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DEGRADATION AND ADSORPTION BEHAVIOR OF DIBUTYL PHTHALATE IN METHANOGENIC PHASE REFUSE

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Abstract

The degradation and adsorption behavior of dibutyl phthalate (DBP) in methanogenic phase refuse was investigated through laboratory microcosm experiments. The results showed that the half-life of DBP in the sterilized refuse was 5.9 times higher than in unsterilized samples, but that it decreased by 35.8% when dominant bacterial strains were added. Different concentrations of DBP did not have obvious effects on its degradation. The half-lives of DBP were decreased by 53.0%, 37.2% and 20.8% when the refuse moisture increased from 20%, 40% and 60% to 80%, respectively. The pH of refuse was an important factor influencing DBP biodegradation, with the optimal pH being around 7.0. The optimal temperature for DBP degradation in refuse was around 30°C. In addition, the Freundlich model fits the adsorption and desorption isotherm of DBP for refuse with *n* values that suggest nonlinear adsorption characteristics. The free energy change ΔG value (−23.5 kJ mol^{-1}) indicates that the adsorption of DBP on refuse was a physical reaction. Desorption hysteresis was observed in the DBP desorption experiments. Overall, the results indicate that DBP may accumulate in refuse, and that its transformation and bio-availability may be limited under landfill conditions.

Key words: adsorption, degradation, dibutyl phthalate, refuse

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1. Introduction

Dibutyl phthalate (DBP) belongs to the family of phthalic acid esters (PAEs), which are widely used as plasticizers (Blount et al., 2000). DBP is suspected to cause cancer and interfere with the reproductive systems and development of humans and animals (Mo et al., 2008; Wu et al., 2011). The United States Environmental Protection Agency, European Union, and China National Environmental Monitoring Center have classified DBP as a top priority pollutant (Lu et al., 2009; Wu et al., 2011). DBP can be released from plastic products and leach into the environment during their use or after disposal (Amir et al., 2005). As a result, DBP has been detected in surface water, sediments, municipal wastewater, sludge and soil (Cai et al., 2007; Chang et al., 2007; Liu et al., 2010; Wang et al., 2008; Xu et al., 2008).

Biodegradation plays an important role in the decomposition of DBP because of its low rate of hydrolysis and photolysis (Xu et al., 2005); therefore, many research regarding the biodegradation of DBP has been conducted (Chi and Cai, 2012; Wang et al., 2004; Xu et al., 2007; Yuan et al., 2010). In addition, several DBP-degrading bacterial strains have been isolated from different environments, including activated sludge, mangrove sediments and wastewater (Li et al., 2005; Lu et al., 2009; Roslev et al., 2007; Wang et al., 2012; Xu et al., 2005, 2007; Yuan et al., 2010).

Most materials containing DBP are disposed of in landfills with other municipal solid waste

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(MSW); accordingly, these facilities are an important DBP pollution source and a sink in the natural environment. Degradation of DBP in landfills is difficult owing to the complex anaerobic environment. Ejlertsson et al. (2003) and Mersiowsky et al. (2001) confirmed that biodegradation plays an important role in the fate of DBP under landfill conditions. Additionally, Jonsson et al. (2003) investigated the degradation of DBP to monobutyl phthalate and phthalic acid under methanogenic conditions in a landfill. In our previous research, the behavior of DBP in simulated landfill bioreactors was evaluated and its concentration was found to decrease greatly during decomposition of waste in bioreactors, with major loss of DBP from landfills with active methanogenic environments being observed (Fang et al., 2009a, 2009b). Furthermore, some bacterial strains capable of using DBP as their sole source of carbon and energy were isolated from MSW (Fang et al., 2010). However, the mechanism of dynamic degradation of DBP in the refuse has yet to be identified.

It is well known that there are methanogens in refuse when a landfill enters the methanogenic phase; however, these organisms cannot degrade complicated organic materials such as DBP. Nevertheless, previous studies confirmed that the loss of DBP from landfills was much higher in active methanogenic environments than acidic environments (Ejlertsson et al., 2003; Fang et al., 2009b; Jonsson et al., 2003; Mersiowsky et al., 2001). Despite this, no studies have investigated the reason for this phenomenon, and the factors influencing DBP degradation in refuse are still unclear. In addition, adsorption is a fundamental process controlling the transformation and biological activity of hydrophobic organic contaminants in the environment (Chefetz and Xing, 2009; Wen et al., 2007). However, few studies have been conducted to investigate the adsorption behavior of DBP and its effects on DBP transformation and fate in landfills.

This study was conducted to measure the dynamic degradation and adsorption behavior of DBP in methanogenic phase refuse through laboratory microcosm experiments. To accomplish this, the influences of microorganisms, DBP initial concentration, moisture, pH of refuse and temperature on DBP degradation in the refuse were investigated. Moreover, the adsorption characteristics of DBP in methanogenic refuse were analyzed with consideration of the adsorption isotherm and desorption hysteresis. The overall goal of this study was to further reveal the mechanism of DBP biodegradation in the refuse and provide a basis for accelerated removal of DBP under landfill conditions.

2. Materials and methods

2.1. Chemicals and instruments

HPLC-grade hexane and isopropanol, as well as reagent grade dibutyl phthalate (≥99%) and all other reagents were obtained from Tianjin Siyou Co. (Tianjin, China). Purified water from a Milli-Q system was used in all experiments.

The following equipment was used in this study: a liquid chromatograph (Agilent 1100, USA), rotatory evaporator (BUCHI R200), biochemical incubator (LRH-250), oven oscillator (HZ-9211K) and ultrapure water equipment (Millipore Milli-Q, USA), etc.

2.2. Tested refuse

The refuse for the test was collected from a leachate recirculation landfill bioreactor located in our lab on day 120 after the refuse was loaded. The landfill bioreactor was constructed of brick and concrete and had an effective size of 0.55 m×0.55 m×2.0 m (L×W×H). The system was comprised of a methanogenic reactor that received leachate from the landfill. The leachate was subjected to methanogenesis in the methanogenic reactor, after which it was recycled into the landfill. Leachate was continuously circulated between the landfill and the methanogenic reactor for 8 h daily using pumps with adjusted flow rates that varied with leachate volume during waste decomposition.

The recycling ratio of leachate was 100%. To avoid the effects of DBP in the refuse itself, the components of the plastics and rubber were removed from the MSW. The initial physical composition of the refuse (by weight) was as follows: kitchen waste 70.0±1.2%; paper 11.7±0.5%; sand and soil 8.1±0.1%; cellulose textile 1.5±0.2%; glass 7.3±0.5%; metal 0.7±0.1%; and wood 0.7±0.1%. Analysis of the refuse indicated that the simulated landfill had completed the acidic phase and entered the methanogenic phase, and refuse samples collected on day 120 are defined as samples from the methanogenic phase. The physicochemical and biochemical properties of the refuse are shown in Table 1.

Table 1. Physicochemical and biochemical properties of refuse used in this study

Diameter (cm)	*Moisture (%)*	*pH*	*VSS (%)*	*BDM (%)*	*CEC (cmol Kg^{-1})*	*Specific surface area (m^2 g^{-1})*	*Population of microorganisms*			*Redox enzyme activities*		
							M1	*M2*	*M3*	*E1*	*E2*	*E3*
≤2	62.3 ±0.3	7.03 ±0.02	14.7 ±0.3	13.4 ±0.6	79.4 ±1.7	4.58 ±0.78	7.59 ±0.07	6.72 ±0.10	5.50 ±0.09	434.5 ±48.6	14.2 ±1.6	4.9 ±1.2

VSS: volatile suspended solids; BDM: biodegradable materials; CEC: cation exchange capacity; M1: bacteria (lg CFU g^{-1}); M2: fungi (lg CFU g^{-1}); M3: actinomycetes (lg CFU g^{-1}); CFU: colony forming units; E1: dehydrogenase (mg TF g^{-1} dw, 12 h); E2: hydrogen peroxidase (mL $KMnO_4$ g^{-1} dw, 1 h); E3: polyphenol oxidase (mg purple gall pigment g^{-1} dw, 2 h)

2.3. Tested bacterial strain

The bacteria strain *Enterobacter* sp. T5 used in this study was previously isolated from MSW obtained from a simulated landfill bioreactor and found to have the ability to use DBP as its sole source of carbon and energy.

The optimal pH and temperature for its biodegradation activities were 7.0 and 35°C, and the degradation half-life was about 20.9 h when the concentration of DBP was < 1000 mg L^{-1} in inorganic salt culture (Fang et al., 2010). When the cultures reached the logarithmic growth phase, samples were centrifuged at 150 rpm and 30°C. The bacteria were then washed three times with buffer solution Na_2HPO_4-NaH_2PO_4 (pH 7.0, 0.02 mol L^{-1}), after which a bacterial suspension with a weight ratio of 1g bacteria: 3 g buffer solution was prepared (Fang et al., 2010).

2.4. Effects of microorganisms on DBP degradation in refuse

Three types of refuse were prepared, sterilized refuse (a), unsterilized refuse (b) and inoculated refuse (c). For sample (a), the refuse was intermittently sterilized for 30 minutes at 121°C and 1.1 kg·cm^{-2}. For sample (c), the refuse was inoculated with 10^8 CFU g^{-1} (*Enterobacter* sp. T5). Each refuse sample was prepared in triplicate. DBP was dissolved in acetone and added to the tested refuse samples to give a concentration of 20 μg g^{-1} (0.05% acetone addition), after which the samples were mixed thoroughly and the acetone was allowed to evaporate. Aliquots of refuse (40 g) were then transferred into serum bottles, tightly sealed and incubated under stationary conditions at 25°C in the dark to avoid photolysation.

To avoid experimental errors caused by non-uniform sampling, all refuse of each sample was withdrawn from the serum bottle on day 0, 1, 3, 7, 14, 21, 28, 35 and 50 and analyzed for residual DBP. Removal of DBP was assessed by measuring disappearance of the parent chemical by HPLC.

2.5. Effects of different concentrations of DBP on its degradation

DBP was added to the tested refuse samples to give concentrations of 5, 10, 20 and 30 μg g^{-1}. Aliquots of refuse were transferred into serum bottles and incubated under stationary conditions at 25°C in the dark. Each refuse sample was prepared in triplicate and sampled for DBP as described in 2.4.

2.6. Effects of refuse moisture on DBP degradation

The refuse was air dried first, after which the moisture contents of the refuse were adjusted to 20%, 40%, 60% and 80% with sterile water. DBP was added to the tested refuse samples to give a concentration of 20 μg g^{-1}. Aliquots of refuse were transferred into serum bottles and incubated under stationary conditions at 25°C in the dark. Each refuse sample was prepared in triplicate and sampled for DBP as described in 2.4.

2.7. Effects of refuse pH on DBP degradation

DBP was added to the tested refuse samples to give a concentration of 20 μg g^{-1}, after which the pH was adjusted to 5.0, 6.0, 7.0, and 8.0, respectively. Aliquots of refuse were then transferred into serum bottles and incubated under stationary conditions at 25°C in the dark. Each refuse sample was prepared in triplicate and sampled for DBP as described in 2.4.

2.8. Effects of the temperature on DBP degradation

DBP was added to the tested refuse samples to give a concentration of 20 μg g^{-1}, after which aliquots of refuse were transferred into serum bottles and incubated under stationary conditions at 15°C, 25°C, 35°C, 45°C and 55°C in the dark. Each refuse sample was prepared in triplicate and sampled for DBP as described in 2.4.

2.9. Adsorption experiment

Adsorption experiments were performed using the batch equilibrium approach. Briefly, DBP solutions of 40.0–400.0 μg L^{-1} (150 mL amended with 0.02% sodium azide to inhibit bacterial growth with pH 7.0) and 0.5 g refuse were placed into a series of 250 mL conical flasks. After initial mixing, flasks were shaken at 200 rpm and 25°C for 24 h (based on the results of a preliminary experiment), then centrifuged at 10,000 rpm for 10 min. Once equilibrium had been reached, the supernatant was used for DBP analysis.

The difference in initial DBP and equilibrium concentration in the liquid phase was the adsorption capacity of the refuse. For the desorption experiments, the supernatant from the adsorption experiments was removed and 150 mL of background solution (0.02% sodium azide in sterilized distilled water) was added to the solid phase, after which the samples were shaken for 24 h, at which time the DBP concentrations in the liquor phase were measured. This test was performed in triplicate. In addition, background samples containing refuse and no DBP and controls containing sample but no refuse were run under the same conditions and the results were considered in the final calculations.

2.10. Analytical methods

Extraction of DBP from the refuse and liquid phase and the subsequent HPLC analysis were conducted as described by Fang et al. (2009b), with minor modification. Briefly, the pH value of sample

of refuse or liquid phase was adjusted to 7–8 with 1N NaOH or 1N HCl if necessary, after which the samples were extracted three times with hexane (2:1, v/v). The hexane extracts were then passed through a small glass hopper containing Na_2SO_4 to eliminate contaminating water. Next, the extracts were concentrated to 1.0 mL prior to analysis by HPLC. This procedure was performed in triplicate for each sample. The samples were then injected onto an AE LICHROM column (CN-5 μm) using a mixture of hexane and isopropanol (99:1, v/v) applied at a flow rate of 1.5 mL min^{-1} as the mobile phase, and DBP was detected using a UV detector at a wavelength of 272 nm. The recovery rates of DBP from refuse and the liquid phase were 82.5%–99.1% and 84.2–98.7%, respectively. The detection limits were 0.1 μg g^{-1} and 0.1 μg l^{-1} for DBP in the refuse and liquid phase, respectively.

3. Results and discussion

3.1. Effects of microorganisms on DBP degradation in refuse

Fig. 1 shows the degradation characteristics of DBP in the sterilized, unsterilized and inoculated refuse from the methanogenic phase. The degradation rate of DBP was significantly higher in the unsterilized refuse than the sterilized refuse ($p<0.05$). The degradation rate of DBP in the refuse from the methanogenic phase increased after addition of the dominant bacterial strain, *Enterobacter* sp. T5. The degradation rate of DBP was significantly higher in the inoculated refuse than the unsterilized refuse ($p<0.05$). On day 50, the removal rate of DBP was 12.3%, 54.7% and 70.1% in the sterilized, unsterilized and inoculated refuse, respectively. DBP biodegradation in the refuse was fit to the first-order kinetic equation (1), where: C is the DBP concentration; K is the first-order kinetic constant; t is the time; A is the constant.

$$\ln C = -Kt + A \quad (1)$$

The kinetic equations are shown in Table 2. The half-life of DBP in the sterilized refuse was 5.9 times higher than that of unsterilized samples. In addition, the half-life of DBP was decreased by 35.8% when the dominant bacterial strains were added. These findings suggest that the effects of hydrolyzation and other chemical degradation on DBP were much lower than biodegradation, again demonstrating that biodegradation plays an important role in DBP decomposition in landfill refuse (Ejlertsson et al., 2003; Mersiowsky et al., 2001). The residual DBP in the refuse was determined based on the metabolic activities of the microbes in the refuse. In previous studies, more loss of DBP from a landfill was observed in active methanogenic environments than in acidic environments (Ejlertsson et al., 2003; Fang et al., 2009b; Jonsson et al., 2003; Mersiowsky et al., 2001), indicating that a methanogenic environment is beneficial to the growth of DBP dominant bacteria.

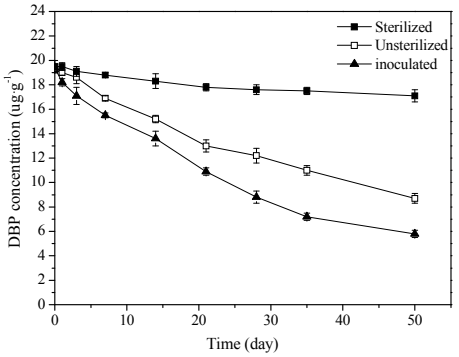

Fig. 1. Effects of microorganisms on degradation of DBP in refuse

3.2. Effects of concentrations of DBP, moisture, pH of refuse and temperature

Variations in the concentration of DBP in the refuse with different initial concentrations, moistures, pH and temperatures are shown in Fig. 2. Plots of the decline of DBP in the refuse all followed the first-order kinetic model (Table 3). The removal rate of DBP was 58.0%, 57.9%, 54.7% and 55.8% in the refuse when the DBP initial concentrations were 5, 10, 20 and 30 μg g^{-1}, respectively. In addition, the half-life periods of DBP in the refuse did not differ significantly among groups, with values of 42.3 d, 42.5 d, 43.3 d and 44.1 d being observed, respectively. The acute toxicity of DBP was not serious (Piersma et al., 2000), and the DBP concentration was relatively low; therefore, the inhibitory effects of DBP on microorganisms in the refuse were weak. Overall, these findings clearly demonstrate that different concentrations of DBP had no effects on its degradation ($p<0.05$).

The removal rate of DBP was influenced by the refuse moisture. The removal rate of DBP was highest in refuse with 80% moisture, while it was lowest in refuse with 20% moisture (Fig. 2b).

Table 2. Degradation kinetic parameters of DBP in sterilized, unsterilized and inoculated refuse

Refuse	*Kinetic equations*	*K (d^{-1})*	*R^2*	*$t_{1/2}$ (d)*
Sterilized	ln C = -0.0027t+2.96	0.0027a*	0.9218	256.7
Unsterilized	ln C = -0.0160t+2.95	0.0160b	0.9946	43.3
Inoculated	ln C = -0.0249t+2.92	0.0249c	0.9878	27.8

**Parameters followed by different letters (a, b, c) in the same column differ significantly at $p<0.05$.*

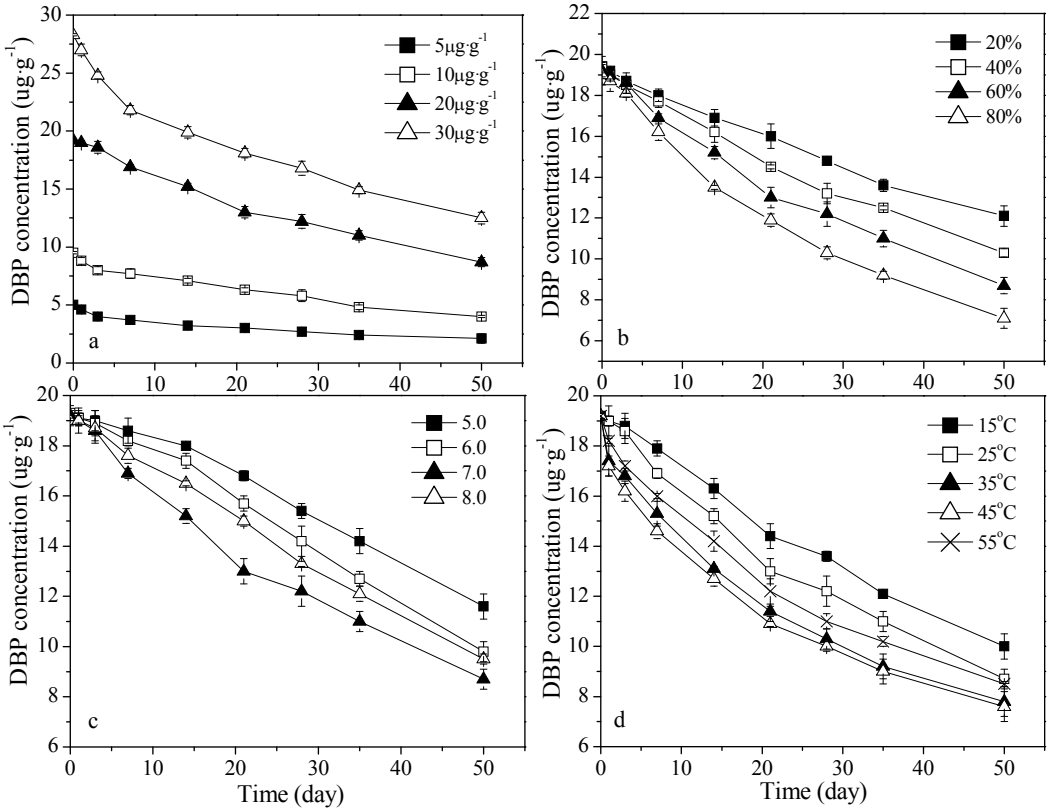

Fig. 2. Effects of DBP concentration, moisture, pH and temperature on degradation of DBP in refuse
(a) DBP concentration; (b) Moisture; (c) pH; (d) Temperature

Table 3. Degradation kinetic parameters of DBP in refuse at different DBP concentrations, moistures, pH and temperatures

DBP concentration (μg/g)	***Kinetic equations***	***K (d^{-1})***	***R^2***	***$t_{1/2}$ (d)***
5	ln C = -0.0164t+1.48	0.0164a	0.9372	42.3
10	ln C = -0.0163t+2.18	0.0163a	0.9820	42.5
20	ln C = -0.0160t+2.95	0.0160a	0.9946	43.3
30	ln C = -0.0157t+3.26	0.0157a	0.9666	44.1
Refuse moisture (%)	***Kinetic equations***	***K (d^{-1})***	***R^2***	***$t_{1/2}$ (d)***
20	ln C = -0.0095t+2.96	0.0095a	0.9974	73.0
40	ln C = -0.0127t+2.96	0.0127b	0.9971	54.6
60	ln C = -0.0160t+2.95	0.0160c	0.9946	43.3
80	ln C = -0.0202t+2.93	0.0202d	0.9931	34.3
Refuse pH	***Kinetic equations***	***K (d^{-1})***	***R^2***	***$t_{1/2}$ (d)***
5.0	ln C = -0.0098t+2.99	0.0098a	0.9666	70.7
6.0	ln C = -0.0132t+2.99	0.0132b	0.9776	52.5
7.0	ln C = -0.0160t+2.95	0.0160c	0.9946	43.3
8.0	ln C = -0.0138t+2.97	0.0138b	0.9931	50.2
Temperature (°C)	***Kinetic equations***	***K (d^{-1})***	***R^2***	***$t_{1/2}$ (d)***
15	ln C = -0.0133t+2.96	0.0133a	0.9971	52.1
25	ln C = -0.0160t+2.95	0.0160b	0.9946	43.3
35	ln C = -0.0178t+2.87	0.0178c	0.9724	38.9
45	ln C = -0.0179t+2.84	0.0179c	0.9610	38.7
55	ln C = -0.0163t+2.90	0.0163b	0.9812	42.5

**Parameters followed by different letters (a, b, c, d) in the same condition differ significantly at $p<0.05$*

The half-lives of DBP were decreased by 53.0%, 37.2% and 20.8% when the refuse moisture increased from 20%, 40% and 60% to 80%, respectively. These results indicate that appropriate refuse moisture was beneficial to the growth and reproduction of microorganisms. In addition, moisture can change the porosity, oxidation-reduction potential of refuse and adsorption effect between the DBP and the refuse (Ingerslev et al., 2001), which will ultimately influence DBP degradation.

Leachate recirculation landfill bioreactors are superior to conventional landfills and provide an advantage for the transformation of organic materials (Calli et al., 2006; He et al., 2007) owing to their effects on microbial populations, as well as the increased refuse moisture in response to circulation of the leachate.

The removal rate of DBP was 39.6%, 49.2%, 54.7% and 50.1% when the refuse pH was 5.0, 6.0, 7.0 and 8.0, respectively. The shortest degradation half-life of DBP was achieved (43.3d) at pH 7.0 (Table 3). The removal rate of DBP decreased significantly when the pH was <7.0 ($p<0.05$). Specifically, the half-life of DBP was increased by 63.3% when the refuse pH decreased from 7.0 to 5.0. This may have been because of the low pH of refuse, which influenced bacterial growth (Fan et al., 2004; Fang et al., 2010). Therefore, the pH of refuse may be an important factor influencing DBP biodegradation. Within the specific limits of the present study, a neutral pH was beneficial for DBP degradation, confirming that the loss of DBP from the landfill would be much higher in an active methanogenic environment than an acidic environment (Ejlertsson et al., 2003; Fang et al., 2009b; Jonsson et al., 2003; Mersiowsky et al., 2001).

The degradation rate constants for DBP loss from the refuse at 15°C, 25°C and 35°C were 0.0133, 0.0160 and 0.0178 d^{-1}, respectively. Accordingly, the half-lives of DBP were 52.1 d, 43.3 d and 38.9 d, respectively (Table 3). Although there was no significant difference in the degradation rates of DBP when the temperature increased from 35°C to 45°C ($p<0.05$), the rate decreased significantly when the temperature increased to 55°C ($p<0.05$). The removal rate of DBP was 59.4%, 60.4% and 55.7% in refuse at 35°C, 45°C and 55°C, respectively. Temperatures between 25°C and 35°C are most suitable for microbial growth (Kurola et al., 2007), and the degradation rate of DBP increased obviously when the temperature increased from 15°C to 35°C ($p<0.05$). Overall, these findings suggested that the optimal temperature for DBP degradation in refuse was around 30°C considering degradation and the energy cost.

3.3. Adsorption behavior of DBP by refuse

DBP is a hydrophobic organic compound with an octanol-water partition coefficient $\lg K_{ow}$ of 4.45 (Cui et al., 2010). Many studies have shown that nonlinear adsorption exists in hydrophobic organic matter (Liu et al., 2011; Pan et al., 2006; Xing and Pingnatello, 1997); therefore, the Freundlich model was used to describe quantitative DBP adsorption and desorption in refuse according to Eq. (2), where: Q_e is the equilibrium adsorption capacity of DBP on refuse (μg kg^{-1}); c_e is the equilibrium concentration of DBP in the liquid phase (μg L^{-1}); K_f is the Freundlich adsorption coefficient ([μg kg^{-1}]/[μg L^{-1}]^n) in the desorption formula, instead of $K_{f,des}$; n is the nonlinear exponent, expressed as n_{ads} and n_{des} in the adsorption and desorption models, respectively.

$$Q_e = K_f c_e^n \quad (2)$$

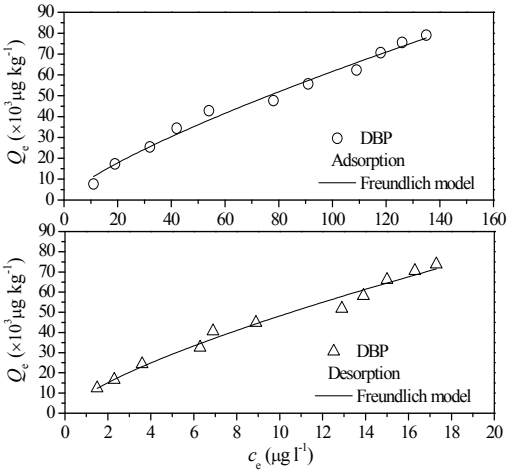

Fig. 3. Results of Freundlich model fits to adsorption and desorption isotherms of DBP on refuse

Table 4. Parameters of Freundlich model of adsorption, free energy change, and desorption isotherms of DBP

Adsorption	r^2	n_{ads}	K_f	
	0.9861	0.772	1.76×10^3	
Free energy change	K_f	K_{oc}	ΔG	
	1.76×10^3	1.31×10^4	-23.5 (kJ mol^{-1})	
Desorption	r^2	n_{des}	$K_{f,des}$	H^*
	0.9811	0.720	9.17×10^3	0.933

*H: hysteresis exponent

As shown in Fig. 3, the Freundlich model fits the adsorption isotherm of DBP on refuse. The fitting parameters of the Freundlich model to the adsorption isotherm of DBP are listed in Table 4. The n_{ads} of DBP adsorption on refuse in the Freundlich model was significantly less than 1, indicating that the adsorption isotherm of DBP has nonlinear characteristics. As refuse contains different organic components with various structures and properties and the adsorption point of organics is not uniform, several mechanisms may exist during adsorption. The nonlinear characteristic adsorption isotherm of DBP was attributed to the organic matter heterogeneity, which has been confirmed as the most important factor in nonlinear adsorption (Jiang et al., 2012).

The maximum removal efficiency of DBP by refuse was a little lower than that reported in most previous studies (Table 5). This difference may have occurred due to differences in the adsorbent type and condition of the experimental operation in each study.

To investigate the adsorption mechanism of DBP by the refuse, the free energy change ΔG for adsorption was calculated using Eqs. (3-4) (Ozgul, 2015):

$$\Delta G = -RT \ln K_{oc} \quad (3)$$

$$K_{oc} = K_f / f_{oc} \times 100 \quad (4)$$

Table 5. Comparison of adsorption behavior of DBP in literature

Constituents								*References*
Wastewater type	***Adsorbent (dosage)***	***Initial DBP concentration***	***Reaction pH***	***Operating temperature***	***Sample volume***	***Contact time***	***Maximum removal efficiency***	
Seawater	Montmorillonite (687 mg)	3930 μgL^{-1}	8.1	30°C	10 mL	12 h	11%	Sullivan et al. (1982)
Seawater	Sediment (0.05 g)	3~12 mgL^{-1}	7.5	25°C	100 mL	4 h	71%	Xu et al. (2008)
Purified water	Sediment (1.0 g)	150~500 mgL^{-1}	7.0	30°C	20 mL	24 h	98%	Guo et al. (2009)
Purified water	Soil (2 g)	400~6000 μgL^{-1}	7.0	20°C	50 mL	10 h	77%	Li et al. (2006)
Purified water	Refuse (0.5 g)	40~400 μgL^{-1}	7.0	25°C	150 mL	24 h	66%	This study

where: T is the solution temperature (K); R is the gas constant (8.314×10^{-3} kJ $mol^{-1}K^{-1}$); K_{oc} is the carbon normalized partition coefficient; K_f is the Freundlich adsorption coefficient ([μg kg^{-1}]/[μg l^{-1}]^n); f_{oc} is the organic carbon fraction of the refuse (%).

As shown in Table 4, the negative value of ΔG indicates that the adsorption of DBP on refuse is spontaneous. In addition, the ΔG value was less than 40 kJ mol^{-1}, indicating that the adsorption of DBP on refuse was a physical reaction (McCall et al., 1980).

3.4. Desorption hysteresis

The adsorption of organic matter often exhibits hysteresis because of its irreversible adsorption on the adsorbent. Several indicators are used for the characterization of adsorption hysteresis (Jiang et al., 2012). The hysteresis exponent (H), which was used in this study, was determined using Eq. (5), where: n_{ads} and n_{des} are the fitting parameters of the Freundlich model for the adsorption and desorption isotherms, respectively.

$$H = n_{des} / n_{ads} \tag{5}$$

The fitting parameters of the Freundlich model to the desorption isotherm of DBP and the hysteresis exponent are listed in Table 4. The Freundlich model can be used to fit the desorption isotherm of DBP on refuse. The $K_{f,des}$ value of DBP from the desorption isotherm was higher than the K_f from the adsorption isotherm, while the nonlinear exponent n_{des} from the desorption process was lower than the n_{ads} from the adsorption process. The hysteresis exponent H of DBP was less than 1, indicating that desorption hysteresis exists in the desorption process.

The desorption hysteresis of the DBP may be attributed to the properties of the refuse. Organic matter content, specific surface area, adsorption points for DBP and bonding strength are key factors contributing to desorption hysteresis in refuse. Pore deformation is also believed to contribute to irreversible desorption (Li et al., 2013). In the desorption process, pore deformation of the refuse formed part of a confined space to fix DBP into deeper pores. This irreversible process prevents the adsorbate from being desorbed completely, causing desorption hysteresis. As a result, large amounts of DBP can be adsorbed for long periods of time by the refuse because of the desorption hysteresis. Therefore, the transformation and bio-availability of this hydrophobic organic compound may be limited in landfill conditions, resulting in accumulation of DBP.

4. Conclusions

Biodegradation plays an important role in DBP decomposition in refuse. The removal of DBP was greatly enhanced in response to the addition of bacterial strains; however, its degradation did not appear to be influenced by its initial concentrations. The half-lives of DBP decreased when the refuse moisture increased.

The optimal pH and temperature for DBP degradation in the refuse were 7.0 and 30°C. The Freundlich model fits the adsorption and desorption isotherm of DBP, and desorption hysteresis occurred in the DBP desorption experiments. Taken together, the results of this study indicate that DBP may be a potential environmental risk in landfills.

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