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Biodegradation of Tetrabromobisphenol-A in Mangrove Sediments

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Abstract: Tetrabromobisphenol-A (TBBPA) is a pollutant which has a devastating impact on our environment and should be removed from earth. This research aims to evaluate the aerobic and anaerobic TBBPA degradation and bacterial community changes in mangrove sediments. TBBPA degradation in the sediments was enhanced with a microcapsuled enzyme extract of spent mushroom compost (MC) under aerobic conditions and with zerovalent iron under anaerobic conditions. The TBBPA aerobic or anaerobic degradation rates were enhanced for three time additions. Four bacterial genera (*Bacillus*, *Erythrobacter*, *Pseudomonas*, *Rhodococcus*) were associated with TBBPA aerobic degradation; and four other bacterial genera (*Desulfovibrio*, *Pseudomonas*, *Sphaerochaeta*, *Sphingomonas*) were associated with TBBPA anaerobic degradation in the sediment. Moreover, nine methanogens were identified under anaerobic conditions that might also be involved in TBBPA anaerobic degradation in the sediment. Our results demonstrate two feasible methods toward TBBPA bioremediation for mangrove sediments under aerobic and anaerobic conditions.

Keywords: aerobic degradation; anaerobic degradation; zerovalent iron; microcapsule; microbial community; tetrabromobisphenol-A

1. Introduction

Mangrove swamps are found in tropical and subtropical tidal regions including estuaries and marine shorelines. Accumulation of a spectrum of anthropogenic pollutants derived from both fresh water river and seawater at these wetlands was found [1]. Halogenated organic compounds, such as tetrabromobisphenol A (TBBPA) are the persistent, ubiquitous, and toxic pollutants in mangrove sediments [2,3]. TBBPA is widely used to make brominated flame retardant in the world. Due to its low water solubility, TBBPA readily attaches onto particles and organic matter in sediments [4]. The toxicity of tetrabromobisphenol A (TBBPA) was subject to study which was concluded with little concern. The low toxicity of TBBPA may be due to low bioavailability [5]. However, TBBPA can interfere with endocrine system, affect metabolism and cause serious health consequences [6]. It is very urgent to explore efficient techniques for TBBPA removal from the environment. Treatments of organic chemicals such as sorption and chemical oxidation show high efficiencies. Advanced treatments such as ozonation and photochemical treatment use less chemicals but have high energy costs. Biological treatments are environmentally-friendly. However, it cannot treat high concentration chemicals. Different remediation techniques for pollutants have advantages and disadvantages [7].

Biodegradation is an effective strategy to remove organic pollutants from sediments. The microbial degradation of the organic contaminants depends on the availability of molecular oxygen in the sediment. Anaerobic reductive dehalogenation is an important mechanism for degradation of

halogenated organic compounds [8]. TBBPA has shown to be degraded in anaerobic and aerobic conditions [9–13]. TBBPA is susceptible to microbial debromination in estuarine sediments [14]. Anaerobic degradation of TBBPA was enhanced by the addition of humic acid, sodium chloride, vitamin B_{12}, and zerovalent iron which exhibited the highest efficient for anaerobic degradation of TBBPA in the sediment [12]. Spent mushroom compost (SMC) is a source of fungal ligninolytic enzymes. The addition of microcapsuled enzyme extract of SMC (MC) has been used to enhance organic pollutant degradation [15]. The degradation of sulfonamides and tetracyclines with MC was reported under aerobic conditions in the sediment [16,17].

Next-generation sequencing could help revolutionize our research on microbial diversity of environmental samples [18]. We need to know more about the microbial communities involved in the degradation of TBBPA in the sediments. This study is to examine degradation of TBBPA in mangrove sediments with MC and zerovalent iron under aerobic and anaerobic conditions, respectively. The microbial communities involved in aerobic and anaerobic degradation of TBBPA in the mangrove sediments were revealed.

2. Material and Methods

2.1. Sample Collection and Culture Medium

Sediment samples were collected from the Guandu and the Bali sampling site at Tamsui, northern Taiwan. Surface sediments (0–5 cm) and deep sediments (5–20 cm) during two different seasons: autumn and spring were collected. The TBBPA concentrations in sediment samples from the Guandu sampling site were spring (0.10 mg/kg) vs autumn (0.22 mg/kg), and for Bali it was spring (0.14 mg/kg) vs. autumn (0.10 mg/kg). The aerobic and anaerobic medium used in experiments were shown in Table 1.

Table 1. Aerobic and anaerobic medium in the experiments.

Medium	Composition (mg/L)
Aerobic medium	K_2HPO_4, 65.3; KH_2PO_4, 25.5; $Na_2HPO_4 \cdot 12\ H_2O$, 133.8; NH_4Cl, 5.1; $CaCl_2$, 82.5; $MgSO_4 \cdot 7H_2O$, 67.5; and $FeCl_3 \cdot 6H_2O$, 0.75.
Anaerobic medium	NH_4Cl, 2.7; $MgCl_2 \cdot 6H_2O$, 0.1; $CaCl_2 \cdot 2H_2O$, 0.1; $FeCl_2 \cdot 4H_2O$, 0.02; K_2HPO_4, 0.27; KH_2PO_4, 0.35, resazurin, 0.001; and titanium citrate, 0.9 mM.

2.2. Preparation of the Microcapsuled Enzyme Extract of Spent Mushroom Compost

SMC of *Pleurotus eryngii* was taken from a mushroom culture farm at Nantou, Taiwan. The microcapsuled enzyme extract of SMC was prepared as described in previous study [15].

2.3. Experimental Design

Two sets experiments (batch and continuous) under aerobic and anaerobic conditions were performed. In the batch experiment, aerobic experiments were performed using 125 mL serum bottles with the following components: 40 mL of medium, 5 g of sediment, 5 mL of the MC, and 2 mg/L TBBPA and incubated on a rotary shaker (120 rpm) at 25 °C in dark. Anaerobic experiments were performed using the same bottle containing 45 mL of medium, 5 g of sediment, 1 g/L zerovalent iron, and 2 mg/L TBBPA and conducted in an anaerobic glove box; capped with butyl rubber stoppers and crimp seals, wrapped in aluminum foil, and then incubated without shaking at 25 °C. Inoculated controls containing 45 mL of medium, 5 g of sediment, and 2 mg/L TBBPA were incubated without the MC or zerovalent iron at 25 °C. Sterile controls containing 45 mL of medium and 5 g of sediment were autoclaved at 121 °C for 30 min. Each experiment was repeated three times.

For the continuous experiments, Bali spring sediment samples were used by adding three times of 2 mg/L TBBPA into it under aerobic or anaerobic conditions. Aerobic settings were filled with 450 mL

of aerobic medium, and 50 g of sediment or 400 mL of aerobic medium, 50 mL of the MC, and 50 g of sediment. Anaerobic settings were filled with 450 mL of anaerobic medium, and 50 g of sediment, with or without 1 g/L zerovalent iron. TBBPA was re-added into each medium when TBBPA was dropped to undetectable level. The aerobic continuous experiments were aerated by air diffuser and the mixtures were stirred. The anaerobic continuous experiments were not aerated by air diffuser and incubated without shaking. The continuous experiments were incubated at 25 °C during a period of 75 d.

2.4. Chemical Analysis

TBBPA was extracted twice from experimental samples by dichloromethane. Residual TBBPA was further analyzed by GC (Hewlett Packard 6890) equipped with an electron capture detector and HP-5 capillary column. Bromide was monitored by ion chromatograms (Metrohm 833). TBBPA remaining percentage was calculated by the formula (residual TBBPA concentration/initial TBBPA concentration) × 100%. The TBBPA degradation data in this study were statistically analysed, and the coefficient of determination (R^2) was 0.911 to 0.979, which fits the first-order kinetics.

2.5. Microbial Community Analysis

The DNA extraction and pyrosequencing analyses were conducted as previously described [17]. These analyses were performed during March 2018. A cluster analysis of the bacterial community compositions between the samples was performed using the heatmap3 package of R 3.5.1 (www.r-project.org). Balloon plots of the bacterial community were plotted by the balloon plot function in the gplots package of R. The principal component analysis of the bacterial community between samples was computed by the PCA function and plotted by the fviz_pca_ind function in the FactoMineR package of R.

3. Results and Discussion

The remaining percentages of TBBPA in the sterile controls were ranged from 90.8 to 97.9% indicated that aerobic and anaerobic TBBPA degradation occurring in all of the following experiments was due to microbial action.

3.1. Batch Experiments of TBBPA Degradation under Aerobic Conditions

As shown in Figure 1, the degradation half-lives of TBBPA without the MC in the spring and autumn were 73.3 and 90.9 d in the Guandu sediment samples and 34.7 and 51.6 d in the Bali sediment samples, respectively. The aerobic degradation half-lives of TBBPA with the MC in the spring and autumn were 29.1 and 34.2 d in the Guandu sediment samples and 14.7 and 25.5 d in the Bali sediment samples, respectively. The degradation rates of the TBBPA were higher in the Bali sediment samples than the Guandu sediment samples, and it is also higher in the spring sediment samples compared with autumn sediment samples. The TBBPA degradation was enhanced with the MC in the sediment samples. The alginate microcapsules created a favorable microenvironment for the enzyme extract. Similar results were revealed in our previous study, which showed that the addition of the MC enhanced the degradation rates of nonylphenol in wastewater sludge [15].

To reveal the microbial community in aerobic conditions, experimental samples using the Bali spring sediment samples were subjected to 16S rRNA gene sequencing. As shown in Figure 2A,B, the diversity of the bacterial community in aerobic conditions decreased after the addition of TBBPA. Moreover, the composition of the bacterial community became similar as experiments proceeded (Mc2 and nMc2 in Figure 2C). As shown in Figure 2D, Gammaproteobacteria dramatically decreased and Alphaproteobacteria, Sphingobacteria, and Flavobacteria increased after addition of TBBPA for 45 days without addition of MC. The observation that the microbial community composition of nMc1 is much different from Mc1 reflected the enhancement of MC on TBBPA degradation within 45 days shown in Figure 1. As the remaining percentage of TBBPA decreased, the microbial community

composition of nMc2 and Mc2 became similar. Moreover, results in Figure 2D indicated that the adapted microbial community after the addition of TBBPA and most of the TBBPA-degrading bacteria may belong to this class. This finding is consistent with Yang et al. (2018) [17] that adaptation occurred after the addition of sulfonamides to mangrove sediments. The microbial communities associated with sulfonamides degradation grew and became the major bacterial populations.

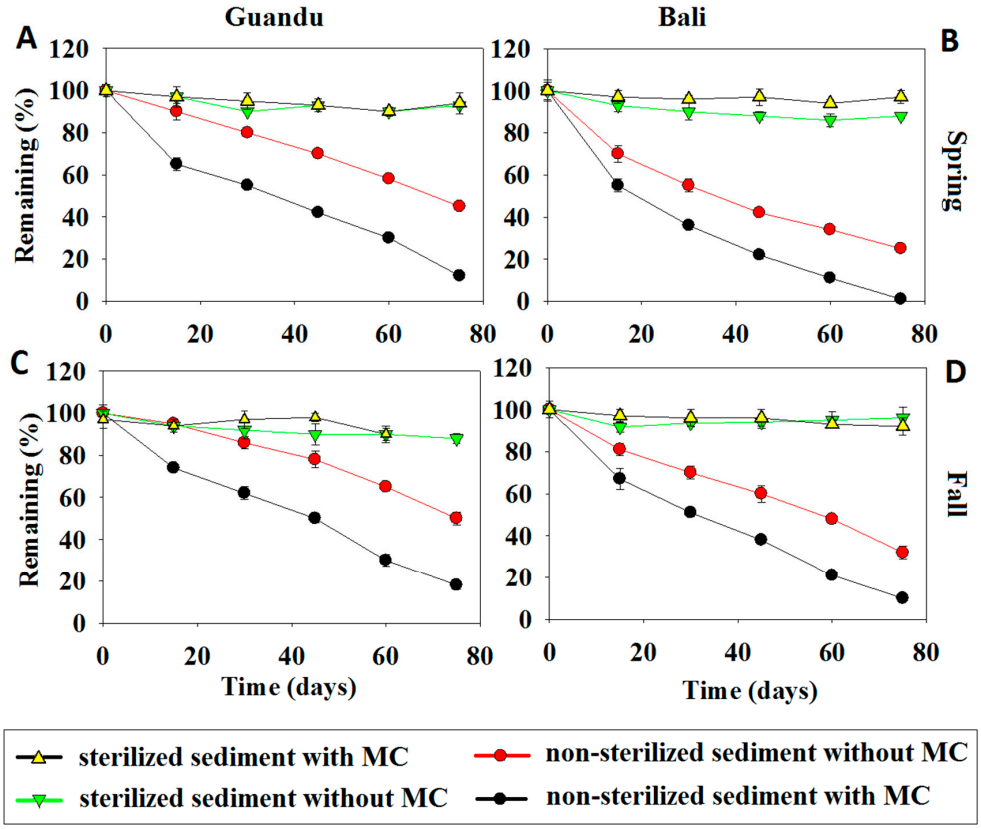

Figure 1. Comparison of TBBPA aerobic degradation from the Guandu sediment samples (A, C) and Bali sediment samples (B, D) within 75 d. MC: microcapsuled enzyme extract of spent mushroom compost. Symbols: Yellow ▲, sterilized sediment with the MC; Green ▼, sterilized sediment without the MC; Black ●, non-sterilized sediment with the MC; Red ●, non-sterilized sediment without the MC.

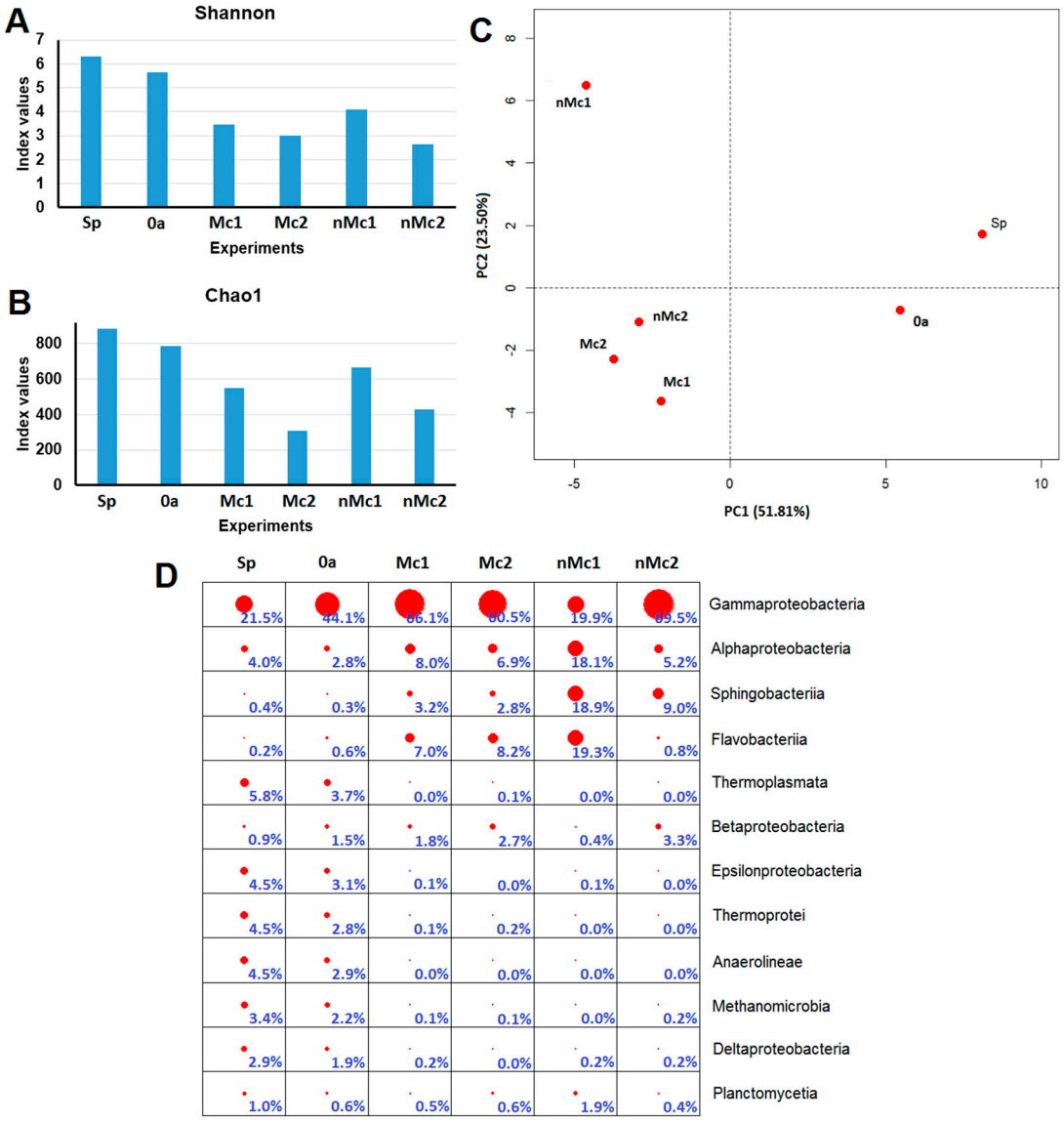

Figure 2. Comparison of the microbial community in the Bali spring sediment samples with and without microcapsuled enzyme extract of spent mushroom compost (MC) under aerobic conditions. (**A**,**B**). Microbial (alpha) diversity indicated by the Shannon and Chao1 diversity index. (**C**) Difference in microbial composition between samples indicated by principal component analysis (PCA). (**D**) Major bacteria and archaea classes in the experimental samples under aerobic conditions. Sp: the Bali samples. 0a: the Bali samples with TBBPA in the initial aerobic experiments. Mc1: the Bali samples with TBBPA and the MC for 45 d. Mc2: the Bali samples with TBBPA and the MC for 75 d. nMc1: the Bali samples with TBBPA and without the MC for 45 d. nMc2: the Bali samples with TBBPA and without the MC for 75 d.

3.2. Batch Experiments of TBBPA Degradation under Anaerobic Conditions

As shown in Figure 3, the anaerobic degradation half-lives of TBBPA without zerovalent iron in the spring and autumn were 41.1 and 65.4 d in the Guandu sediments and 31.4 and 42.9 d in the Bali sediments, respectively. The anaerobic degradation half-lives of TBBPA with zerovalent iron in the spring and autumn were 22.1 and 31.8 d in the Guandu sediments and 9.7 and 14.4 d in the Bali sediments, respectively. The TBBPA degradation was enhanced by zerovalent iron in the sediments. The addition of zerovalent iron could reduce TBBPA to less brominated compounds by the actions of

anaerobic microbes [19]). Additionally, adsorption on zerovalent iron also plays a role on the removal of TBBPA [20].

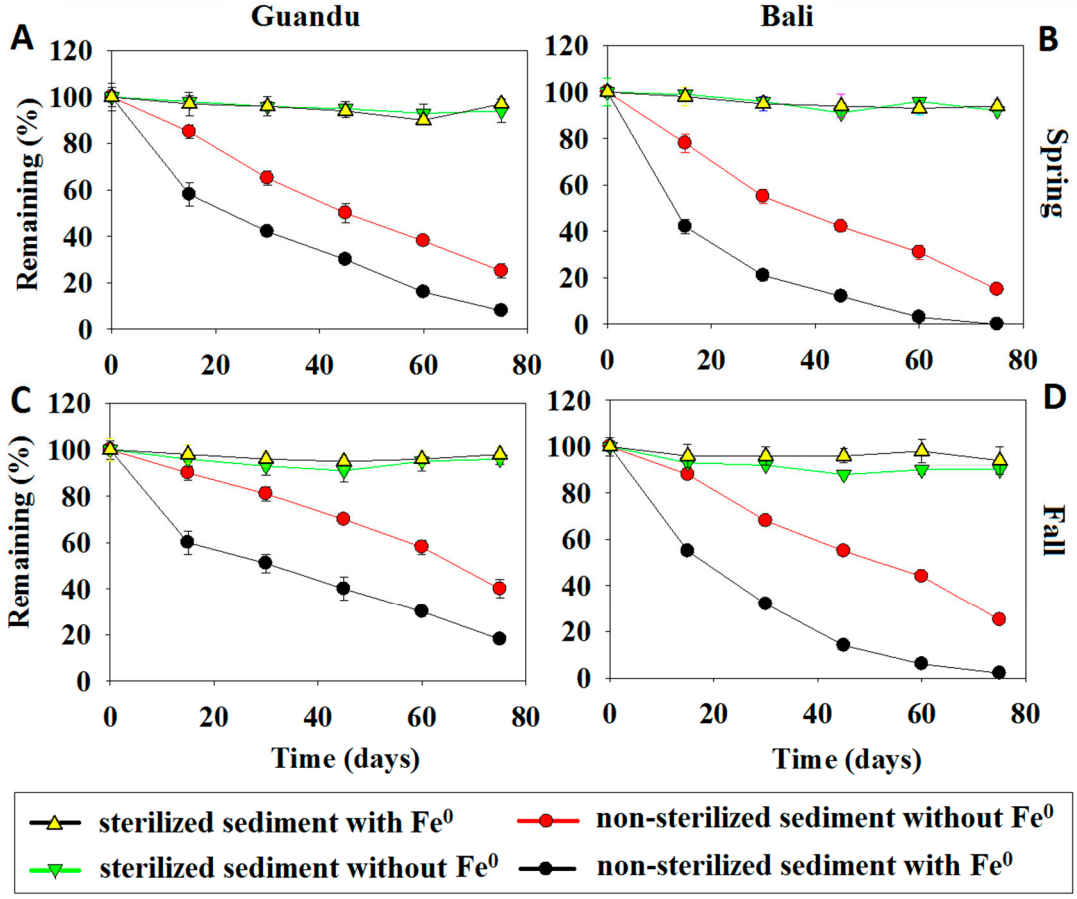

Figure 3. Comparison of anaerobic TBBPA degradation from the Guandu sediment samples (**A**,**C**) and Bali sediment samples (**B**,**D**) sampling sites with 75 d. Symbols: Yellow ▲, sterilized sediment with Fe°; Green ▼, sterilized sediment without Fe°; Black ●, non-sterilized sediment with Fe°; Red ●, non-sterilized sediment without Fe°.

The bromide ion concentrations increased from 0.9 to 2.1 mg/L without zerovalent iron and from 2.1 to 5.2 mg/L with zerovalent ion. Bromide ions were produced from TBBPA debromination. Debromination of TBBPA is likely a stepwise process with the sequential removal of bromine atoms. Based on this finding, we proposed the following biochemical pathway: TBBPA → → dibromobisphenol-A → → BPA. This observation is consistent with previous finding of the debromination of TBBPA in sediment [12]. The bromide ion concentrations were higher with zerovalent iron than without zerovalent iron.

The results also revealed that TBBPA anaerobic degradation rates in the spring sediment samples were higher than in the autumn sediment samples, and were higher in the Bali sediment samples than in the Guandu sediment samples. TBBPA anaerobic degradation rates were higher than aerobic degradation rates in the sediment. PCBs degradation are resistant to aerobic condition but degraded through dehalogenation under anaerobic environment [21]. The salinity at the Guandu and Bali sampling site in spring and autumn were different. Salinity may affect organic pollutant degradation in environment [22]. Additionally, the concentration of TBBPA was detected in the sediments of the two sampling sites. The adaptation process could enhance TBBPA degradation [8]. The TBBPA could be degraded without the MC or zerovalent iron.

To reveal the microbial community in anaerobic conditions, experimental samples using the Bali spring sediment samples were subjected to 16S rRNA gene sequencing. As shown in

Figure 4A,B, the diversity of the bacterial community in anaerobic conditions fluctuated after addition of TBBPA. Moreover, the composition of microbial community varied as experiments with zerovalent iron proceeded (Fe2 and nFe2 in Figure 4C). The Gammaproteobacteria and Deltaproteobacteria increased first in anaerobic TBBPA degradation experiments with zerovalent iron (Figure 4D). However, both the Alphaproteobacteria and Clostridia increased at the end of the experiments. These results indicated continuous changes in the microbial community during TBBPA anaerobic degradation with zerovalent iron.

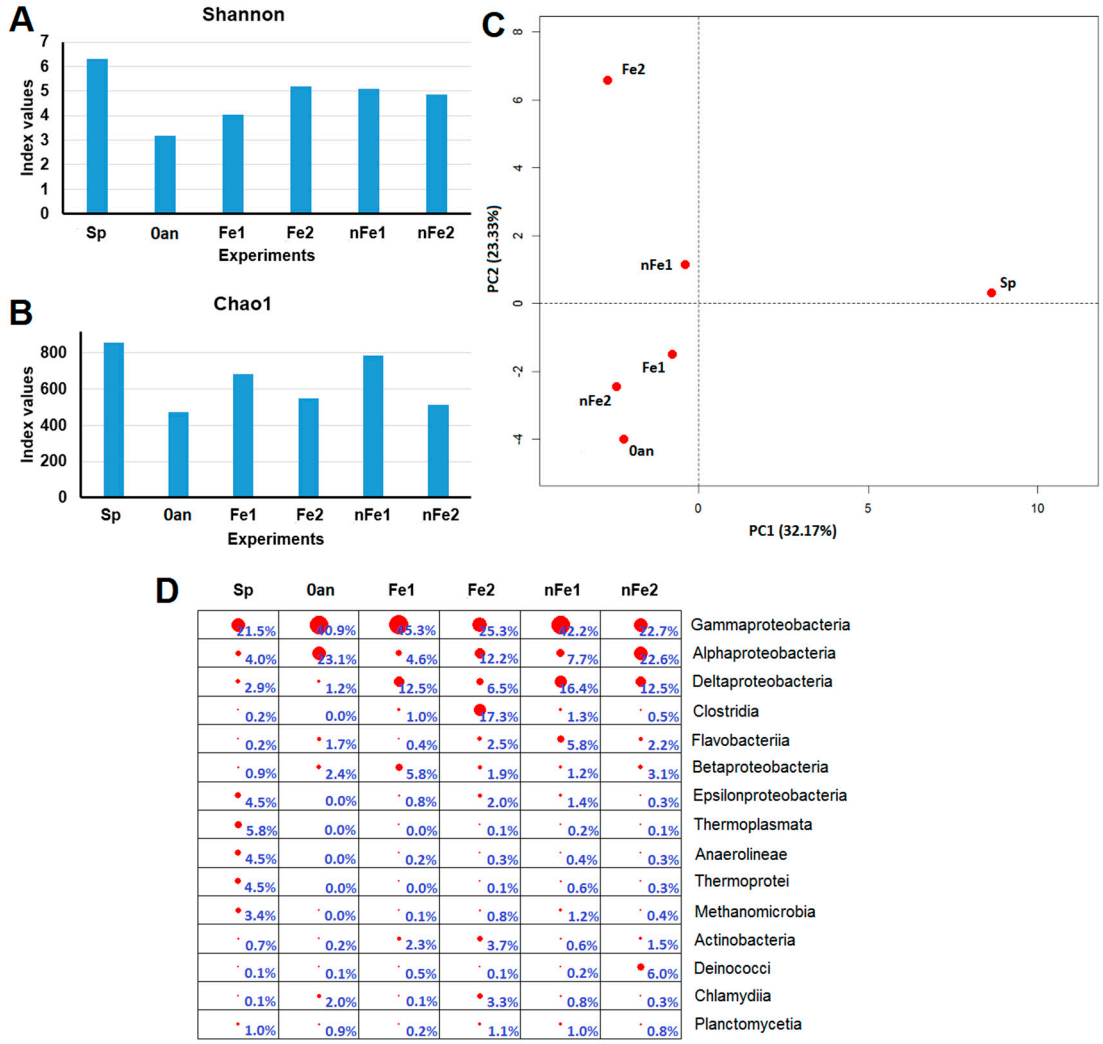

Figure 4. Comparison of the microbial communities in the Bali spring sediment samples with and without zerovalent iron (Fe°) under anaerobic conditions. (**A**,**B**) Microbial (alpha) diversity indicated by the Shannon and Chao1 diversity index. (**C**) Difference in microbial composition between samples indicated by principal component analysis (PCA). (**D**) Major bacteria and archaea classes under anaerobic conditions. Sp: the Bali samples. 0an: the Bali samples with TBBPA in the initial anaerobic experiments. Fe1: the Bali samples with TBBPA and Fe° for 45 d. Fe2: the Bali samples with TBBPA and Fe° for 75 d. nFe1: the Bali samples with TBBPA and without Fe° for 45 d. nFe2: the Bali samples with TBBPA and without Fe° for 75 d.

To get deeper insight into the differences in the microbial community between aerobic and anaerobic TBBPA degradation, the microbial community compositions of aerobic and anaerobic experiments were combined to perform a cluster analysis. As shown in Figure 5, two groups of bacteria and archaea genera were identified. The first group represents the major microbial community of aerobic TBBPA degradation and could be further divided into two subgroups. Group I-1 was

composed of eight bacterial genera (*Brevundimonas*, *Escherichia/Shigella*, *Idiomarina*, *Methylobacillus*, *Methyloversatilis*, *Phycisphaera*, *Pseudomonas*, *Roseivirga*) that were present in aerobic TBBPA degradation with the MC. Group I-2 was composed of nine bacterial genera (*Altererythrobacter*, *Balneola*, *Erythrobacter*, *Halobacteriovorax*, *Halomonas*, *Hanstruepera*, *Muricauda*, *Rhodopirellula*, *Robiginitalea*) that were decreased in the aerobic TBBPA degradation with the MC (Mc1 and Mc2).

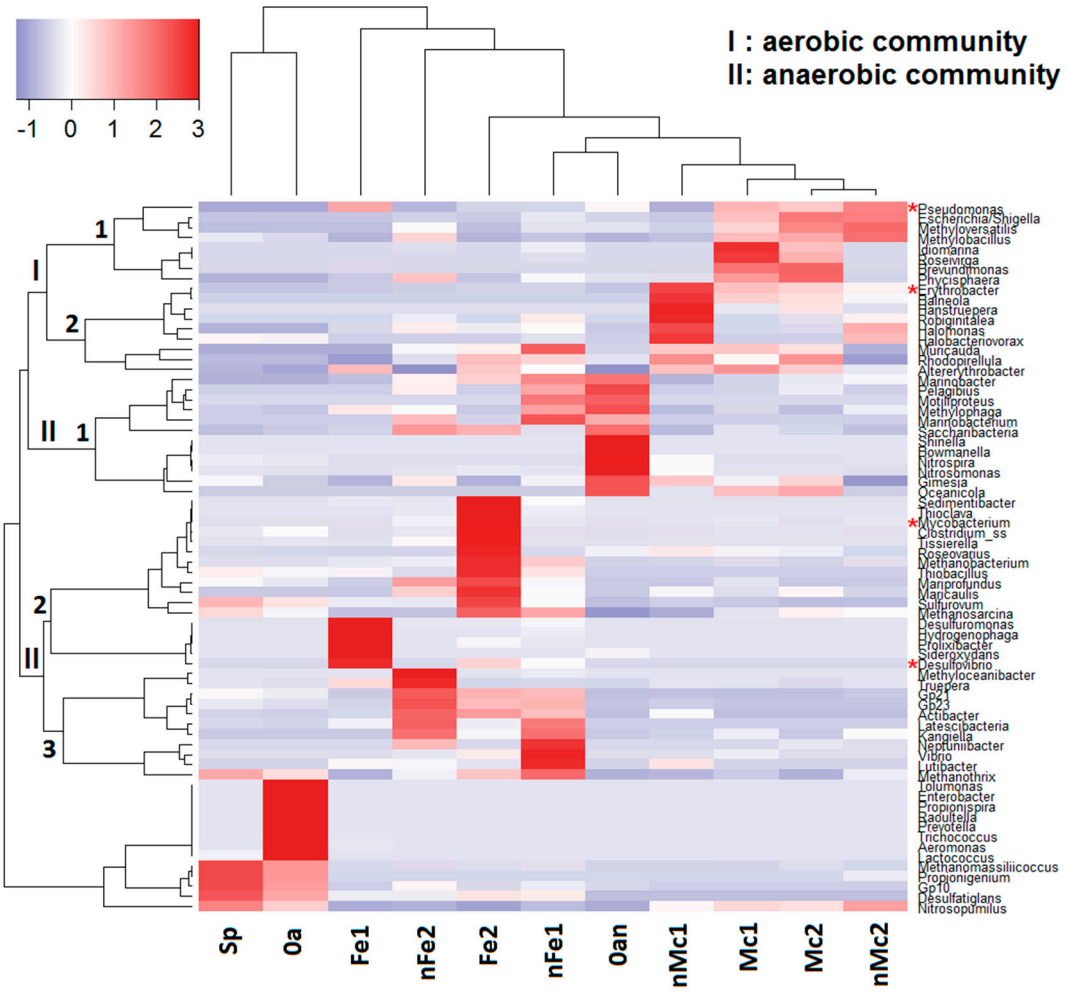

Figure 5. Comparison of the microbial communities in the Bali spring sediment samples under aerobic and anaerobic conditions. MC: microcapsuled enzyme extract of spent mushroom compost. Sp: the Bali samples, 0a: the Bali samples with TBBPA in the initial aerobic experiments. Mc1: the Bali samples with TBBPA and the MC for 45 d. Mc2: the Bali samples with TBBPA and the MC for 75 d. nMc1: the Bali samples with TBBPA and without the MC for 45 d. nMc2: the Bali samples with TBBPA and without the MC for 75 d. 0an: the Bali samples with TBBPA in the initial anaerobic experiments. Fe1: the Bali samples with TBBPA and Fe° for 45 d. Fe2: the Bali samples with TBBPA and Fe° for 75 d. nFe1: the Bali samples with TBBPA and without Fe° for 45 d. nFe2: the Bali samples with TBBPA and without Fe° for 75 d. Red stars indicate reported TBBPA degrading-bacteria.

The second group represents the major microbial community of anaerobic TBBPA degradation and could be further divided into three subgroups. Group II-1 was composed of 12 bacterial genera (*Bowmanella*, *Gimesia*, *Marinobacter*, *Marinobacterium*, *Methylophaga*, *Motiliproteus*, *Nitrosomonas*, *Nitrospira*, *Oceanicola*, *Pelagibius*, *Saccharibacteria*, *Shinella*) that were present in the initial stage of TBBPA anaerobic degradation with zerovalent iron. Group II-2 was composed of 17 bacterial and archaeal genera (*Clostridium_ss*, *Desulfovibrio*, *Desulfuromonas*, *Hydrogenophaga*, *Maricaulis*, *Mariprofundus*, *Methanobacterium*, *Methanosarcina*, *Mycobacterium*, *Prolixibacter*, *Roseovarius*,

Sedimentibacter, *Sideroxydans*, *Sulfurovum*, *Thiobacillus*, *Thioclava*, *Tissierella*) that were present in the midst and late stages of TBBPA anaerobic degradation with zerovalent iron. Likewise, group II-3 was composed of 11 bacterial and archaeal genera (*Actibacter*, *Gp21*, *Gp23*, *Kangiella*, *Latescibacteria*, *Lutibacter*, *Methanothrix*, *Methyloceanibacter*, *Neptuniibacter*, *Truepera*, *Vibrio*) that were present in the late stage of TBBPA anaerobic degradation without zerovalent iron. Among the microbial community, four bacterial genera (*Desulfovibrio*, *Erythrobacter*, *Mycobacterium*, *Pseudomonas*) were reported to be TBBPA degrading bacteria [23–26].

3.3. TBBPA Degradation in the Continuous Addition Experiments

The TBBPA degradation in the continuous experiments under aerobic or anaerobic conditions are illustrated in Figure 6. In aerobic conditions, after the first addition of TBBPA at d 0, TBBPA decreased to ND with the MC and degraded 96.1% without the MC at 63 (Figure 6A). After the second addition of TBBPA at d 70, the TBBPA decreased to ND with the MC and degraded 98.3% without the MC at d105. After the third addition of TBBPA at d 112, the TBBPA decreased to ND with or without the MC at d 147. In anaerobic conditions, after the first addition of TBBPA at d 42, TBBPA decreased to ND with zerovalent iron and degraded 3.2% without zerovalent iron. After the second addition of TBBPA at d 49, the TBBPA decreased to ND with zerovalent iron and degraded 2.1% without zerovalent iron at d 84. After the third addition of TBBPA at d 91, the TBBPA decreased to ND with zerovalent iron and degraded completely at d 126. The results indicated that the aerobic degradation half-lives of TBBPA were 7.1, 6.2, and 5.3 d with the MC, and 12.1, 7.8, and 6.1 d without the MC by first, second and third additions, respectively. The anaerobic degradation half-lives of TBBPA were 7.0, 5.6, and 3.9 d with zerovalent iron, and 9.7, 6.8, and 5.1 d without zerovalent iron by first, second, and third additions, respectively.

Anaerobic TBBPA degradation rates were enhanced by addition of zerovalent iron in sediments. This result is consistent with the anaerobic BDE-209 degradation with zerovalent iron in the sediment [27]. The aerobic TBBPA degradation was enhanced by addition of the MC in sediments. The degradation rate increased with each successive TBBPA addition. A second and third addition may increase microorganisms with TBBPA-degrading activity. This result was similar to investigate dibromodiphenyl ether degradation in sediments [28]. Various sampling sites, seasons and treatments could affect bacterial communities, and thus affect degradation of TBBPA in the sediments.

First of all, the differences between aerobic TBBPA degradation with and without the MC is shown in Figure 7A. The diversity (number of microbial genera) decreased and the composition of microbial genera changed after addition of TBBPA with and without the MC. This result consistent with the finding from the batch experiments (Figure 1). Four bacterial genera (*Bacillus*, *Erythrobacter*, *Pseudomonas*, *Rhodococcus*) identified in aerobic TBBPA degradation with the MC were found to be TBBPA-degrading bacteria [13,25,26]. Secondly, the differences between TBBPA anaerobic degradation with and without zerovalent iron is shown in Figure 7B. The diversity (number of microbial genera) of anaerobic re-addition experiments with zerovalent iron was greater than it without zerovalent iron. Nine methanogens were identified in the re-addition experiments with zerovalent iron. It has been reported that TBBPA degradation was enhanced under anaerobic methanogenic conditions [8]. These results provide strong evidence that the methanogens might be involved in TBBPA degradation in this study. Moreover, four bacterial genera (*Desulfovibrio*, *Sphaerochaeta*, *Sphingomonas*, *Pseudomonas*) identified from anaerobic TBBPA degradation with zerovalent iron were found to be TBBPA-degrading bacteria [24,25,29,30]. Thirdly, the differences between TBBPA aerobic degradation with the MC and anaerobic degradation with zerovalent iron is shown in Figure 7C. This Venn diagram clearly illustrates that two different microbial communities were developed from the same source of the Bali sediment samples under aerobic conditions with the MC and anaerobic conditions with zerovalent iron.

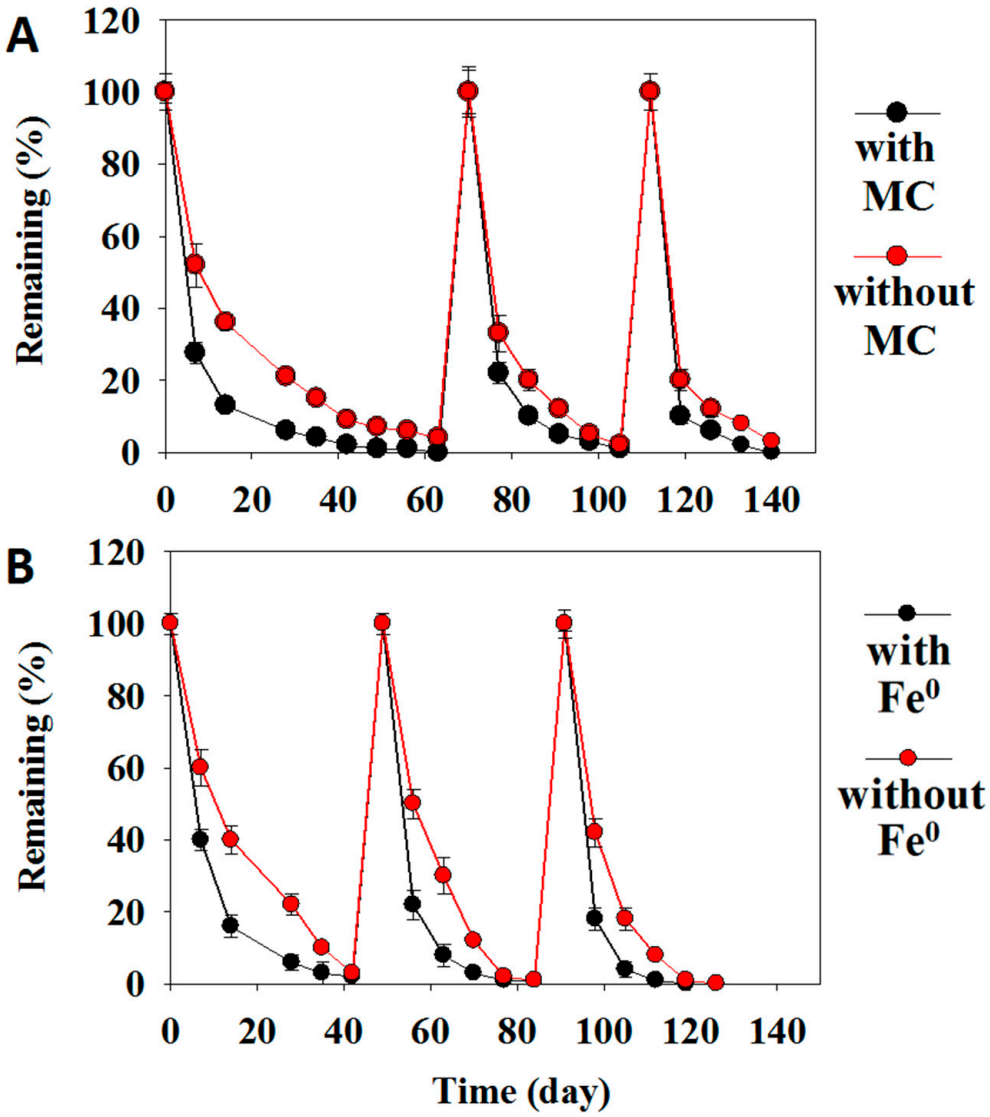

Figure 6. The remaining percentages after three additions of TBBPA in the Bali spring sediment samples under (**A**) aerobic conditions and (**B**) anaerobic conditions. MC: microcapsuled enzyme extract of spent mushroom compost. Fe°: zerovalent iron.

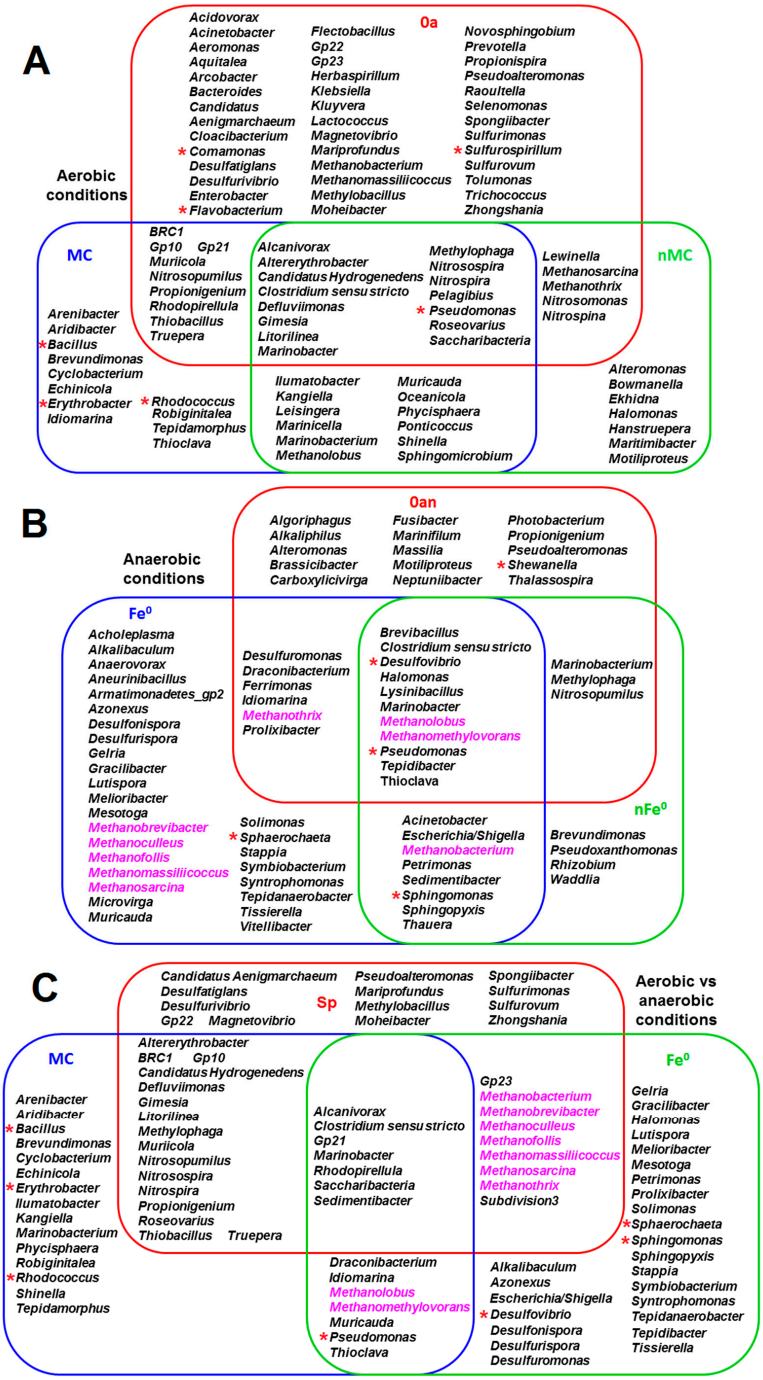

Figure 7. Comparison of the microbial communities in TBBPA continuous addition experiments using the Bali spring sediment samples under aerobic and anaerobic conditions. MC: microcapsuled enzyme extract of spent mushroom compost. Fe°: zerovalent iron. (**A**) Microbial community differences between experiments with and without the MC under aerobic conditions. (**B**) Microbial community differences between experiments with and without Fe° under anaerobic conditions. (**C**) Microbial community differences between aerobic and anaerobic conditions. Genera indicated by pink words are methanogenic archaea. Red stars indicate reported TBBPA degrading bacteria. 0a: the Bali samples with TBBPA in the initial aerobic experiments. MC: the re-addition experiments using Bali samples with TBBPA and MC. nMC: the re-addition experiments using Bali samples with TBBPA and without the MC. 0an: the Bali samples with TBBPA in the initial anaerobic experiments. Fe°: the re-addition experiments using Bali samples with TBBPA and Fe°. nFe°: the re-addition experiments using Bali samples with TBBPA and without Fe°. Sp: Bali samples.

4. Conclusions

This study revealed methods using microbial degradation of TBBPA as major processes for decontamination of the mangrove sediments. TBBPA degradation was enhanced with MC and zerovalent iron under aerobic and anaerobic conditions in mangrove sediments, respectively. Various sampling sites, seasons, and treatments could affect bacterial communities, and thus affect the TBBPA degradation efficiency in the mangrove sediments. Four bacterial genera (*Bacillus, Erythrobacter, Pseudomonas, Rhodococcus*) were the major bacterial communities involved in TBBPA aerobic degradation in the sediments. Another four bacterial genera (*Desulfovibrio, Pseudomonas, Sphaerochaeta, Sphingomonas*) were the major bacterial communities involved in TBBPA anaerobic degradation in the sediments. This study provides two feasible methods (addition of fungi enzymes in aerobic condition and addition of zerovalent iron in anaerobic condition) for the TBBPA bioremediation of mangrove sediments.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

References

1. Bayen, S. Occurrence, bioavailability and toxic effects of trace metals and organic contaminants in mangrove ecosystems: A review. *Environ. Int.* **2012**, *48*, 84–101. [CrossRef] [PubMed]
2. Haggblom, M.M.; Knight, V.K.; Kerkhof, L.J. Anaerobic decomposition of halogenated aromatic compounds. *Environ. Pollut.* **2000**, *107*, 199–207. [CrossRef]
3. Hale, R.C.; La Guardia, M.J. Emerging contaminants of concern in coastal and estuarine environments. In *Coastal and Estuarine Risk Assessment*; CRC Press: Boca Raton, FL, USA, 2002; pp. 41–72.
4. Wantanabe, I.; Sakai, S. Environmental release and behavior of brominated flame retardants. *Environ. Int.* **2003**, *29*, 665–682. [CrossRef]
5. Lai, D.Y.; Kacew, S.; Dekant, W. Tetrabromobisphenol A (TBBPA): Possible modes of action of toxicity and carcinogenicity in rodents. *Food Chem. Toxicol.* **2015**, *80*, 206–214. [CrossRef] [PubMed]
6. Koike, E.; Yanagisawa, R.; Takano, H. Brominated flame retardants, hexabromocyclododecane and tetrabromobisphenol-A, affect proinflammatory protein expression in human bronchial epithelial cells via disruption of intracellular signaling. *Toxicol. In Vitro* **2016**, *32*, 212–219. [CrossRef] [PubMed]
7. Zhou, Y.; Wu, S.; Zhou, H.; Huang, H.; Zhao, J.; Deng, Y.; Wang, H.; Yang, Y.; Yang, J.; Luo, L. Chiral pharmaceuticals: Environment sources, potential human health impacts, remediation technologies and future perspective. *Environ. Int.* **2018**, *121*, 523–537. [CrossRef]
8. Fetzner, S. Bacterial dehalogenation. *Appl. Microbiol. Biotechnol.* **1998**, *50*, 633–657. [CrossRef]
9. Yang, C.W.; Chen, W.Z.; Chang, B.V. Biodegradation of tetrabromobisphenol-A in sludge with spent mushroom compost. *Int. Biodeter. Biodeg.* **2017**, *119*, 387–395. [CrossRef]
10. McAvoy, D.C.; Pittinger, C.A.; Willis, A.M. Biotransformation of tetrabromobisphenol-A (TBBPA) in anaerobic digester sludge, soils, and freshwater sediments. *Ecotoxicol. Environ. Saf.* **2016**, *131*, 143–150. [CrossRef]
11. Ronen, Z.; Abeliovich, A. Anaerobic-aerobic process for microbial degradation of tetrabromobisphenol-A. *Appl. Environ. Microbiol.* **2000**, *66*, 2372–2377. [CrossRef]
12. Chang, B.V.; Yuan, S.Y.; Ren, Y.L. Anaerobic degradation of tetrabromobisphenol-A in river sediment. *Ecol. Eng.* **2012**, *49*, 73–76. [CrossRef]
13. Chang, B.V.; Yuan, S.Y.; Ren, Y.L. Aerobic degradation of tetrabromobisphenol-A by microbes in river sediment. *Chemosphere* **2012**, *87*, 535–541. [CrossRef] [PubMed]

14. Voordeckers, J.W.; Fennell, D.E.; Jones, K.; Haggblom, M.M. Anaerobic biotransformation of tetrabromobisphenol A, tetrachlorobisphenol A, and bisphenol A in estuarine sediments. *Environ. Sci. Technol.* **2002**, *36*, 696–701. [CrossRef] [PubMed]
15. Hsu, F.Y.; Wang, Z.Y.; Chang, B.V. Use of microcapsules with electrostatically immobilized bacterial cells or enzyme extract to remove nonylphenol in wastewater sludge. *Chemosphere* **2013**, *91*, 745–750. [CrossRef] [PubMed]
16. Chang, B.V.; Ren, Y.L. Biodegradation of three tetracyclines in river sediment. *Ecol. Eng.* **2015**, *75*, 272–277. [CrossRef]
17. Yang, C.W.; Tsai, L.L.; Chang, B.V. Fungi extracellular enzyme-containing microcapsules enhance degradation of sulfonamide antibiotics in mangrove sediments. *Environ. Sci. Pollut. Res.* **2018**, *25*, 10069–10079. [CrossRef] [PubMed]
18. Pattanasuttichonlakul, W.; Sombatsompop, N.; Prapagdee, B. Accelerating biodegradation of PLA using microbial consortium from dairy wastewater sludge combined with PLA-degrading bacterium. *Int. Biodeterior. Biodegrad.* **2018**, *132*, 74–83. [CrossRef]
19. Kim, Y.M.; Murugesan, K.; Chang, Y.Y.; Kim, E.J.; Chang, Y.S. Degradation of polybrominated diphenyl ethers by a sequential treatment with nanoscale zero valent iron and aerobic biodegradation. *J. Chem. Technol. Biotechnol.* **2011**, *87*, 216–224. [CrossRef]
20. Shih, Y.H.; Tai, Y.T. Reaction of decabrominated diphenyl ether by zerovalent iron nanoparticles. *Chemosphere* **2010**, *78*, 1200–1206. [CrossRef]
21. Borja, J.; Taleon, D.M.; Auresenia, J.; Gallardo, S. Polychlorinated biphenyls and their biodegradation. *Process Biochem.* **2005**, *40*, 1999–2013. [CrossRef]
22. Castillo-Carvajal, L.C.; Sanz-Martín, J.L.; Barragán-Huerta, B.E. Biodegradation of organic pollutants in saline wastewater by halophilic microorganisms: A review. *Environ. Sci. Pollut. Res. Int.* **2014**, *21*, 9578–9588. [CrossRef] [PubMed]
23. George, K.W.; Häggblom, M.M. Microbial O-methylation of the flame retardant tetrabromobisphenol-A. *Environ. Sci. Technol.* **2008**, *42*, 5555–5561. [CrossRef] [PubMed]
24. Lefevre, E.; Cooper, E.; Stapleton, H.M.; Gunsch, C.K. Characterization and adaptation of anaerobic sludge microbial communities exposed to tetrabromobisphenol-A. *PLoS ONE* **2016**, *11*, e0157622. [CrossRef] [PubMed]
25. Li, G.; Xiong, J.; Wong, P.K.; An, T. Enhancing tetrabromobisphenol-A biodegradation in river sediment microcosms and understanding the corresponding microbial community. *Environ. Pollut.* **2016**, *208*, 796–802. [CrossRef]
26. Peng, X.; Zhang, Z.; Luo, W.; Jia, X. Biodegradation of tetrabromobisphenol-A by a novel *Comamonas* sp. strain, JXS-2–02, isolated from anaerobic sludge. *Bioresour. Technol.* **2013**, *128*, 173–179. [CrossRef] [PubMed]
27. Yang, C.W.; Hsiao, W.C.; Chang, B.V. Biodegradation of sulfonamide antibiotics in sludge. *Chemosphere* **2016**, *150*, 559–565. [CrossRef] [PubMed]
28. Huang, H.W.; Chang, B.V.; Cheng, C.H. Biodegradation of dibromodiphenyl ether in river sediment. *Int. Biodeterior. Biodegrad.* **2012**, *68*, 1–6. [CrossRef]
29. Iasur-Kruh, L.; Ronen, Z.; Arbeli, Z.; Nejidat, A. Characterization of an enrichment culture debrominating tetrabromobisphenol A and optimization of its activity under anaerobic conditions. *J. Appl. Microbiol.* **2010**, *109*, 707–715. [CrossRef] [PubMed]
30. Peng, X.; Wang, Z.; Huang, J.; Pittendrigh, B.R.; Liu, S.; Jia, X.; Wong, P.K. Efficient degradation of tetrabromobisphenol A by synergistic integration of Fe/Ni bimetallic catalysis and microbial acclimation. *Water Res.* **2017**, *122*, 471–480. [CrossRef]