Solar photo-catalytic degradation of endocrine disruptor di-n-butyl phthalate in aqueous solution using zinc oxide

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Abstract

The photocatalytic degradation of endocrine disruptor dibutyl phthalate in aqueous solution with zinc oxide was investigated under sunlight illumination. The influence of various degradation parameters, such as photocatalyst loading, initial pH, and solar illumination time, on the photocatalytic degradation was evaluated. It was found that the primary photocatalytic decomposition reaction followed a pseudo first-order kinetic law according to the Langmuir–Hinshelwood model. During the photocatalytic degradation, the first-order rate constant k_{obs} was 0.182 min^{-1}. From the comparison of photocatalytic degradation with zinc oxide and titanium dioxide, the ZnO photocatalyst was preferable to TiO$_2$ for the solar photocatalytic degradation of dibutyl phthalate. The solar photocatalytic degradation treatment is simple, easy handling and cheap. Therefore, since the artificial lamp devices, for example Hg-Xe lamp, are particularly expensive in the local and poor areas, the proposed technique appears to become a very powerful method for the treatment of wastewater including dibutyl phthalate in those areas.

Keyword: Sunlight; Photocatalytic degradation; di-*n*-butyl-ortho-phthalate; ZnO semiconductor; Endocrine disruptor

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Introduction

Phthalic acid esters (PAEs, esters of 1,2-benzenedicarboxylic acid, phthalates) are used in virtually every major product category including construction, automotive, household products, package, and medicine products. They represent a large family of chemicals, which are widely used as plastisizers primarily in the production of polyvinyl chloride (PVC)

resins. Plasticizers are used predominantly in building materials, home furnishings, transportation, clothing, and to a limited extent in food and medical product packaging [1]. However, in order to provide the required flexibility, the phthalate is not bounded covalently to the resin and is able to migrate into the environment [2,3]. PAEs have been reported to be etiological agents in several human diseases, including disorders of the male reproductive tract, breast and testicular cancers, disruptors of the neuroendocrine system, and skeletal effects [4,5]. Therefore, several regulatory bodies, such as, the European Union [6] and the US Environmental Protection Agency (US EPA) [7] classified phthalate esters as a top priority pollutant for risk assessment, mandating the reduction and control of phthalate pollution.

Numerous studies have proposed the biodegradability of several PAEs from soil [8-10]. However, because PAEs are becoming a class of concerning water pollutants and are still accumulating in the environment though they can be biological degraded within 1–100 days [11], there is a strong need to look for alternative and faster treatment processes for

PAEs. Recently, some researchers [12-16] have reported the photocatalytic degradation of PAEs in a TiO_2 aqueous suspension using an artificial light source such as a Hg-Xe lamp. The artificial lamp device is particularly expensive in the local and poor areas. Thus far, little information on the solar photocatalytic degradation of PAEs has been presented.

Although TiO_2 in the anatase form has been used for many environmental applications, ZnO is a suitable alternative to TiO_2 so far as band gap energy is concerned. The greatest advantage of ZnO is that it absorbs large fraction of the solar spectrum than TiO_2. Sakthivel et al. [17] have reported the light absorption characteristics of both ZnO and TiO_2 with UV-Vis diffuse reflectance spectrophotometer. In the study, it was observed the absorption of light by ZnO in the visible region is more compared to TiO_2. Consequently, they have concluded that ZnO is more active than other photocatalysts when sunlight is used as energy sources.

This work deals mainly with the solar photocatalytic degradation of dibutyl phthalate (DBP) in aqueous solutions with zinc oxide.
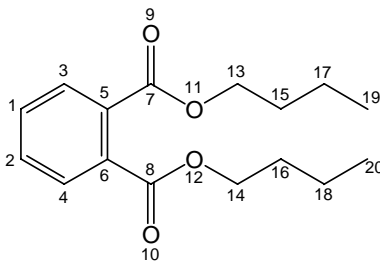
di-*n*-butyl-ortho-phthalate (DBP)

2. Experimental

DBP (di-*n*-butyl-ortho-phthalate, *o*-C₆H₄-[COO(CH₂)₃CH₃]₂,CAS#84-74-2) used in this study was purchased from Nacalai Tesque, Inc., Kyoto, Japan (GC grade >98%). DBP aqueous solutions were prepared with ultra-pure water, which was purified by an ultrapure water system (Advantec MFS, Inc., Tokyo, Japan) resulting in a resistivity > 18 MΩ cm. It has been reported in the previous work [2] that the solubility of DBP in water is 11.2 μg/mL.

Since the DBP 5 μg/mL (18 μM) concentration was selected as the initial sample concentration, the sample solution was a single phase. A 100 mL aqueous solution containing DBP was put into a Pyrex reaction vessel (200 mL capacity) ZnO powder (purity 99.9%, diameter < 5 μm, specific surface area 9.2 m²/g, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was added to the solution to produce a given concentration of their suspensions. The temperature was kept constant with a water bath. The detailed experimental conditions were shown in Table 1.

The ZnO suspension containing DBP was irradiated under sunlight illumination. In this case, the short ultraviolet radiation (λ<300 nm) was filtered out by the vessel wall. The intensity of light was measured by a UV radio meter with a sensor of 320 to 410 nm wavelengths (UVR-400, Iuchi Co., Osaka, Japan). The variations of sunlight intensity for 30 min were less than 10 %.

After the illumination, ZnO powder was separated through the 0.45 μm Advantec membrane filter. The amount of DBP in the aqueous solution was measured using a high-performance liquid chromatograph (HPLC, JASCO Co., Tokyo, Japan), equipped with a JASCO UVIDEC-100-VI optical detector and a Chromspher 5 Poly C18 column (Chrompack, VARIAN Inc., California, USA). The elution was monitored at 276 nm. The eluent used was a mixed solvent of acetonitrile and water (1/1, v/v). The flow rate of the mobile phase was 1.5 mL/min. The degradation efficiency of DBP was calculated with the following equation.

$$\text{Degradation efficiency}\,(\%) \;=\; \frac{100\times(q_0-q_1-q_2)}{q_0-q_1}, \qquad (1)$$

where q_0, q_1 and q_2 were the initial amount of DBP, the amount adsorbed onto the catalyst at equilibrium and the residual amount undegraded after the treatment, respectively. The reproducibility of the degradation (relative standard deviation, RSD, for the degradation efficiency of DBP) was

better than RSD 15% for more than three repeated measurements.

3. Results and discussion

Nakai et al. [18] has studied the conformation of dialkyl phthalate. Judging from ^{1}H-NMR measurements, dibutyl phthalate was found to be in a C2 symmetry conformation, in which two ester-alkyl chains are not distinguished spectrometrically from each other. The chemical shift of the methyl and methylene groups of alkyl chains emerged at the ordinary regions in ^{1}H-NMR spectra, demonstrating that the methylene chains are extended straightforwardly. This conformation was supported by ab initio molecular orbital (MO) calculations to estimate the most energetically stable conformation of di-*n*-alkyl phthalates. In the proposed conformation, two alkyl groups linked by the ester bond to the adjacent carboxyl groups are extending to the different directions, which are deviated from the benzene plane to the upward and downward, respectively.

3.1 Effect of photocatalyst loading

It is very interesting to determine the minimum amount of catalyst required to degradation of DBP at an expmental condition. Therefore, in order to optimize the ZnO suspension concentration, the effect of photo-catalyst loading on the degradation of DBP in aqueous solution was investigated. The results are illustrated in Fig. 1. With increasing the catalyst amounts up to 30 mg, the degradation efficiency increased, and then the efficiency was nearly flat. The increase in the amount of photocatalyst increased the total surface area, namely number of active sites, available for the photocatalytic reaction as the dosage of photocatalyst increased. This indicates the increase in the number of hydroxyl and superoxide radicals. However, the suspension concentration of ZnO catalyst increased above the limiting value, the number of active sites on the ZnO surface may become almost constant because of the decreased light penetration, the increased light scattering and the loss in surface area occasioned by agglo-meration (particle-particles inter-actions) at high solid concentration [19]. When a blank experiment without ZnO photocatalyst was performed until 3 illumination hours, the degradation efficiency for DBP was of $r_f = 1.7\%$. Therefore, it could be concluded that the degradations was attributed to the photocatalytic reaction, not to thermal one. As a consequence, 30 mg of ZnO was chosen as the optimal amounts of photocatalyst for the sequential experiment.The ZnO amounts corresponded the suspension concentration of 0.3 mg/mL (3.7

μmol/mL).
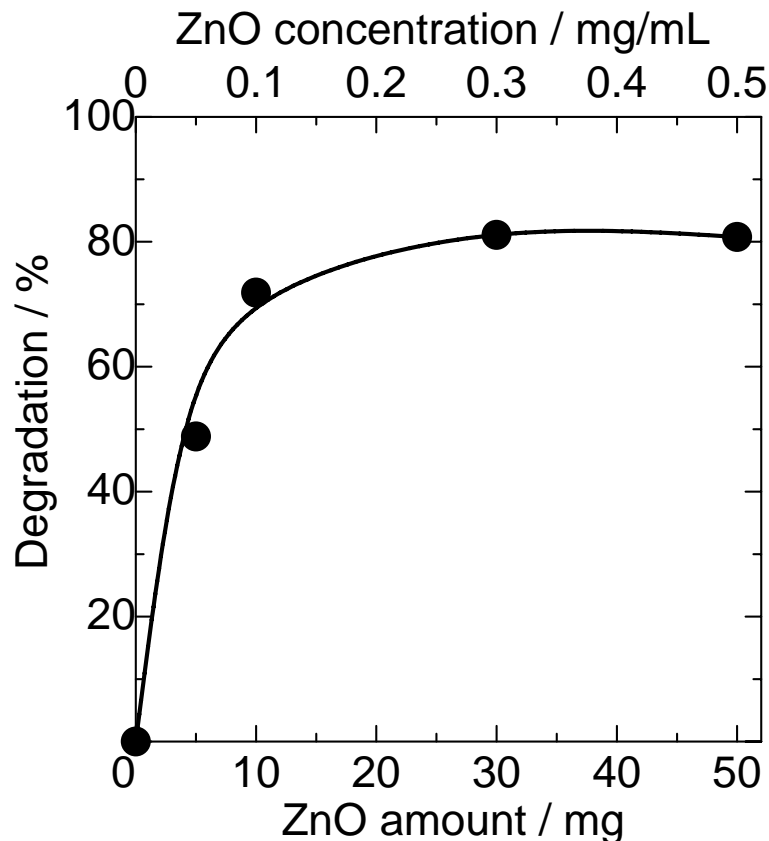

Figure 1:   Effect of ZnO amount on the solar photocatalytic degradation of DBP in aqueous solution.   [DBP   5 μg/mL; Illumination time :10 min;   Light intensity : 1.1 mW/cm^2;   Temperature: 20 ^{o}C: pH: 6]

3.2 *Effect of initial pH*

Owing to the amphoteric behavior of most semiconductor oxides, a significant parameter governing the reaction rate taking place on semiconductor particle surfaces is the pH of the dispersions, because it affects the surface-charge-properties of the photocatalysts.   Therefore, the role of initial pH on the degradation efficiency for DBP was investigated in the pH range 4 to 10, as illustrated in Fig. 2.   The degradation efficiency curve was convex, and the maximum (r_f = 81%) was observed at pH 6.   The treated aqueous solution was a transparent color after the removal of ZnO through the membrane filter. The zero point charge (zpc) pH_{zpc} of ZnO particles is around 9 [17].   ZnO

surface is positively charged in acidic media (pH<9) whereas it is negatively charged under alkaline condition (pH>9). Generally, the pH changes can have a non-insignificant result not only on the mode of adsorption of the DBP substrate on ZnO surface, but also on the selectivity of the photodegradative reaction occurring on the particle surface since redox reactions are very sensitive to changes in the surface potential [20]. In the previous work [16], the calculation of molecular partial charge of DBP structure has been performed in MOPAC version 6.01 with a CAChe package (Fujitsu Co. Ltd.), in order to estimate the mode for the adsorption of DBP onto the ZnO surface. The most negative partial charge atoms in the DBP structure were the two carbonyl oxygen atoms (9O and 10O), with the next ones being two ether oxygen atoms (11O and 12O). Therefore, we conclude that in alkaline media (pH>9) the DBP substrate is likely adsorbed on the negatively charged particle surface through all positive hydrogen atoms in such a way that the DBP molecule lies relatively flat against the particle surface, and in

acidic condition (pH<9) on the positively one through the four negative oxygen atoms that the side-chain parts of DBP molecule are adsorbed onto the surface. On the other hand, at high initial pH, more hydroxide ions (OH^-) in the solution induced the generation of hydroxyl free radicals (HO•), which came from the photooxidation of OH^- by holes forming on the zinc oxide surface. In this study, the reasons for the pH effect on the degradation efficiency may be attributable to the complex relation between a number of factors, such as the extent and mode of adsorption of DBP on the ZnO surface and the number of hydroxyl and hydroperoxide radicals. It has been known that the photocorrosion of ZnO is complete at pH lower than 4 and at pH higher than 10 no photocorrosion takes place [21]. The dissolution of ZnO is due to a classical chemical process. Consequently, the neutral conditions (pH 6) were selected for the optimal experimental conditions, because of trade off between the photocorrosion of ZnO and the unnecessary of chemical treatment including neutralization process.
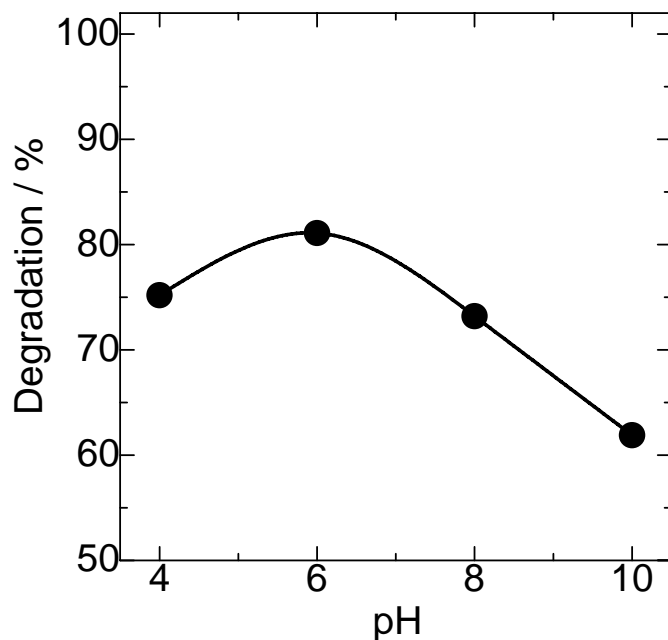
Figure 2: Effect of initial pH concentration on the solar photocatalytic degradation of DBP in aqueous solution using ZnO. [ZnO : 30 mg (0.3 mg/mL); DBP : 5 μg/mL; Illumination time: 10 min; Light intensity : 1.1 mW/cm^2; Temperature: 20 ^{o}C]

Table 1.   Experimental conditions.

DBP	5 μg/mL (100 mL)
ZnO	0 ~ 50 mg (0 ~ 500 μg/mL)
Temperature	20 ^{o}C
pH	4 ~ 10
Light source	Sunlight
Light intensity	1.1 mW/cm^2
Illumination time	0 ~ 30 min

3.3 Effect of illumination time

The effect of illumination time on the photocatalytic degradation of DBP in water with ZnO was investigated. The results are illustrated in Fig. 3. The photo-catalytic decomposition process proceeded rapidly until 10 min.   At 30 min illumination time, DBP disappeared and degraded in aqueous solutions.

The photo-catalytic degradation of various organic compounds by means of illuminated ZnO can be formally described by the Langmuir–Hinshelwood (L–H) kinetics model.
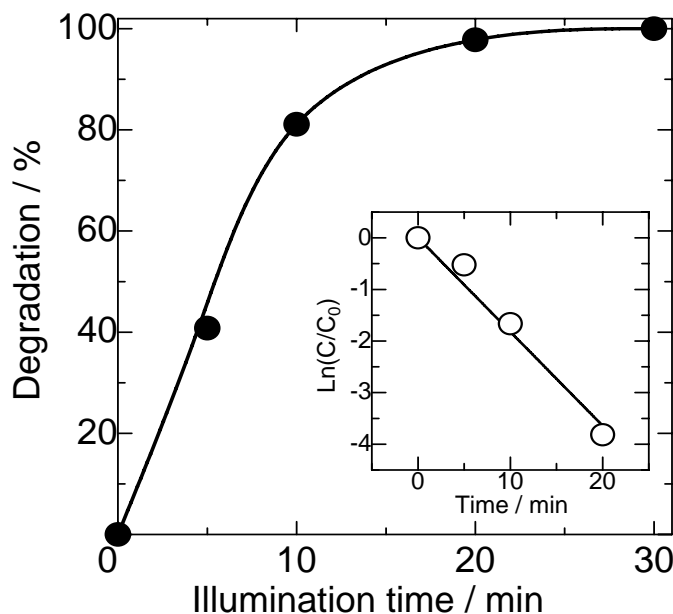
Figure 3: Effect of illumination time on the solar photocatalytic degradation of DBP in aqueous solution using ZnO. [ZnO : 30 mg (0.3 mg/mL; DBP : 5 μg/mL; Light intensity: 1.1 mW/cm^2 ; Temperature : 20 ^{o}C; pH   : 6; Insert figure : plot of –Ln(C/C$_0$) versus time.]

$$-\frac{dc}{dt} = \frac{kKC}{1+KC},$$ (2)

where dc/dt is the rate of degradation, k the reaction rate constant, K the adsorption coefficient of the substance to be degraded and C its concentration. In the case that the concentrations of the

substances to be degraded exceed the saturation coverage of the ZnO surface, Eq. (2) (i.e. KC >> 1) simplifies to a zero-order rate equation.

$$-\frac{dc}{dt} = k .$$ (3)

For very low concentrations (i.e. KC<< 1) the L–H equation simplifies to a pseudo-first-order kinetic law (Eq. (4))

where k_{obs} is being the apparent pseudo first-order rate constant.

$$-\frac{dc}{dt} = kKt = k_{obs}t \qquad \text{or} \qquad C_t = C_0 e^{-k_{obs}t}$$ (4)

The primary degradation reaction is estimated to follow a pseudo-first-order kinetic law, according to the Eq. (4). In order to confirm the speculation,

–Ln(C/C$_0$) was plotted as a function of illumination time (the insert figure in Fig. 3).   Since the linear plots were observed in the insert figure as expected,

the kinetics of DBP in the ZnO suspension solution followed the first-order degradation curve which was consistent to the L–H model resulting from the low coverage in the experimental concentration range (5 µg/mL). The degradation parameters such as pseudo first-order rate constant, correlation coefficient, and substrate half-live are shown in Table 2. In order to compare the photocatalytic degradation power of ZnO with TiO_2, some experimental data for TiO_2 are added in Table 2. From the data in Table 2, the kinetics of disappearance of DBP was faster with ZnO than with TiO_2. Lizama et al. have described that ZnO showed greater degradation activity than TiO_2 in the optimized photo -degradation of reactive blue 19 with a commercial lamp [23]. According to Kormann et al. [24], one possible explanation for the high photocatalytic activity of ZnO could be the higher production of hydrogen peroxide production on the catalyst surface compared with TiO_2 when illuminated. Sakthivel et al. [17] have presented the comparison of photocatalytic activity of different semiconducting materials, which has clearly indicated that ZnO is the most active photocatalyst in the degradation of acid brown 14 using sunlight as an energy source. The main reason for this greater activity of ZnO is that it absorbs large fraction of the solar spectrum. In addition, the UV-Vis absorption spectra show that ZnO absorbs more quantum of light. Hence, it is evident that considerable amount of visible light could be utilized when ZnO is used as catalyst. Therefore, it may be concluded that for solar applications ZnO will be the best catalyst for the pollutants degradation.

Table 2. Photocatalytic degradation parameters for DBP.

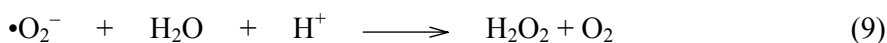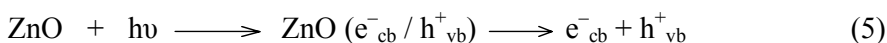|	k_{obs} (min^{-1})	R^2	$t_{1/2}$ (min^{-1})
ZnO	0.182	0.986	3.8
TiO_2[a]	0.126	0.999	5.5

[a] Ref. [22]. The optimized degradation conditions were as follows: concentration of DBP; 5 µg/mL, sample volume; 100 mL, TiO_2 amount; 5 mg (50 µg/mL), temperature 20 °C, pH 6.2, sunlight intensity 1.3 mW/cm^2. TiO_2 powders (anatase, purity 99.9%, diameter 230 nm, surface area 8.7 m^2/g) were purchased from Nacalai Tesque, Inc., Kyoto, Japan, whose photocatalytic activities were almost similar to those of TiO_2 P25.
k_{obs} : pseudo-first-order rate constant.: R^2 : correlation coefficient; $t_{1/2}$: substrate half-live.

3.4 Photodegradation mechanism

A general ZnO photocatalytic mechanism is proposed as follows [25]: Under the irradiation of energy greater than the band gap, valence band electrons are promoted to the conduction band leaving a hole behind (Eq. (5)). These electron (e^-_{cb}) – hole (h^+_{vb}) pairs can either recombine (Eq. (6)) or interact separately with other molecules. The holes at the ZnO valence band can oxidize adsorbed water or hydroxide ions to produce •OH radicals (Eq. (7)). Electron in the conduction band on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. (8)). This radical may form hydrogen peroxide or hydroperoxy radical •OOH (Eqs. (9) and (10)). The hydroxyl radical is a powerful oxidizing agent and attacks to DBP, and intermediate products are formed. These intermediates react with more hydroxyl radicals to produce final products CO_2 and H_2O (Eq. (11)).

$$ZnO + h\upsilon \longrightarrow ZnO \, (e^-_{cb} / h^+_{vb}) \longrightarrow e^-_{cb} + h^+_{vb} \qquad (5)$$

$$e^-_{cb} + h^+_{vb} \longrightarrow heat \qquad (6)$$

$$h^+_{vb} + OH^- \, (or \, H_2O)_{ads} \longrightarrow •OH \, (+ H^+) \qquad (7)$$

$$e^-_{cb} + O_2 \longrightarrow •O_2^- \qquad (8)$$

$$•O_2^- + H_2O + H^+ \longrightarrow H_2O_2 + O_2 \qquad (9)$$

$$•O_2^- + H^+ \longrightarrow •OOH \qquad (10)$$

$$•OH \, (or \, •OOH) + DBP \longrightarrow \longrightarrow Oxidative \, products \longrightarrow CO_2 + H_2O \qquad (11)$$

In the photocatalytic degradation of DBP in the aqueous TiO_2 suspension [16], six intermediate products could be identified by GC–MS analysis. In the degradation of DBP by homogeneous photocatalysis with Fe(III) in aqueous solution [26], seven intermediates were detected by HPLC/ES/MS and GC/MS, which could not be detected in the photocatalytic degradation with TiO_2. The photocatalytic degradation of DBP is, apparently, a very complex process whose mechanism is not yet fully clarified. It may be speculated from the literature reports [12-17, 18-26] that the solar photocatalytic degradation pathway of DBP in water with zinc oxide is roughly similar to that observed in the aqueous TiO_2 suspension.

4. Conclusion

The optimization of solar photcatalytic degradation conditions of DBP in water using zinc oxide was investigated. Although sunlight has only 5% of optimal energy for the

photocatalytic excitation and ultimately degradation of DBP [17], it could be safe and cost effective source. UV source is not only hazardous but also expensive because of large input of electric power to generate UV irradiation. In the tropical countries, intense sunlight is available throughout the years and, hence it could be effectively used for the photocatalytic degradation of pollutants in wastewater. In case of large surface demanding photocatalytic degradation, sunlight would be the ultimate source.

Moreover there is no material deterioration in case that sunlight is used as a radiation source. Therefore, the solar photocatalytic degradation technology with zinc oxide may become a promising method for the treatment of wastewater containing DBP.

Acknowledgment

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Figure 3