic degradation of PA was reported through decarboxylation to benzoate (Kleerebezem et al. 1999b; Liu and Chi 2003). Benzoate is then cleaved and degraded via β-oxidation, to hydrogen, carbon dioxide, and acetate (Elder and Kelly 1994). Usually, the rate-limiting step in anaerobic phthalates' degradation is from PA to benzoate (Kleerebezem et al. 1999c).

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