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Water purification in a fluidized bed photocatalytic reactor using TiO_2-coated ceramic particles

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Abstract

TiO_2-coated mm-size spherical ceramic particles which are very stable for dynamical impact and whose specific density is very near to unity were developed and applied to a fluidized bed reactor for water purification. Two types of test-scale fluidized bed photocatalytic reactors were prepared: the reactor *a* which holds the ultra violet light source (254 nm) inside it and the reactor *b* which holds the light source (365 nm) outside it. The latter one is supposed to be operated under solar light. Phenol and bisphenol A were selected for target contaminants and the decomposition experiments by fluidized bed photocatalytic reactor were conducted. It was shown with the reactor *a* that aqueous phenol and bisphenol A with 10 mg/dm^3 in 2 L water can be decomposed rapidly in about 200 min and TOC originated from their byproducts can eventually be mineralized in short time in 300 min. It was also shown through the decomposition experiment using the reactor *b* that water purification under solar light can be possible, though the decomposability is less effective: it took about 20 h to mineralize the aqueous contaminants with10 mg/dm^3 in 1 L water.

Keywords: TiO_2 photocatalyst; Fluidized bed reactor; Water purification; Solar light

1. Introduction

The environmental technologies against atmospheric and aqueous contaminants exhausted from industries, vehicles, municipal utilities, household wastes, etc. have so far been successfully developed. The calcium-gypsum scrubber for deSOx, ammonia catalytic process for deNOx, and the biological process for wastewater treatment are representative illustrations of such technologies. In these days, however, it is reported that there are many known or unknown chemicals that would cause serious damage against human health even if their concentrations are extremely lower. Dioxine and related environmental endocrine disrupters, EED's, like nonylphenol, bisphenol A are typical representatives of such chemicals. To make it worse, these chemicals cannot be treated well by the conventional biological processes. It is therefore important to develop some physical or physicochemical processes for water purification. Photochemical processing is one of the candidates by which these chemicals can be safely and effectively decomposed.

In this decade, titanium dioxide, TiO_2, one of the semiconductors has aroused much interest of many chemical engineers who have engaged in catalyst and reactor engineering and/or in environmental and energy technologies for its striking photocatalytic functions [1]. Trial of its application to water purification was initiated by using the slurry reactor in which commercialized TiO_2 powder is suspended in contaminated water [2–4]. We previously developed TiO_2-catalyst film and applied to photocatalytic rotating-drum and tube reactors for water purification [5–7].

In this research, we newly fabricated the TiO_2-coated ceramic particles of about 0.7 mm diameter whose apparent density is very near to unity so that they can suspend very

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freely in water, and used them for photocatalyst carrier particles. Our challenges are to develop a fluidized bed photocatalytic reactor which is effective for water purification and to provide a technology for water purification using solar light, with least energy consumption. We conducted here decomposition experiments using two types of fluidized bed photocatalytic reactors, one is the reactor *a* with the light source (254 nm) inside it and the other one is the reactor *b* with the light source (365 nm) outside it as an imitated solar light. In decomposition experiments, phenol and bisphenol A were selected for target chemical compounds. It was shown that these hazardous chemicals are effectively mineralized by the fluidized bed reactor, particularly by the reactor of type *a*. It was also shown from the decomposition experiments using the reactor of type *b*, that water purification using solar light can possibly be put into practical use, though the decomposition performance is less than that of the reactor of type *a*.

2. Fabrication of TiO_2 carrier particles

The carrier particles were fabricated according to the process as shown in Fig. 1. Bentonite, nepheline, syenite were first mixed with micro ceramic balloons and granulated to about 1 mm spherical grains. The grains were dried at room temperature and calcined at 1300 °C to form spherical porous ceramic particles in diameter of about 0.7 mm. The particles were then coated with TiO_2 fine crystals by sol–gel treatment by a dip-coating method, and were dried and calcined again at 600 °C (temperature elevation rate = 50 °C/h, holding time at 600 °C = 5 h). The TiO_2 carrier particles developed here have several specific properties: (1) the carrier particles are spherical and about 0.7 mm in diameter so that they can be easily separated from the treated water; (2) the specific weight is very near to unity so that the carrier particles can suspend very freely in water and are very easy to be treated in water; (3) the carrier particles are very stable against dynamical damage since TiO_2 fine crystals are stuck strongly in the micro pores of the surface of the ceramic particles; and (4) the carrier particles are highly effective for photo catalyst, because TiO_2 fine crystals are immobilized at high density at the surface of the particles. Regarding the stability of the immobilized TiO_2, we did not obtain quantitative data for evaluation. Nevertheless, it was remarkable that the treated water was kept transparent during the fluidizing the TiO_2 carrier particles.

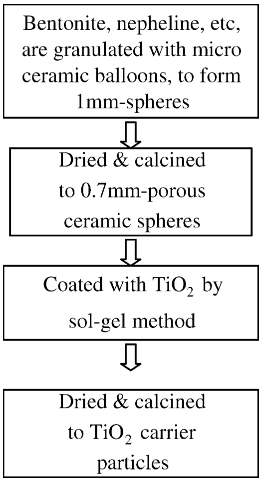


Fig. 1. Fabrication of TiO_2 carrier particles.

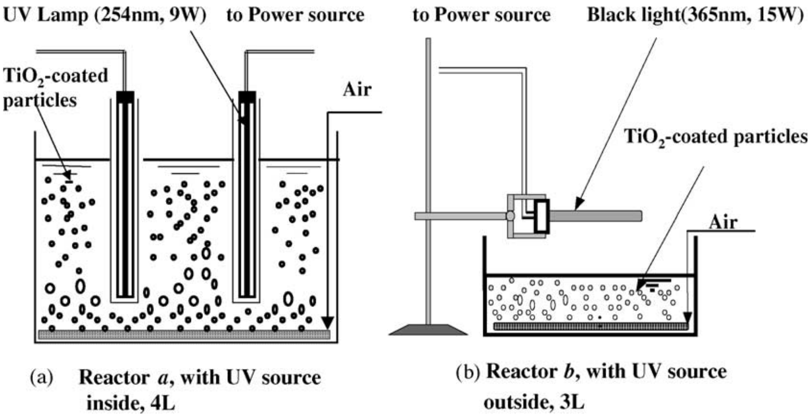
3. Experimental

We prepared two types of reactors. One is the reactor *a*, rectangular parallelepiped one with the volume of 4 dm^3 with the cross area of 10 cm × 20 cm and the height of 20 cm, in which two ultra violet lamps of 9 W with the wave length 254 nm are immersed vertically in the water phase as shown in Fig. 2a. The other one is the reactor *b*, which is also a rectangular parallel piped but with the volume of about 3 dm^3 with the cross area of 15 cm × 15 cm and the height of 10 cm. The reactor *b* was designed in image to be operated under solar light. The two black lights of 15 W with a wavelength 365 nm were placed horizontally over the surface of the water separated by a distance of about 8 cm, as shown in Fig. 2b. The intensity of light was adjusted to be 3 mW/cm^2 at the surface of the water. The TiO_2-coated particles were put into the both reactors at the volume fraction at 7–12%. Within this range, the higher fraction showed the faster degradation rate of bisphenol A by approximately 8%. The TiO_2-coated particles were fluidized uniformly just by aerating from the bottom of the respective reactor at the rate of 0.5 dm^3 (STP)/min. Both reactors were operated batch wise.

Phenol and bisphenol A were selected for target contaminant chemicals. The initial concentration of each chemical was adjusted at 10 mg/dm^3. The contaminated water was poured at 2 dm^3 in the reactor *a* and at 1 dm^3 in the reactor *b*. The concentrations of each source contaminant and its intermediate products were measured by HPLC (SPD-10Avvp, Shimazu Ltd., with columns: ODS-UG-5, Nomura Chem. Ltd. and RP18-GP, Kanto Chem. Ltd.) and the total carbons were measured by TOC analyzer (TOC-5000, Shimazu Ltd.) at adequate time intervals.

4. Results and discussion

Aqueous phenol and bisphenol A are known to be decomposed by illumination of UV light alone [8]. In order to check the reliability of this information, we conducted the decomposition experiments of aqueous phenol by illuminations of UV light (254 nm) and of black light (365 nm). In our pre-experiments, a 400 mL tall beaker was used for UV reactor, with the respective light source being immersed vertically in water. We found that phenol can be decomposed fairly rapidly just by illumination of UV light (254 nm) alone but



(a) Reactor *a*, with UV source inside, 4L

(b) Reactor *b*, with UV source outside, 3L

Fig. 2. Experimental apparatus, fluidized bed photocatalytic reactors.

could not be decomposed by illumination of UV (365 nm). The results are shown in Fig. 3. In addition, it was shown that TOCs originated from phenol and bisphenol A and from their byproducts can scarcely be decomposed even by illumination of UV (254 nm) as shown in Fig. 4. This supports the possibility that the TiO_2 photocatalyst plays a principal in the mineralization of aqueous phenol and bisphenol A, and their byproducts as described below.

In order to evaluate the photocatalytic effectiveness of the developed TiO_2 carrier particles, we conducted pre-experiment of decomposition of aqueous acetic acid using a beaker scale suspension reactor with the volume of 0.4 dm^3. Fig. 5 illustrates the comparison between decomposition rates when our TiO_2 carrier particles were used and when commercialized TiO_2 powder of anataze structure (TP-2, 7 nm averaged diameter, Fuji Titanium Co. Ltd.) was used. The decomposition rate when powder was used reaches a maximum around the suspension density at 500 mg/dm^3. Despite the fact that powder has an advantage of maintaining the largest contact area, the figure shows that the decomposition rate when the carrier particles were used is rather faster than that maximum rate when powder was used. This result is ascribed to the fact that the light can reach only to the region adjacent to the lamp in case of fine powders because the water becomes clouded in white with the powders. Thus, the decomposition performance of the reactor as well as the op-

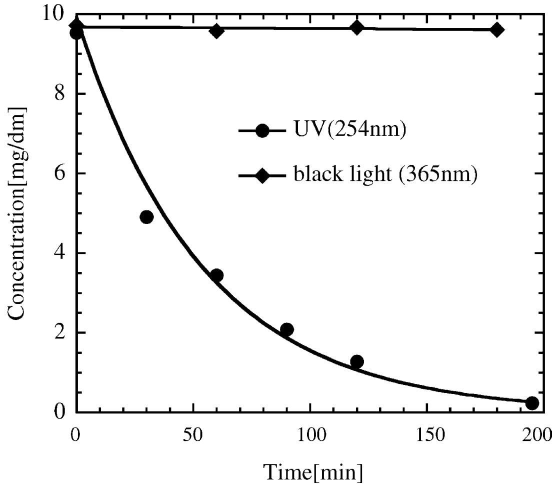


Fig. 3. Decomposition of phenol by UV illumination, UV (254 nm), black light (365 nm), 400 mL.

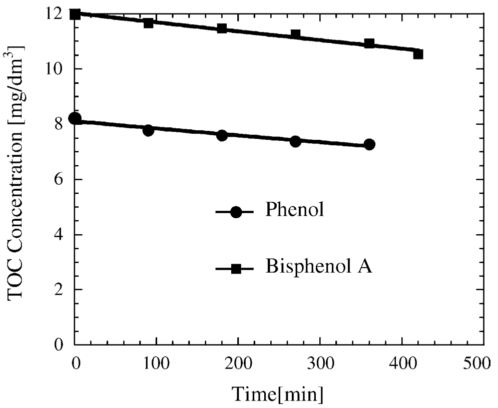


Fig. 4. Mineralization of phenol and bisphenol A by illumination of UV (254).

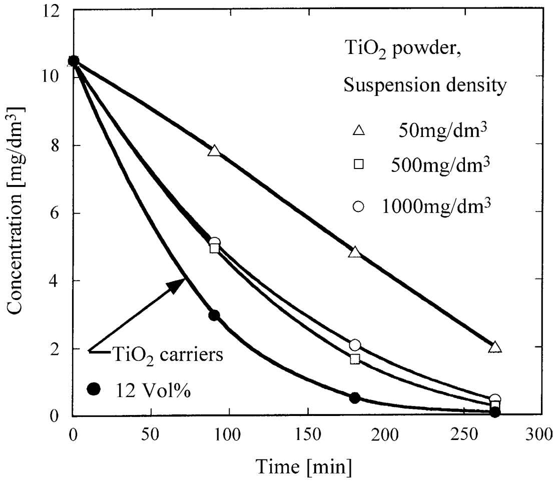


Fig. 5. Decomposition of aqueous acetic acid, comparison with decomposition rate when TiO_2 powder was used.

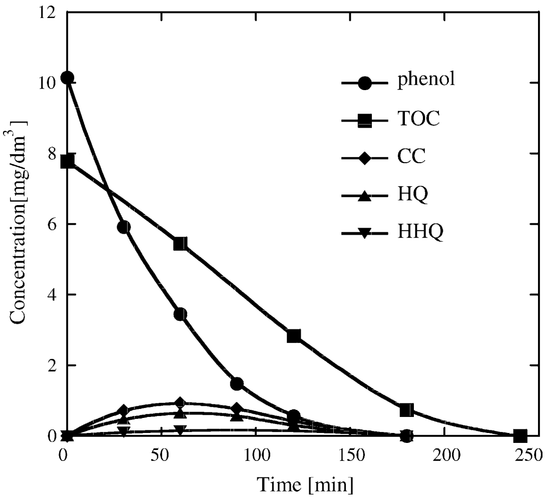


Fig. 6. Decomposition of phenol by reactor *a*, 2 dm^3, carriers: 7 vol.%, UV (254 nm, 2 × 9 W).

erational condition is much improved by using the developed TiO_2 carrier particles.

Fig. 6 shows the results of decomposition experiment of aqueous phenol by the fluidized bed reactor of type *a*, namely changes in phenol and TOC concentrations with operation time. In this experiment, the intermediate byproducts, catechol (CC), hydroquinone (HQ) and hydroxyhydroquinone (HHQ) were identified. The other peaks found on the HPLC chart were not identified, but are supposed to be organic acids like acetic acid. The figure shows that phenol (10 mg/dm^3 in 2 Lwater) can be decomposed relatively fast in about 150 min and be mineralized in about 250 min, with TOC concentration being reduced down to less than 0.1 mg/dm^3 by that time. The intermediate species CC and HQ both appear immediately after phenol starts to be decomposed and HHQ follows them a bit later. These byproducts would be further oxidized to organic acids and eventually be mineralized to carbon dioxide and water. Phenol is therefore, thought to be photochemically oxidized through the intermediate path as shown in Fig. 7. This is compatible with the report by Okamoto et al. [9].

Fig. 8 shows the experimental results when aqueous bisphenol A was treated by the reactor *a*. As seen in the figure, the concentration of bisphenol A (10 mg/dm^3 in 2 L water) decreases rapidly: more than 99% of it can be decomposed within about 200 m and TOC disappears in around 400 m.

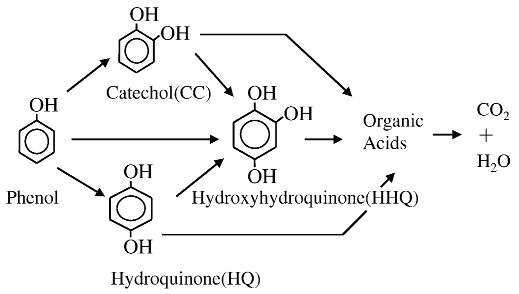


Fig. 7. Pathway for photochemical decomposition of phenol.

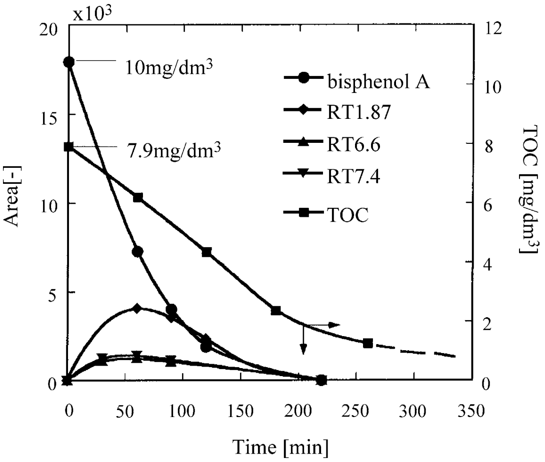


Fig. 8. Decomposition of bisphenol A by reactor *a*, 2 dm^3, carriers: 7 vol.%, UV (254 nm, 2 × 9 W).

Three peaks on HPLC chart were detected in process of decomposition of bisphenol A. According to LC–MS analysis, two species among them with the retention time designated as RT6.6, RT7.4 were found to be isomers and their mass was determined as $M = 244$ (ionized fragment mass (with OH being removed away) is $m/z = 227$). This indicates that these two species are 2,2-bis(4-hydroxyphenyl)-1-propanol and 1,2-bis(4-hydroxyphenyl)-2-propanol, respectively. These byproducts are identical with those that are generated in the pathway of bacteria metabolism of bisphenol A [10]. Their chemical forms and an assumed intermediate path are shown in Fig. 9. Unfortunately, we could not calibrate the areas of HPLC peak of these chemicals into the corresponding concentrations because of lack of their standard chemicals. Note that in Fig. 8 the concentrations of these byproducts are shown in the term of peak area in relative value. Nevertheless, in comparison with Fig. 6, we can say that the decomposition of bisphenol A should proceed in the similar

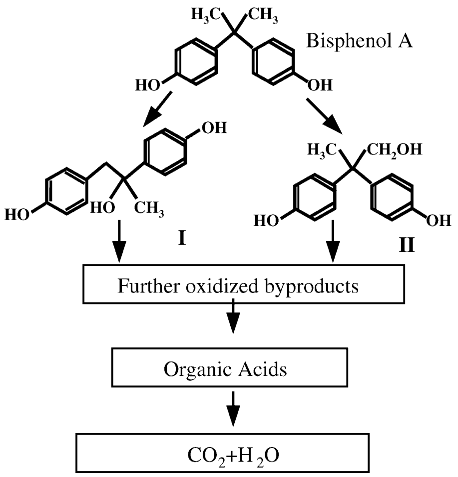


Fig. 9. Pathway of photochemical decomposition of bisphenol A, I: 1, 2-(bis(4-hydroxphenyl)-2-propanol, II: 2, 2-bis(4-hydroxyphenyl)-1-propanol.

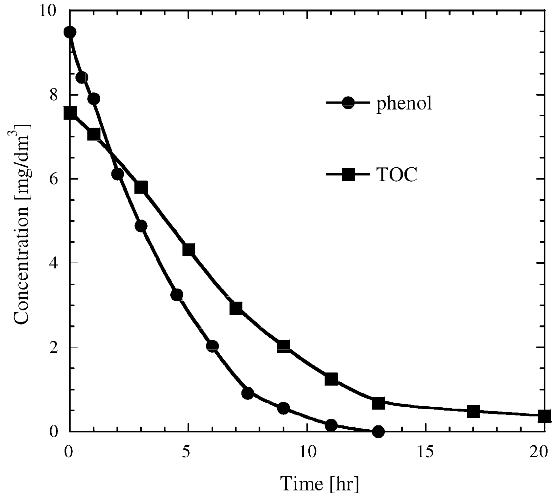


Fig. 10. Decomposition of phenol by reactor *b*, 1 dm^3, carrier: 8 vol.%, UV (365 nm, 2 × 15 W).

manner to that of phenol, thus that aqueous bisphenol A can effectively be treated by the fluidized bed photocatalytic reactor.

The results for decomposition experiments of phenol and bisphenol A by the reactor *b* using black light (365 nm) are shown in Figs. 10 and 11, respectively. As seen from these figures, both of phenol and bisphenol A (10 mg/dm^3 in 1 Lwater) can be decomposed in about 12 h and their TOCs can be reduced down to less than 1 mg/dm^3 in about 20 h. The black light (365 nm) is included in the tailing of shorter wavelength of the spectrum of solar light. This implies that these aqueous contaminants can be mineralized under solar light. Although it takes about 4 times as longer as the treating time by the reactor a, we can conclude that the water purification under solar light can be possible. Thus, some hazardous aqueous organic compounds such as phenol, bisphenol A and so on that cannot be biologically degraded, can possibly be mineralized under solar light using the fluidized bed photocatalytic reactor of type *b*.

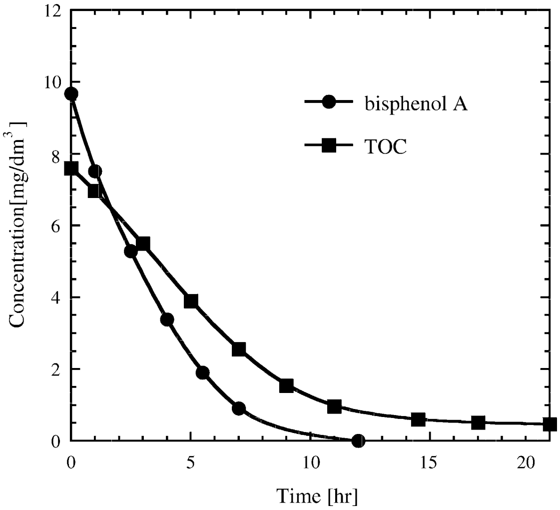


Fig. 11. Decomposition of bisphenol A by reactor *b*, 1 dm^3, carriers: 8 vol.%, UV (365 nm, 2 × 15 W).

5. Conclusion

TiO_2 carrier particles were newly fabricated and applied to fluidized bed photocatalytic reactors. Based on the experimental results and discussion above, we can make the following concluding remarks:

1. The decomposition performance, as well as the operational condition, is much improved by applying the developed carrier particles to a fluidized bed reactor for photocatalyst than using the commercialized TiO_2 powder. The fluidized bed photocatalytic reactor proposed here has the superiority in the points of operation and energy conservation.
2. Aqueous phenol and bisphenol A, can effectively be decomposed by the present reactor of type *a:* phenol (10 mg/dm^3 in 2 L) can be decomposed in about 150 min and be mineralized in about 250 min, and bisphenol A (10 mg/dm^3 in 2 L) can be decomposed in about 200 min and be mineralized in about 350 min.
3. In treatments of phenol and bisphenol A, several byproducts are generated in the individual processes of decomposition of them, but they can further be oxidized into organic acids, and eventually be mineralized into carbon dioxide and water. For the processes of decomposition of these chemicals, assumed intermediate pathways are proposed.
4. From the decomposition experiment of aqueous phenol and bisphenol A using the reactor of type *b* illuminated with black light outside, possibility of water purification under solar light was proved. In particular, the reactor *b* proposed here has the potentiality to be put into practical use and even to be widely commercialized.

Acknowledgements

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