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REMEDIATION OF SOIL CONTAMINATED WITH DECABROMINATED DIPHENYL ETHER USING WHITE ROT FUNGI

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Abstract. Biodegradation of decabrominated diphenyl ether (BDE-209) in soil by white rot fungi under various experimental conditions was investigated in this study. It was found that BDE-209 in soil could be rapidly and efficiently degraded by white rot fungi, and the biodegradation fits the pseudo-first-order kinetics during a 15-day incubation period. The residues of BDE-209 in soil decreased with the increased amount of white rot fungi addition. It can be seen from the results that white rot fungi have a good degradation ability with one-step and two-step addition method. In native soil, the degradation of BDE-209 reached 52.65%, which was higher than that in sterilized soil. About 37.76–53.74% of BDE-209 degradation was observed in different soil types after 15 days. In addition, it was confirmed in this study that the presence of Cu^{2+}, Cd^{2+} could enhance the remediation of soil contaminated with BDE-209, and the residues decreased by 69.20% and 54.65% for Cu^{2+} and Cd^{2+} treatment, respectively. However, the superior ability of white rot fungi to degrade BDE-209 was not obvious at low pollution level (<0.5 mg kg^{-1}).

Keywords: white rot fungi, decabrominated diphenyl ether (BDE-209), biodegradation, soil.

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Introduction

Decabrominated diphenyl ether (BDE-209) which is a member of the class of compounds well known as polybrominated diphenyl ethers (PBDEs) is widely used as flame retardants in producing fabrics and electronic products (Liu *et al.* 2005). With fast-developing electronics industry, outdated products are frequently discarded. Unsuitable handling of e-waste would not only pose risks to the surrounding environment, but also to human health. Pearl River Delta, Taizhou area and other regions in China became e-waste recycling areas. Chen *et al.* (2011) reported the amount of PBDEs of 0.625 mg kg^{-1}, in which the content of BDE-209 was in excess of 85%. Higher concentrations were observed by Yang *et al.* (2008) in soil of the Pearl River Delta, with BDE-209 levels range from 1.31 to 6319 ng kg^{-1}. Soil contaminated with PBDEs in some Europe countries such as Norway and Sweden, were reported by Hassanin (Hassanin *et al.* 2004). Because of its low water solubility, low volatility, high lipophilicity and other properties, BDE-209 is regarded as one of the persistent organic pollutants (POPs) (Tanabe 2004). Large number of experiments proved that PBDEs including BDE-209 persist in the environment for long time (de Wit 2002), and bioaccumulate and biomagnify as they move through the food chain (Law *et al.* 2006; Wolkers *et al.* 2004). They are released to the environment and converted into several toxic compounds through their photodecomposition and biologic degradation (Schenker *et al.* 2008; Watanabe, Sakai 2003; Robrock *et al.* 2008; He *et al.* 2006). Due to the production and use of BDE-209, and potential toxicity to humans, BDE-209 has raised public safety concerns.

It is reported that current technologies used to treat contaminated soil and sediment, such as photo degradation (Crosby *et al.* 1971), thermal desorption (De Percin 1995), biodegradation by fungi, base catalyzed dechloronation (Takada *et al.* 1996), plasma arc systems, have been rapidly developed to various extent (Rubin, Burhan 2006). However, little research work on biodegradation of BDE-209 in soil has been done.

White rot fungi have the unique ability to decompose lignin, and they are also capable of degrading some compounds with similar structure. Many studies on successful fungal remediation in soil have been reported (Eggen, Majcherczyk 1998; Kubatova *et al.* 2001; Ogbo, Okhuoya 2008). Although the main mechanism involved in the fungal degradation is not yet clear, it is believed that the produce of the ligninolytic systems composed of the lignin peroxidases (LiPs), manganese dependent peroxidases (MnPs) and

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laccase might be the main reason (Reddy 1995). LiPs and MnPs directly involved in most of the oxidation reaction are extracellular, which offer the potential to oxidize substrates that have low water solubility like PBDEs. A positive correlation has been found between biodegradation and ligninolytic enzyme activity in soil. Thus, it is not surprising that the ligninolytic system of white rot fungi is useful for the remediation of soil contaminated with BDE-209.

The objective of this study is to investigate the biodegradation of BDE-209 in soil by white rot fungi. Since the potential could be influenced by a range of environmental factors in the laboratory, we have been studying the effects of different conditions (the amount of white rot fungi addition, ways of white rot fungi addition, pollution levels of BDE-209, sterilized soil and native soil, soil types, the presence of heavy metals) on biodegradation kinetics.

1. Methods

1.1. Chemicals and fungi

BDE-209 used throughout this study was purchased from Jinan Enter Chemical Co., LTD. The five BDE-209 standards at different concentrations (0.2 mg kg^{-1}, 0.5 mg kg^{-1}, 1 mg kg^{-1}, 2 mg kg^{-1} and 5 mg kg^{-1}) were purchased from South China Institute of Environmental Sciences (Guangzhou, China). Hexane, acetone, dichloromethane of analytical grade were obtained from Damao Chemical Reagent Factory (China).

White rot fungi was purchased from Guangzhou Chemical Company L.T.D. of Chinese Academy of Sciences (Guangzhou, China). The fungi was incubated at 28 °C on potato dextrose agar medium containing peeled potato 200 g, dextrose 20 g, KH_2PO_4 3 g, $MgSO_4$ 1.5 g, vitamin B_1 0.01 g, and agar 20 g in 1 L distillated water for 7 days before being used in the experiments of this study. In all cases, round pieces of 10 mm-diameter from the fungal lawn were cut and tested for the effects of different conditions on the biodegradation of BDE-209.

1.2. Soil

The experimental soil was collected from different places in Guangdong Province (China). They had different organic matter contents and pH. Their physical-chemical properties are shown in Table 1. Before being used, the soil was air-dried, passed through a 2 mm sieve.

To prepare BDE-209 contaminated soil, BDE-209 was added into a volumetric flask adjusting to 250 mL with hexane. Apply the BDE-209 solution into soil. The mixture of BDE-209 solution and soil was kept at room temperature, the indoor ventilated places for a period of four weeks. Keep the water-holding capacity at 15% throughout all experiments.

1.3. Degradation of BDE-209 by fungi

The effects of different factors, including the amount of white rot fungi addition, ways of white rot fungi addition, pollution levels of BDE-209, native soil and sterilized soil, soil types, and the presence of heavy metals, on the degradation of BDE-209 in soil by fungi were investigated in the laboratory.

At the beginning, different amounts of white rot fungi (3 pieces, 6 pieces, 9 pieces in 15 g of soil) were added into 15 g of soil contaminated with BDE-209 at the same initial concentrations of 4.6256 mg kg^{-1}, while the soil without fungi was used as a control.

In the experiment with one-step addition method, 6 pieces of white rot fungi were added into 15 g of soil on the first day. The control was without white rot fungi. In the experiment with two-step addition method, 3 pieces of white rot fungi were applied to 15 g of soil on the first day and another 3 pieces were added on the 7th day. The BDE-209 concentration in samples was 4.6256 mg kg^{-1}.

White rot fungi (6 pieces in 15 g of soil) were added into different soil with three different BDE-209 pollution levels. The three levels were Level 1, Level 2, and Level 3, which represented the concentrations of BDE-209 in soil were 0.4882 mg kg^{-1}, 2.0571 mg kg^{-1} and 4.6256 mg kg^{-1}. The controls were without fungi.

Experiments on biodegradation of BDE-209 in native and sterilized soil were carried out in the laboratory. Six pieces of white rot fungi were added into 15 g of sterilized soil that was sterilized in an autoclave at 1.2 MPa for 30 min or native soil. The controls were without fungi. The BDE-209 concentration in samples was 4.6256 mg kg^{-1}.

In this study, we used lateritic red soil, laterite, red soil, paddy soil and vegetable soil at the BDE-209 concentration of 4.6256 mg kg^{-1}, 4.7123 mg kg^{-1}, 4.6348 mg kg^{-1}, 4.6982 mg kg^{-1}, 4.6537 mg kg^{-1}, respectively. For each case, one degradation experiment with fungi (6 pieces in 15 g of soil) and one control experiment without fungi were conducted.

Table 1. Physical-chemical characteristics of experimental soil

Soil	Lateritic Red Soil	Red Soil	Laterite	Paddy Soil	Vegetable Soil
Fe (mg kg^{-1})	45.00	91.21	22.77	35.00	34.00
Organic matters (g kg^{-1})	0.45	4.26	3.15	6.27	6.66
pH	4.8	5.1	5.2	5.8	5.8

To study the effects of the presence of heavy metals on soil remediation, we added 6 pieces of fungi and Cu^{2+} or Cd^{2+} at the concentration of 0.5 mg kg^{-1} into 15 g of soil separately. The BDE-209 concentration was 4.7428 mg kg^{-1} in the experiments of Cu^{2+} treatment. The BDE-209 concentration was 4.8217 mg kg^{-1} in the experiments of Cd^{2+} treatment. A set of experiments without fungi was set up as control.

All the experiments were performed in triplicate for 15 days of incubation period. The BDE-209 residues were analyzed by GC-MS on 0 d, 3 d, 6 d, 9 d, 12 d, and 15 d.

1.4. Sample pretreatment

After adding ^{13}C-PCB141 and 2 g of copper for desulfurization, the samples were extracted with hexaneacetone (1:1) solution in a Soxhlet extraction apparatus for 48 h. And then, the extract liquid was transferred to a rotary evaporator, washed three times with hexane, concentrated to 2 mL. Subsequently, the concentrate was purified with a chromatography column filled with activated silica gel. The order of wet-loaded columns from top to bottom was: 6 cm of neutral alumina, 2 cm of neutral silica gel, 5 cm of alkali silica gel, 2 cm of neutral silica gel, 8 cm of acidic silica gel, and 1 cm of anhydrous sodium sulfate. Then the elution took place with 30 mL of hexane and 70 mL of hexanedichloromethane (1:1) solution in succession. Until there was no liquid dripping, the eluent should be concentrated to 1 mL, and kept at 4 °C in darkness.

1.5. GC-MS analysis

The GC-MS analysis was conducted on Thermo Fisher TRACE-DEQ gas chromatograph-mass spectrometer with column DB-5MS (15 m × 0.25 mm.i.d, 0.1 μm), and a NCI detector at temperature of 230 °C. The column temperature was programmed to increase from 110 to 300 °C at a flow rate of 10 °C min^{-1}. The carrier gas was high purity nitrogen (99.999%). The speed of gas flow was 1 mL min^{-1}. Continuous injection (1 μL) was applied. ^{13}C-PCB141 was used as a recovery indicator to control the recovery rate during the whole operation procedure. The recovery standard was used to control the sample recovery rate. The recovery rate of the indicator range from 78% to 88.6%, and that of BDE-209 was between 88.4% and 98.7%.

2. Results and discussion

2.1. Effects of different amount of white rot fungi addition

In this study, pieces of 10 mm-diameter from the fungal lawn were cut and tested for the effects on the removal of BDE-209 in samples with different amount of white rot fungi addition. An initial BDE-209 concentration of 4.6256 mg kg^{-1} was used for all these samples and other conditions were kept constant during the whole incubation period. Figure 1 shows that the residues of BDE-209 in soil declined and reduced by 50.07%, 52.65% and 52.74% for 3 pieces, 6 pieces, and 9 pieces of fungi, respectively during the whole incubation period.

The results indicated that the removal was directly related to the amount of inoculums in this experiment. With the increasing amount of fungi addition, the residues of BDE-209 decreased. However, the residues of BDE-209 in soil declined and reduced by 52.65% and 52.74% for 6 pieces, and 9 pieces of fungi, which were very close. It can be concluded that there was an optimal amount of added fungi in the degradation process. Thus, the optimal amount should be taken into account in practice to obtain efficiency as well as cost savings.

2.2. Effects of different ways of white rot fungi addition

The effects of addition ways of fungi were shown in Figure 2. In the experiment with one-step addition method, incubation of soil with an initial addition of 6 pieces of white rot fungi led to 45.16% removal of BDE-209 after 6 d, and it increased to 52.65% after 15 d. However, the soil treated with the two-step addition approach demonstrated a different situation. Three pieces of white rot fungi were added on the first day, and the residues decreased by 23.63% from 4.6256 mg kg^{-1} to 3.533 mg kg^{-1} after 6 days. Further experiments showed that residues continued to decrease when 3 more pieces of white rot fungi were added on the 7th day. The residues were decreased by 59.01% to 2.0639 mg kg^{-1}, which was lower than that in the soil treated with one-step approach (2.2146 mg kg^{-1}) during the 15 days of incubation period.

The way of white rot fungi addition does affect the biodegradation. The research (Zhao *et al.* 2008)

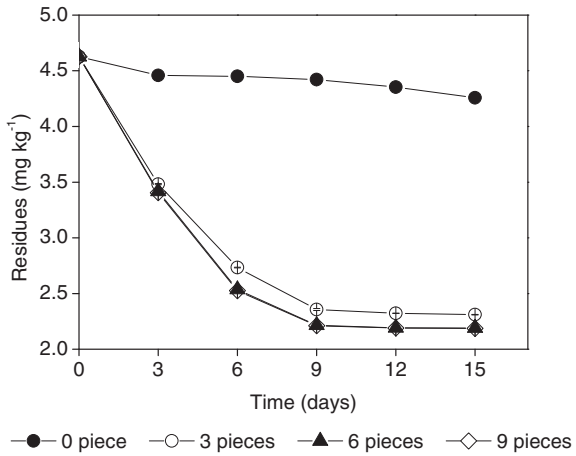

Fig. 1. Residues of BDE-209 in soil with different amount of white rot fungi addition on 0d, 3 d, 6 d, 9 d, 12 d, and 15 d. All data are means ± SE (n = 3)

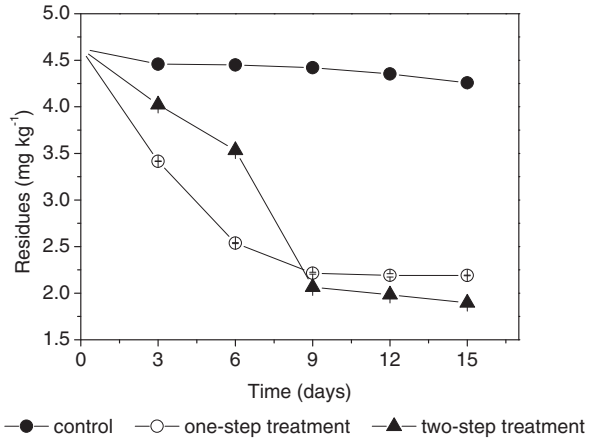

Fig. 2. Residues of BDE-209 in different ways of white rot fungi addition on 0 d, 3 d, 6 d, 9 d, 12 d, and 15 d. All data are means ± SE (n = 3)

on remediation of soil contaminated with DDTs by laccase extracted from white rot fungi showed that two-step method can bring a higher degradation rate compared with one-step method. Some other similar results were also reported (Hu *et al.* 2008). Various environmental conditions, such as soil temperature, mineral and metal ions, could affect the chemical degradation indirectly by affecting enzyme and microorganisms' activity. The divided addition method can reduce the impact of these factors by splitting white rot fungi into 2 equal portions, and adding into soil separately. It may enhance the utilization of white rot fungi as well as biodegradation.

2.3. Degradation of BDE-209 at different pollution levels

All the data of the research based on the different concentrations of BDE-209 in soil were shown in Figure 3, which also indicated that a better biodegradation by white rot fungi occurred at higher concentration. The highest removal occurred at a BDE-209 concentration of 4.6256 mg kg^{-1} (Level 3) after 15 days, reduced by 52.65% from 4.6256 mg kg^{-1} to 2.1903 mg kg^{-1}. In the experiment of Level 2, the amount of BDE-209 decreased by 48.43% during the 15-day incubation period. In contrast, when the BDE-209 concentration was lower than 2.5 mg kg^{-1}, the degradation was worse. Figure 3 shows the removal of BDE-209 at an initial concentration of 0.4882 mg kg^{-1} (Level 1) after 15 days was reduced by only 11.04% from 0.4882 mg kg^{-1} to 0.4343 mg kg^{-1}.

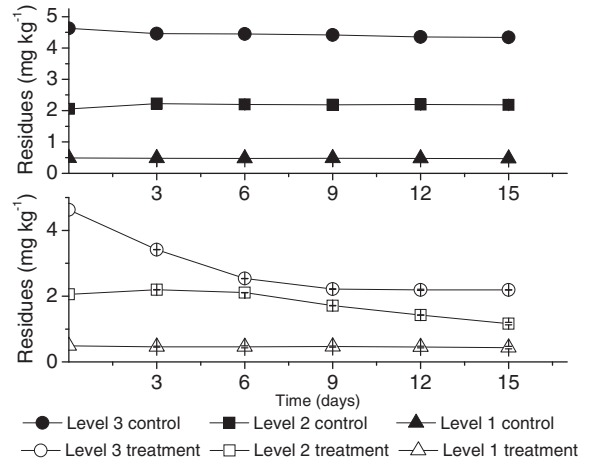

Fig. 3. Residues of BDE-209 in soil at different pollution levels on 0 d, 3 d, 6 d, 9 d, 12 d, and 15 d. All data are means ± SE (n = 3)

It was reported that white rot fungi could effectively degrade PAHs; and the initial concentration of PAHs in 1 kg dry soil was up to 609.8 mg before any treatment (Sasek *et al.* 2003). Zhou *et al.* (2007) carried out a research on the degradation of BDE-209 in liquid culture medium at a concentration of 160 mg L^{-1}. It appears that the high concentration of pollutant is favorable for the degradation. In this study, however, the superior ability of white rot fungi to degrade BDE-209 was not obvious at low pollution level (<0.5 mg kg^{-1}).

2.4. Effects of native and sterilized soil

The experiments were carried out with native and sterilized soil. Incubation of soil led the removal of BDE-209 to decline rapidly in the first 6 days and then slowly (Fig. 4). White rot fungi induced 34.02% degradation of BDE-209 after 6 days, and then the degradation of BDE-209 increased to 44.8% with the residues of 2.5496 mg kg^{-1} in sterilized soil after 15 days. Nevertheless, an improved degradation was observed in native soil. A 6-day incubation in native soil led to 45.16% removal. After 15 days, the removal reached 52.65%, which was higher than that in sterilized soil.

Matthias (Kastner *et al.* 1998) investigated the degradation of PAHs in native and sterilized soil. The report showed that anthracene and phenanthrene degraded enormously in native soil, while only a slight

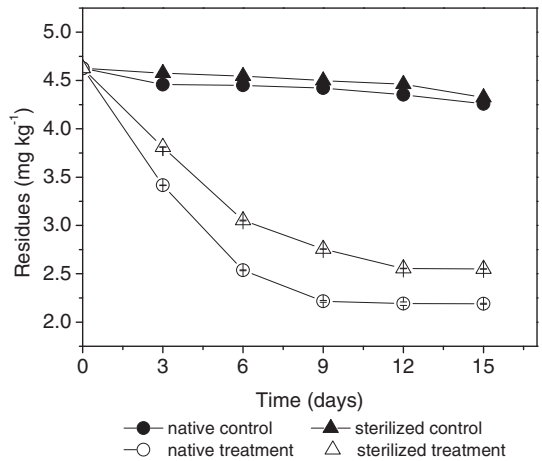

Fig. 4. Residues of BDE-209 in native and sterilized soil on 0 d, 3 d, 6 d, 9 d, 12 d, and 15 d. All data are means ± SE (n = 3)

abiotic loss was observed in sterilized soil during the whole incubation period. However, the experiments designed by Bishnoi (Bishnoi *et al*. 2008) showed that maximum degradation of PAHs in sterilized soil was higher than that in unsterilized native soil. Obviously, the conditions for biodegradation were quite different in sterilized and native soil. Although the mechanism is still unclear, we concluded that the key influencers on the biodegradation may be pH value, soil moisture, organic matter content, indigenous microorganisms and so on. In native soil, there may be competitions between introduced and indigenous microorganisms, when fungi were inoculated.

2.5. Degradation of BDE-209 in different soils

Lateritic red soil, laterite, red soil, paddy soil and vegetable soil were used in this study. During 15 days of incubation, the residues of BDE-209 in soil decreased by 52.65%, 47.92%, 52.94%, 53.74%, 37.76% for lateritic red soil, laterite, red soil, paddy soil and vegetable soil, respectively (Fig. 5). The increasing order of BDE-209 removal was paddy soil > red soil > lateritic red soil > laterite > vegetable soil. In addition, the paddy soil was flooded for a long time, leading to a lower redox potential (Eh). The reductive soil may benefit the degradation of BDE-209 by white rot fungi.

2.6. Effects of the presence of heavy metals

A comparison of the degradation results for Cu^{2+} and Cd^{2+}-BDE209 appears in Figure 6. As shown in Figure 6, the residues of BDE-209 in soil incubated with white rot fungi decreased by 69.20% and 54.65% for Cu^{2+} and Cd^{2+} treatment, respectively.

The fungal metabolism requires trace amounts of many heavy metals. Such as copper, iron, manganese, molybdenum, zinc, and nickel are necessary for fungal

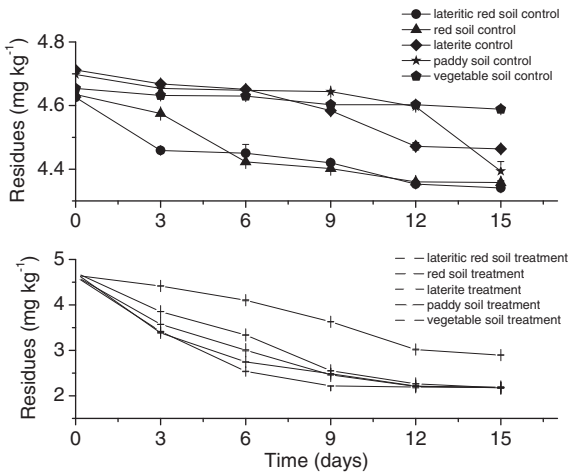

Fig. 5. Residues of BDE-209 in lateritic red soil, laterite, red soil, paddy soil and vegetable soil on 0 d, 3 d, 6 d, 9 d, 12 d, and 15 d. All data are means ± SE (n = 3)

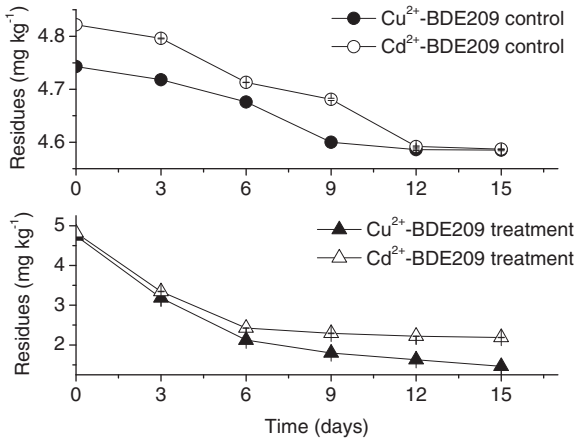

Fig. 6. Residues of BDE-209 in soil in the presence of heavy metals on 0 d, 3 d, 6 d, 9 d, 12 d, and 15 d. All data are means ± SE (n = 3)

growth, while chromium, cadmium, lead, mercury and silver are nonessential metals (Gadd 1994). In this study, we investigated whether the biodegradation can be enhanced as a result of the presence of copper and cadmium. In white rot fungi, the produce of the ligninolytic systems, which composed of LiPs, MnPs, and laccase, are useful for the remediation of environmental contaminants (Call, Muecke 1997). Copper, which served as a cofactor in the catalytic center of laccase, directly participates in the process of lignin degradation (Baldrian 2003). On the other hand, it has been reported that the presence of copper could improve the production of laccase (Tychanowicz *et al*. 2006; Tinoco *et al*. 2011). Thus, the presence of copper was likely to enhance the biodegradation. However, Cd^{2+} is in general the most toxic metal for white rot fungi, the presence of Cd^{2+} may inhibit fungal growth (Baldrian 2003). Atagana (2009) investigated biodegradation of PAHs by fungi in contaminated soil containing cadmium; the fungi tested were capable of removing PAHs in the presence of cadmium. One possible explanation for this is that the addition of Cd^{2+} and Cu^{2+} leads to an increase of laccase activity. The results demonstrated that the presence of Cu^{2+}, Cd^{2+} can enhance the remediation of soil contaminated with BDE-209.

2.7. Kinetic studies

In this study, the degradation of BDE-209 in soil fits the pseudo-first-order kinetics and follows the equation of $\ln C_t = -kt + \ln C_0$, where t is the degradation time, C_0 is the initial concentration of BDE-209, C_t is the concentration of BDE-209 on the t days, k is the degradation rate constant, and the half-life of BDE-209 is $0.693/k$ (Tables 2–7).

The residues of BDE-209 in soil treated with white rot fungi decreased rapidly during the first 6 days and then slowly during the 15-day incubation period. There

was a relation between the half-life of BDE-209 and the amount of white rot fungi addition. Higher amount of white rot fungi in soil led to lower half-life. But there were no apparent declines in half-life when the addition was more than 6 pieces. In soil treated with 6 and 9 pieces of white rot fungi, the half-life was about 14.14 days, which was lower than that in soil treated with 0 and 3 pieces fungi (Table 2). Two-step method had a lower half-life than the one-step method, and their half-life values of BDE-209 were 10.21 days and 14.14 days, respectively (Table 3). The half-life values were 14.14, 15.10, 117.46 days for soil with initial BDE-209 concentration of 4.6256, 2.2573, 0.4882 mg kg^{-1}, respectively. Obviously, we cannot achieve a better biodegradation using white rot fungi at low pollution level (< 0.5 mg kg^{-1}) (Table 4). The data indicated there was a faster rate in native soil than sterilized soil, which was reflected in the half-life values, where $t_{1/2}$ values were 14.14 and 16.99 days, respectively (Table 5). This strongly supported that native soil was more favorable to remediation of BDE-209 in the laboratory. The half-life increased in the order red soil (13.46 days) < paddy soil (13.92 days) < lateritic red soil (14.14 days) < laterite (15.10 days) < vegetable soil (20.03 days) (Table 6). Compared with the half-life (13.89 days) of Cd^{2+}, a lower half-life (9.02 days) was figured out in soil treated with Cu^{2+} (Table 7).

The findings were consistent with many investigators (Tayal *et al*. 1999; Huang *et al*. 2004) who reported that the biodegradation for PCP using white rot fungi follows the pseudo-first-order kinetics, and the residues decreased sharply in the first 6 days. Studies showed

Table 2. Kinetic parameters of degradation of BDE-209 with different amount of white rot fungi addition

Degradation experiment	Pseudo-first-order kinetic equation $\ln C_t = -kt + \ln C_0$	Half-life/d	Degradation rate constant/d	Regression coefficient R
Control	$\ln C_t = -0.0047t + 1.523$	138.60	0.0047	0.910
3 pieces treatment	$\ln C_t = -0.046t + 1.399$	15.07	0.046	0.838
6 pieces treatment	$\ln C_t = -0.049t + 1.381$	14.14	0.049	0.816
9 pieces treatment	$\ln C_t = -0.049t + 1.378$	14.14	0.049	0.813

Table 3. Kinetic parameters of degradation of BDE-209 in different ways of white rot fungi addition

Degradation experiment	Pseudo-first-order kinetic equation $\ln C_t = -kt + \ln C_0$	Half-life/d	Degradation rate constant/d	Regression coefficient R
Control	$\ln C_t = -0.0047t + 1.523$	147.45	0.0047	0.910
One-step treatment	$\ln C_t = -0.049t + 1.381$	14.14	0.049	0.816
Two-step treatment	$\ln C_t = -0.0679t + 1.550$	10.21	0.0679	0.902

Table 4. Kinetic parameters of degradation of BDE-209 at different pollution levels

Degradation experiment	Pseudo-first-order kinetic equation $\ln C_t = -kt + \ln C_0$	Half-life/d	Degradation rate constant/d	Regression coefficient R
5 mg kg^{-1} control	$\ln C_t = -0.0047t + 1.523$	147.45	0.0047	0.910
5 mg kg^{-1} treatment	$\ln C_t = -0.049t + 1.381$	14.14	0.049	0.816
2.5 mg kg^{-1} control	$\ln C_t = -0.0020t + 0.808$	138.60	0.0020	0.799
2.5 mg kg^{-1} treatment	$\ln C_t = -0.0459t + 0.099$	15.10	0.0459	0.922
0.5 mg kg^{-1} control	$\ln C_t = -0.0033t + 0.720$	210.00	0.0033	0.810
0.5 mg kg^{-1} treatment	$\ln C_t = -0.0059t + 0.732$	117.46	0.0059	0.760

Table 5. Kinetic parameters of degradation of BDE-209 in native and sterilized soil

Degradation experiment	Pseudo-first-order kinetic equation $\ln C_t = -kt + \ln C_0$	Half-life/d	Degradation rate constant/d	Regression coefficient R
Native soil control	$\ln C_t = -0.0047t + 1.523$	147.45	0.0047	0.910
Native soil treatment	$\ln C_t = -0.049t + 1.381$	14.14	0.049	0.816
Sterilized soil control	$\ln C_t = -0.0029t + 1.531$	238.97	0.0029	0.997
Sterilized soil treatment	$\ln C_t = -0.0408t + 1.451$	16.99	0.0408	0.898

Table 6. Kinetic parameters of degradation of BDE-209 in various soils

Degradation experiment	Pseudo-first-order kinetic equation $\ln C_t = -kt + \ln C_0$	Half-life/d	Degradation rate constant/d	Regression coefficient R
Lateritic soil control	$\ln C_t = -0.0047t + 1.523$	147.45	0.0047	0.910
Lateritic soil treatment	$\ln C_t = -0.049t + 1.381$	14.14	0.049	0.816
Red soil control	$\ln C_t = -0.0044t + 1.527$	157.50	0.0044	0.874
Red soil treatment	$\ln C_t = -0.0515t + 1.450$	13.46	0.0515	0.935
Laterite control	$\ln C_t = -0.0039t + 1.554$	177.69	0.0039	0.940
Laterite treatment	$\ln C_t = -0.0459t + 1.487$	15.10	0.0459	0.909
Paddy soil control	$\ln C_t = -0.0035t + 1.554$	198.00	0.0035	0.690
Paddy soil treatment	$\ln C_t = -0.0498t + 1.416$	13.92	0.0498	0.894
Vegetable soil control	$\ln C_t = -0.0037t + 1.542$	187.30	0.0037	0.971
Vegetable soil treatment	$\ln C_t = -0.0346t + 1.575$	20.03	0.0346	0.963

Table 7. Kinetic parameters of degradation of BDE-209 in the presence of heavy metals

Degradation experiment	Pseudo-first-order kinetic equation $\ln C_t = -kt + \ln C_0$	Half-life/d	Degradation rate constant/d	Regression coefficient R
Cu^{2+}-BDE-209 control	$\ln C_t = -0.0026t + 1.535$	266.54	0.0026	0.919
Cu^{2+}-BDE-209 treatment	$\ln C_t = -0.077t + 1.556$	9.02	0.077	0.910
Cd^{2+}-BDE-209 control	$\ln C_t = -0.0037t + 1.451$	187.30	0.0037	0.782
Cd^{2+}-BDE-209 treatment	$\ln C_t = -0.0499t + 1.395$	13.89	0.0499	0.963

that the kinetics of biodegradation was greatly improved by the presence of manganese ions, H_2O_2 and glucose in the medium. In our experiments, the presence of Cu^{2+} and Cd^{2+}, which has positive effect on the production of laccase, enhanced the biodegradation. This strongly suggests the involvement of ligninolytic systems mechanism in the process of biodegradation.

Conclusions

1. By using white rot fungi, a rapid and efficient remediation of soil contaminated with BDE-209 could be expected. The biodegradation fits the pseudo-first-order kinetics under different experimental conditions. The residues of BDE-209 in soil treated with white rot fungi decreased rapidly during the first 6 days and then slowly during the 15-day incubation period.

2. In this study, 6 pieces of added fungi for 15 g of soil are optimal amounts in the degradation process.

3. White rot fungi have a good degradation ability with one-step and two-step addition method.

4. In native soil, the removal rate reached 52.65%, which was higher than that in sterilized soil.

5. For 15 days of incubation, 52.65%, 52.94%, 47.92%, 53.74%, 37.76% of BDE-209 was degraded by white rot fungi for lateritic red soil, laterite, red soil, paddy soil and vegetable soil, respectively.

6. The presence of Cu^{2+}, Cd^{2+} can both enhance the remediation of soil contaminated with BDE-209. The residues of BDE-209 decreased by 69.20% and 54.65% for Cu^{2+} and Cd^{2+} treatment, respectively.

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