Degradation of Dibutyl Phthalate in Water by the Aid of Metals under γ-Ray Irradiation

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The degradation of dibutyl phthalate (DBP), one of endocrine disruptors, by γ-ray irradiation was enhanced by the effective energy conversion of γ-ray through the interaction with some kind of metal materials.

Some organic compounds called endocrine disruptors have been spread over the environment and they influence the generative function of some kinds of living things on the earth.[1] Although it is still under discussion whether such chemicals influence human being or not, they must be eliminated or degradated as early as possible.

Photocatalytic reactions over TiO_2 catalysts[2–7] have been reported as one of the powerful methods to degradate organic compounds, which is effective even for the endocrine disruptors[8] in water, because diluted organic pollutants can be decomposed without separation from water. However, the photocatalytic systems seem difficult to apply to practical waste water, when it is colored, turbid or containing a lot of impurities, and hence strongly reduces the efficiency of UV radiation.

γ-Ray irradiation has been reported to effectively degradate some organic pollutants in water.[9–13] This technique seems to be promising for the degradation of the endocrine disruptors, because the high transparency of γ-ray makes it possible to degradate turbid waste waters even in the vessel made of a metallic material.

In the present study, we first confirmed to use γ-ray for degradation of dibutyl phthalate (DBP), one of the endocrine disruptors, diluted in water, then tried to improve the efficiency by the addition of metal pieces in the system.

A 10-mL DBP aqueous solution of 17 mg/L (6.1×10^{-5} M) in a stoppered vessel (ca. 25 mL) made by stainless steel (SUS316) or Pyrex glass was irradiated by γ-ray from ^{60}Co source at Nagoya University at room temperature. After the γ-ray irradiation, the DBP concentration was evaluated by means of gas chromatography.

The concentration of DBP drastically decreased by γ-ray irradiation, whereas no change was observed without the irradiation. Even after a low dose irradiation of 750 Gy (150 Gy/min, for 5min), 97% of DBP disappeared in a stainless steel vessel, clearly indicating that the γ-ray irradiation is effective for the decomposition of DBP. No other by-products were confirmed by gas chromatography and no water-insoluble materials were observed in the vessel. Most possible is that the degradation of DBP and the mineralization to the small molecular like CO_2 proceeded by the γ-ray irradiation.

Then, we have tried to improve the efficiency by converting γ-rays to lower energy electrons and photons which are more effective for chemical reactions.[14] The γ-rays in solid first lose their energy by Compton effect, producing high energy electrons and photons. Subsequently, these high energy electrons and photons produce another one with lower energy, to be finally thermalized. Therefore, we employed metals in this system to convert the γ-rays to such low electrons and photons. The heavier the mass, the more the production should be.

To confirm this, the following experiments were carried out: six metal pieces (the size of one piece, $50 \times 10 \times 0.2$ mm) were put into 10-mL DBP solution of 17 mg/L (6.1×10^{-5} M) in a Pyrex glass vessel and irradiated by γ-ray. Conversion of DBP in the early stage of γ-ray irradiation (50 Gy ; 10 Gy/min, for 5min) in the presence of some kinds of metal pieces are summarized in Table 1. To elucidate the effect of the metals, the difference in conversion from the case for no metal pieces (i.e., only using Pyrex vessel) was evaluated, and the degradation efficiency was normalized by the number of metal atoms in the system. Obviously, the degradation of DBP was successfully enhanced by addition of metal pieces, simultaneously, this result would suggest that the stainless steel vessel mentioned above, also made some enhancement in the degradation of DBP.

Table 1. Degradation of DBP after 50 Gy γ-ray irradiation in a Pyrex vessel[a]

Metal piece	Conversion / %	Relative[b] conversion / %	Conversion per one[c] metal atom / 10^{-22} %
None[d]	11.4	—	—
Al	8.9	−2.5	—
SUS316[e]	25.1	13.7	2.6
Ni	18.8	7.4	1.3
Mo	56.3	44.9	11.0
W	56.3	44.9	12.8
Pb	23.1	11.7	6.2

[a]10 mL DBP solution of 17 mg/L(6.1×10^{-5} M) in a Pyrex vessel was irradiated by γ-ray with 10 Gy/min for 5 min. The estimated error of conversion is ± 5%. [b]The difference from the conversion in a Pyrex vessel containing no metal pieces. [c]Conversion per one metal atom = (Relative conversion) / (number of metal atoms included in 6 metal pieces, calculated from the size of metal pieces and atomic density). [d]Only a Pyrex vessel without metal pieces. [e]SUS316 : Cr 17%, Ni 12%, Mn 2%, Si 1.5%, Mo 2%, Fe 65.5%

Moreover, Table 1 clearly shows that the degradation rate of DBP in the solution with heavier metal such as Mo, W and Pb was higher than that with lighter one such as Al, SUS316 and Ni. Thus, the effective conversion from γ-ray to electrons and other radiations was confirmed and it really enhanced the degradation of DBP. On the other hand, after the 50 Gy irradiation, the dissolution of a metal into DBP solution was found only for Mo and W by UV–vis spectroscopy, which may be one of the reasons why the degradation rate of DBP in the solutions

with Mo and W is higher than that with Pb that is the heaviest metal in this experiment. The investigation in details is now in progress.

In conclusion, γ-ray irradiation was found to be available for the degradation of DBP in water, and the degradation was enhanced with the assistance of the interaction between γ-ray and metals. Especially high mass materials were more effective. The present results are promising to develop a new method for the degradation of organic pollutants such as endocrine disruptors in our environment.

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