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Photocatalytic and adsorptive treatment of 2, 4-dinitrophenol using a TiO_2 film covering activated carbon surface

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Abstract

Anatase titanium dioxide (TiO_2) in particle sizes of roughly 0.5-20 μm was prepared from amorphous TiO_2 in an aqueous H_2O_2 solution by heating at 90 °C for 9 h and directly deposited on a PET film. On the other hand, granular activated carbon (AC) particles in sizes of 1-2 mm in diameter were adhesively deposited on a PET film, and their surfaces were also coated with TiO_2. The resulting three preparations (TiO_2-, AC-, and TiO_2/AC-PET films) were set up in an annular-flow reactor to treat aqueous solutions of 2, 4-dinitrophenol (DNP) in a batch-recirculation mode. The rate of DNP adsorption onto the TiO_2/AC-PET film without UV irradiation was almost the same as that onto the AC-PET film, indicating that the attraction of DNP to AC was not lowered in the presence of TiO_2 film. Observation of SEM photographs suggests that this result is attributed to the porous structure of the thin TiO_2 film covering AC particles. The rate of DNP removal by the TiO_2-AC PET film under UV irradiation was 2.9 times higher than that by the TiO_2-PET film under UV irradiation, and was 1.1 times higher than the rate of DNP adsorption onto the AC-PET film. The rate of DNP removal by the AC-PET film decreased by 40 % after six runs, while that by the TiO_2/AC-PET film decreased by 22%. Durable experiments using the TiO_2/AC-PET and AC-PET films clarified that the lifetime of the TiO_2/AC-PET film is at least two times longer than that of the AC-PET film. This result suggests that DNP molecules are photocatalytically decomposed when passing through the porous TiO_2-PET film, which lessens a burden of DNP adsorption on AC. Moreover, the DNP treatments in the batch-recirculation flow system suggested that the TiO_2/AC-PET film saturated with DNP can be successfully regenerated at 60 ^oC.

Keywords: photocatalytic reaction; titanium dioxide; activated carbon; adsorption; batch-recirculation reactor

Introduction

The removal of nitrophenols from wastewater is of increasing concern because of their potential toxicity. Their complete biodegradation usually requires several days or weeks. The decomposition and mineralization of nitrophenols in wastewater by the conventional methods, such as microbial and electrochemical treatments, are rather arduous due to their high stability and low solubility in water [1-4]. The organic compound 2, 4-dinitrophenol (DNP), which is a yellow, crystalline solid and slightly soluble in water (0.14 g/100 ml water at 54.5 °C), is detected in urban or agricultural wastewaters including those from the manufacture of textiles, dyes, wood preservatives, photographic developer, explosives, and pesticides [1,5]. DNP is a serious environmental contaminant and has been specified as a persistent, bioaccumulative and high acute toxic chemical compound by the United States Environmental Protection Agency [5-7]. Recently, several studies have elucidated that the photocatalytic decomposition of nitrophenols in aqueous solutions is an effective method to treat wastewaters containing these toxic and stable compounds compared to the conventional methods [6-10].

Titanium dioxide (TiO_2) excited by the irradiation with UV light can mineralize a wide range of organic compounds and is the most popular semiconductor catalyst. This is because TiO_2 is chemically inert, photocatalytically stable, relatively easy to prepare and to use, able to efficiently catalyze oxidative reactions, cheap, and usable without risks to human health. Irradiation of TiO_2

particles with UV light generates highly reactive oxidants, such as hydroxyl radicals, superoxide anions, hydrogen peroxide, and other reactive oxygen species, as a result of oxidative and reductive reactions. These highly reactive oxidants cause oxidative decompositions of organic compounds adsorbed on the TiO_2 surface [11-13]. The organic compounds decomposed by these photocatalytic reactions are finally mineralized to CO_2, H_2O, and other mineral ions, such as PO_4^{3-}, SO_4^{2-}, Cl^-, and a mixture of NH_4^+, NO_2^-, and NO_3^- if such compounds contain P, S, Cl, and N, respectively [14].

The simplest way to carry out the photocatalytic reaction is to suspend TiO_2 particles in an aqueous solution. However, it is not easy to separate TiO_2 particles from the solution after the treatment, because TiO_2 particles usually range from 10 to 300 nm in size. Moreover, the suspended particles interfere with the UV light penetrating into the deep water layer, which leads to a decrease in the reactor performance. Consequently, TiO_2 particles are usually immobilized onto various solid supports and the resulting TiO_2 preparations are used in various types of reactors [8,12,14-16].

Many researchers have immobilized TiO_2 on various porous solid particles, such as activated carbon (AC), silica beads, and so on to utilize their high adsorption capabilities [9,15,17-21]. They suspended these TiO_2 preparations in aqueous solutions and photocatalytically decomposed organic compounds under UV irradiation. When the TiO_2-depositing solid particles are suspended in an aqueous solution, on the other hand, it is difficult to sufficiently excite TiO_2 with UV light. After the treatment, moreover, the solid particles with TiO_2 must be separated from the solution, although this operation may not be so laborious compared to when only TiO_2 particles are suspended.

The purpose of the present work is to develop a high-performance photocatalytic reactor system in order to efficiently treat aqueous solutions of various organic compounds including DNP. To achieve this purpose, the performances of three preparations (TiO_2-, AC-, and TiO_2/AC-PET films) are investigated through the treatment of aqueous DNP solutions in a batch-recirculation flow system with an annular-flow photocatalytic reactor. The regeneration of TiO_2/AC-PET film saturated with DNP is also investigated through the treatment of aqueous DNP solutions at several temperatures higher than room temperature.

Experimental

Materials

DNP used as a reactant was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). A nonionic surfactant (polyoxyethylene lauryl ether with a degree of polymerization of 23) used to increase the affinity of aqueous coating solution of TiO_2 to the PET film was also the product of Wako Pure Chemical Industries, Ltd. This surfactant was selected from several candidates including ionic surfactants. The coating solution (aqueous H_2O_2 solution) containing anatase TiO_2 fine particles with diameters of 0.5-20 μm was a product of Sundecor Co. Ltd. (Fukuoka, Japan). The details of this solution are available elsewhere [12]. The 6-W blacklight blue fluorescent lamp with a wavelength distribution of 300-400nm was products of Matsushita Electric Industrial Co., Ltd. (FL6BL-B; Osaka, Japan). Granular activated carbon particles of roughly 1-2 mm in size were purchased from Japan EnviroChemicals Ltd. (WH2CSS; Osaka, Japan).

Preparations of PET films depositing TiO_2, AC, and AC coated with TiO_2

PET films of 0.085×0.195 m in size and 0.014 mm thick were used as a support for depositing TiO_2, activated carbon, and activated carbon coated with TiO_2. Prior to preparations, the films were washed with 70% ethanol and dried at room temperature.

The coating solution to which 0.01 wt% surfactant was added in order to increase the affinity of coating solution to the PET film was sprayed onto the surface of the PET film and dried for 1 h in a drier at 100 °C. The same procedure was repeated four times. As a result, a PET film coated with a TiO_2 film, was obtained; this is referred to as TiO_2-PET film.

A silicon adhesive was uniformly applied to the surface of PET film with a brush and activated carbon particles were then sprinkled over the adhesive film. The preparation thus obtained was pressed with a flat plate to firmly glue the particles to the PET film and then dried for one night. As a result, a PET film, whose one side is covered with activated carbon particles, was obtained; this is referred to as AC-PET film.

The coating solution was sprayed on the AC-PET film and dried for 1 h in a dryer at 100 °C. The same procedure was repeated four times. As a result, a PET film depositing activated carbon particles the surfaces of which were coated with a titanium dioxide film, was obtained; this is referred to as TiO_2/AC-PET film.

Let us assume that the GAC particle is of a cube with 0.0015 m in side length. Since seven faces of the cube are covered with a thin TiO_2 film, the total algebraic surface area of 7370 GAC particles loaded on a PET film becomes equal to 0.1160 m^2, which value is much larger than the surface area of a PET film, 0.01658 m^2. After four-time coating, TiO_2 particles of about 200 mg in total weight were deposited on an AC-PET film. Consequently, the weight of TiO_2 particles deposited per unit surface area of AC on a PET film is estimated to be 1724 mg/m^2.

Although the true mechanism for TiO_2 immobilization is unknown, there is no doubt that H_2O_2 has an important role. The TiO_2 coating solution used in the present work provided an easy way to fix TiO_2 particles to the surfaces of various kinds of materials by simply heating at above 100 °C. However, its adhesive power is not so high that the particles may easily be detached when exposed to high shear stress. For this reason, a reaction mixture was recirculated at a flow rate that did not cause detachment of a thin TiO_2 film.

It is known that TiO_2 particles dissolved in an aqueous H_2O_2 solution are present in the form of titanium peroxide. We therefore presume that heating the coating solution simply dried on a PET film results in further removal of water, formation of a thin TiO_2 film by use of H_2O_2 as a binder, and partial binding of this film with AC.

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Batch-recirculation flow system with an annular-flow photocatalytic reactor

To characterize the TiO_2/AC-PET film, removals of DNP from aqueous solutions were investigated in the batch-recirculation flow system (Figure 1), which consisted of the annular-flow photocatalytic reactor, a mixed-flow container, and peristaltic pump (RP-2; EYELA, Tokyo, Japan). The plastic reactor consists of a cylindrical vessel, 0.20m long and 0.0285m inlet diameter, equipped with a 6-W blacklight blue fluorescent lamp as a light source. A reaction mixture flows through the annulus between the inside wall of the cylindrical vessel and the quartz glass tube, 0.024m outer diameter, set for the protection of the UV lamp. The PET film depositing activated carbon particles and/or titanium dioxide was inserted into the annulus such that it contacts closely to the inside wall of the cylindrical vessel. The volume of the annulus in the photocatalytic reaction zone was 3.7×10^{-5} m^3.

Experimental procedures

To evaluate the performances of TiO_2-, AC- and TiO_2/AC-PET film, a 5.0×10^{-4} m^3 aqueous solution of DNP at various concentrations ranging from 1 to 15 g m^{-3} was circulated at a constant flow rate. The photocatalytic reaction was started by switching-on the UV lamp. The TiO_2/AC-PET film was also used to remove DNP at the temperature ranging from 30 to 60 ^{o}C.

The amount of DNP where the AC- and TiO_2/AC-PET films can treat until activated carbon loses its ability to adsorb DNP was estimated from repeated DNP treatment experiments. A 5.0×10^{-4}

m^3 aqueous solution of DNP at about 250 g m^{-3} was circulated at a constant flow rate and the experiment repeatedly conducted until the performance of AC- and TiO_2/AC-PET film decreased remarkably due to the saturation of the activated carbon.

The TiO_2/AC-PET film, whose activated carbon was saturated with DNP, was regenerated in the batch-recirculation flow system. A 5.0×10^{-4} m^3 distilled water was circulated in the system for 24 h and then the UV lamp was switched on to start the decomposition of DNP released from activated carbon particles. During the experiment at room temperature of about 20 ^{o}C, the temperature in the plastic reactor was measured with a thermometer. On the other hand, the regeneration of TiO_2/AC-PET film at 60^{o}C was conducted in a constant-temperature water bath.

In every experiment, an aliquot of the reaction mixture in the well-mixed flow vessel was withdrawn at appropriate time intervals and its absorbance was measured at 357 nm with a spectrophotometer (Ultrospec 1100Pro; Amersham Biosciences, Sweden) to determine the DNP concentration.

In our experiment, no pH control of a reaction mixture was conducted, although the pH value of a DNP solution reduced from 6.0 to 4.5 during the decomposition experiment. We have confirmed that in this pH range, there is little pH effect on the photocatalytic decomposition of DNP. Also, there was no pH effect on the TiO_2/AC-PET film. The descriptions regarding these facts have been given in the text.

Results and discussion

Characterization of a TiO_2/AC-PET film

Figure 2 shows SEM photographs of both the activated carbon loaded on the PET film and the TiO_2 film covering the surface of the activated carbon. It is obvious that the TiO_2 film has nonuniformly distributed pores and uneven surface. It is presumed that the porous structure is based on the use of large TiO_2 crystal particles in sizes of 0.5-20 μm, which greatly contributed to forming clearance gaps in the TiO_2 film. Thus, one may be able to expect that the DNP molecules are strongly attracted by the activated carbon without losing its attraction force and then decomposed when passing through the porous TiO_2 film. It is also clear that such large TiO_2 particles greatly contributed to forming the even surface of TiO_2 film. We have already confirmed that this even surface structure is very useful to enhance the rate of photocatalytic decomposition of gaseous formaldehyde compared to the very flat surface of anatase TiO_2 film prepared from nano-sized amorphous TiO_2 particles by heating at 500 °C [22].

Effect of flow rate on DNP removal using a TiO_2/AC-PET film

A 5.0×10^{-4} m^3 aqueous solution of DNP at an initial concentration of 8.5 g m^{-3} was circulated at flow rates ranging from 1.7×10^{-4} to 3.6×10^{-4} m^3 min^{-1} in the batch-recirculation flow system and treated using the annular-flow reactor with the TiO_2/AC-PET film. Figure 3 shows the time courses of DNP concentrations in these treatments. The simultaneous action of photocatalyst and activated carbon at a flow rate of 3.6×10^{-4} m^3 min^{-1} decreased 98.8 % of DNP at 105 min. On the other hand, the treatment at a flow rate of 1.7×10^{-4} m^3 min^{-1} required 160 min to achieve almost the same percentage of DNP removal. These results indicate that a higher flow rate can remove DNP more rapidly. In general, the photocatalytic reaction in an aqueous solution is significantly affected by the film-diffusional resistance that may appear in the neighbourhood of photocatalyst, especially when the reactant concentration is low [11,23,24]. In the present reaction system, it is therefore considered that an increase in the flow rate reduced the film-diffusional resistance and in turn contributed to increasing not only the rate of photocatalytic decomposition but also the rate of DNP adsorption onto the activated carbon.

Although the activated carbon particles were fixed onto one side of the PET film with a silicon adhesive, a little of them was separated from the film when the flow rate exceeded 4×10^{-4} m^3 min^{-1}. Moreover, it should be considered that the operation at a higher flow rate consumes a larger amount of electricity. In the following experiment, therefore, the flow rate was fixed at 3.6×10^{-4} m^3 min^{-1}.

Performances of TiO_2-, AC-, and TiO_2/AC-PET films with and without UV irradiation for DNP removal

Figure 4 shows the results of DNP removal experiments in the batch-recirculation flow system with the annular-flow photocatalytic reactor with the TiO_2-, AC-, or TiO_2/AC-PET film irradiated with UV light. A 5.0×10^{-4} m^3 aqueous solution of DNP at an initial concentration of 10 g m^{-3} was circulated at a flow rate of 3.6×10^{-4} m^3 min^{-1}. The TiO_2/AC-PET film removed 99.4% of DNP at 135 min. On the other hand, the TiO_2-PET film removed, or decomposed, 54.2 % of DNP at 150 min and 96.7 % of DNP at 6.5 h. The initial rate of DNP removal for the TiO_2/AC-PET film is 2.9 times higher than that for the TiO_2-PET film. The AC-PET film removed DNP at a slightly slower rate than did the TiO_2/AC-PET film. The rate of DNP removal for the TiO_2-PET film is not satisfactorily high, suggesting that there is a noticeable limitation to the treatment of DNP using UV-irradiated TiO_2 alone. It should be also noted that the DNP concentration can decrease to a value near zero in the treatment using TiO_2, whereas its decrease stops at a small but nonzero value in the adsorption using activated carbon only.

Figure 5 shows the results of DNP adsorption experiments in the batch-recirculation flow system equipped with the annular-flow photocatalytic reactor with the TiO_2-, AC-, or TiO_2/AC-PET film under the same condition as in Fig.4, except there was no UV irradiation. The TiO_2-PET film hardly decreased the DNP concentration, indicating that TiO_2 has a low ability to adsorb DNP. By contrast, both the AC- and TiO_2/AC-PET films quickly decreased the DNP concentration at almost the same rate, indicating that the activated carbon on the PET films can adsorb DNP at almost the same rate in spite of the presence or absence of the TiO_2 film. In other words, the DNP adsorption onto the activated carbon is hardly affected by the TiO_2 film. This can be attributed to the porous structure of the TiO_2 film.

The remarkably high performance of the TiO_2/AC-PET film irradiated with UV light is probably due to the cooperative work of UV-irradiated TiO_2 and activated carbon. In the TiO_2/AC-PET film, the activated carbon particles loaded on the PET film are entirely covered with a porous TiO_2 film, which provides a large reaction field for the photocatalytic decomposition and, in turn, leads to a high rate of photocatalytic decomposition. Moreover, since the distance between the light source and photocatalyst surface is only 5 mm, the reactor has a very high UV intensity per unit surface area, which greatly contributed to increasing the rate of photocatalytic reaction.

Even when the photocatalyst preparation is highly active, the efficiency of photocatalytic decomposition is reduced as a result of lowering a contact between reactant molecules and TiO_2 in the presence of film-diffusional resistance. This problem becomes serious especially at a low reactant concentration [11,24]. In the case of TiO_2/AC-PET film, however, this problem could be solved if the activated carbon has a high adsorption capacity. This is because when DNP molecules are rapidly attracted by the activated carbon and then pass through the porous TiO_2 film, the DNP concentration in the neighbourhood of TiO_2 surface is increased.

Figure 6 shows the time course of DNP concentration in the treatment of an aqueous solution of 10 mg m^{-3} DNP using the TiO_2/AC-PET film over 210 min. In this case, the UV light was turned-off until 150 min and turned-on thereafter. At around 140 min, the system reached an equilibrium between the aqueous solution and activated carbon, so that the DNP concentration stopped decreasing. When the light was turned on at 150 min, however, the DNP concentration started decreasing again toward a zero value. This experimental result indicates that the TiO_2 film coated on the activated carbon certainly contributed to the photocatalytic decomposition of DNP.

Characterization of experimental data after six runs using TiO_2/AC- and AC-PET films

When DNP molecules pass through the porous structure of TiO_2 film coated on the activated carbon, they are probably decomposed to some extent by UV-irradiated TiO_2. After a long period of time, however, the activated carbon on the TiO_2/AC-PET film would be saturated with DNP molecules passing through the TiO_2 film without being decomposed. In this case, the lifetime of the activated carbon should be prolonged as a result of the occurrence of photocatalytic reaction.

Figure 7 shows the time courses of DNP concentrations in six runs where DNP at an initial concentration of 10 g m^{-3} was adsorbed onto the AC-PET film and decomposed by or adsorbed onto the TiO_2/AC-PET film. The AC-PET film required 180 and 210 min in the third and sixth runs, respectively, to adsorb more than 97% of DNP; their removal time became longer by 1.2 and 1.4 times, respectively, than that of the first run. On the other hand, the TiO_2/AC-PET film required 165 min in both third and sixth runs to remove more than 98% of DNP; its removal time became longer by 22% than that of the first run. With increasing the number of runs, the AC-PET film lowered its performance compared to the TiO_2/AC-PET film. At the sixth run, the adsorption capacity of the AC-PET film decreased by 40 %, while that of the TiO_2/AC-PET film decreased by 18.1 %.

Figure 8 shows variations in the initial rates of DNP removal for the AC- and TiO_2/AC-PET films during six runs. The initial rate of removal for the AC-PET film decreased from 0.204 to 0.157 g m^{-3} min^{-1} (a reduction of 23%), while that for the TiO_2/AC-PET film decreased from 0.246 to 0.212 g m^{-3} min^{-1} (a reduction of 13.6%). The removal operations of DNP using the AC- and TiO_2/AC-PET films were further repeated until the activated carbon particles on these films were saturated with DNP. As a result, the maximum treatment amount of DNP was determined to be 0.95g for the AC-PET film and 1.87g for the TiO_2/AC-PET film. It is thus clear that the activated carbon on the TiO_2/AC-PET film is slowly saturated with DNP and its lifetime is expectedly prolonged as a result of photocatalytic decomposition.

Effect of temperature on DNP removal using a TiO_2/AC-PET film

Figure 9 shows the time courses of DNP concentration in the treatment of aqueous solutions of DNP at an initial concentration of 10 g m^{-3} in the batch recirculation flow system equipped with the TiO_2/AC-PET film. The solution temperatures were set up at 30-60 °C. The rate of decrease in the DNP concentration increased with increasing the temperature and levelled off at a temperature above 50 °C. As a consequence, the DNP concentration at 120 min increased in the range of 30-50 °C and became almost equal above 50 °C. In general, both the rate and amount of adsorption by the activated carbon decrease with increasing the temperature [25]. The photocatalytic activity also increases with increasing the temperature unless the reactant concentration is remarkably high [26]. These facts indicate that the increase in the rate of removal of DNP with the TiO_2/AC-PET film is due to the fact that the increase in the TiO_2 activity with increasing the temperature became larger than the decrease in the rate of adsorption of DNP onto the activated carbon.

Regeneration of a DNP-saturated TiO_2/AC-PET film

A repeated treatment of aqueous DNP solutions with the TiO_2/AC-PET film results in a saturation of activated carbon with DNP. Of course, TiO_2 decomposes DNP even under this condition, but its rate of removal would not be so high. It is therefore useful to investigate a regeneration method of the activated carbon on the TiO_2/AC-PET film. Distilled water was added to the batch recirculation flow system equipped with the annular-flow reactor with the TiO_2/AC-PET film and then recirculated to desorb DNP from the activated carbon and photocatalytically decompose it in free form.

Figure 10 shows the experimental result for the regeneration of TiO_2/AC-PET film over 24 h without controlling the solution temperature. A temperature increase from 24 to 36 ^{o}C was observed during the 24 hour treatment (Figure 11(a)). The DNP concentration reached a maximum value of about 10 g m^{-3} after 1 h and then decreased to 1.4 g m^{-3} as a result of photocatalytic decomposition. The time required to decompose DNP in this regeneration experiment is much longer than that of the DNP decomposition in Fig.7. This is considered due to the continuous desorption of DNP from the activated carbon into the solution during the regeneration experiment. After the experiment, the regenerated TiO_2/AC-PET film quickly decomposed DNP at an initial concentration of 10 g m^{-3} compared to before the regeneration experiment (Figure 11(b)). However, this result is quite different from the experimental data for the first run (the data indicated by a broken line), indicating that the degree of regeneration was not of a satisfactory level.

Figure 11 shows the experimental result for the regeneration of TiO_2/AC-PET film over 24 h at a constant solution temperature of 60^oC. The DNP concentration increased up to 17.5 g m^{-3} at maximum after 0.5 h because of higher solution temperature, decreasing to 1.4 g m^{-3} as a result of photocatalytic decomposition, as seen in Figure 12(a). Similarly, the time required to decompose DNP in this regeneration experiment is much longer that that for the DNP decomposition in Fig.7. This is considered due to the continuous release of DNP from the activated carbon as a result of reduction in the DNP concentration during the photocatalytic decomposition of DNP. After the regeneration experiment, the TiO_2/AC-PET film treated the DNP solution more rapidly than before the regeneration; the DNP concentration continuously decreased even after 180 min (Figure 12(b)). This result suggests that at the regeneration temperature of 60 ^oC, DNP was rapidly desorbed and then photocatalytically decomposed at a higher rate. It is thus obvious that the regeneration at 60 ^oC is more efficient than that at room temperature.

Evaluation of an annular-flow reactor with a TiO_2/AC-PET film

It is useful to compare the performance of the annular-flow reactor with a TiO_2/AC-PET film with those of the reactors reported by other researchers. Unfortunately, however, there are few reports on the photocatalytic decomposition of 2,4-DNP. Moreover, the purpose of using an experimental reactor is different among researchers. For examples, Nakano et al. [9] constructed their reactor to investigate the performance of TiO_2/SiO_2 beads, so that their reactor has not necessarily been optimized. Furthermore, the experimental condition, including the liquid volume, initial reactant concentration, number of UV lamps, electrical consumption of an UV lamp, and amount of TiO_2, is different. The result of comparison given here is therefore not absolute.

Table 1 compares the performances of the annular-flow reactors with TiO_2- and TiO_2/AC-PET films with those of the reactors reported by two other research groups. To remove the difference in the experimental condition, comparison is made in terms of the reactivity [mmol h^{-1} W^{-1}] calculated from each initial rate of decomposition. The reactivity of the TiO_2-PET film is similar to those of other TiO_2 preparations. Slight discrepancy can be attributed to differences in the film-diffusional effect, UV intensity, how to use TiO_2 particles, and so on. On the other hand, the reactivity of the TiO_2/AC-PET film is 4.3 times larger than that of the TiO_2 suspension and 10.2 times larger than that of the TiO_2/SiO_2 beads. This is because the treatment of DNP by the TiO_2/AC film is based on not only the photocatalytic decomposition but also the AC adsorption. The difference between the amounts of DNP required to saturate AC particles on the TiO_2/AC- and AC-

PET films suggests that the substantial rate of the decomposition of DNP by TiO_2 on the TiO_2/AC-PET film is roughly one half of the rate of the treatment of DNP by the TiO_2/AC-PET film. The reactivity for this case is therefore estimated to be 3.07×10^{-3} ($= 6.13\times10^{-3}/2$) mmol h^{-1} W^{-1}, the value of which is more than three times of the reactivity of the TiO_2-PET film, 9.01×10^{-4} mmol h^{-1} W^{-1}. This is obviously due to an increase in the DNP concentration at the TiO_2 surface on the TiO_2/AC-PET film as a result of rapid attraction of DNP by AC.

In conclusion, the result of comparison clearly shows that the TiO_2/AC-PET film is useful to decompose DNP.

Conclusions

The TiO_2/AC-PET film has almost the same ability to adsorb DNP as the AC-PET film despite the fact that the activated carbon is covered with a thin film of TiO_2. This can be attributed to the porous structure of the TiO_2 film. The maximum amount of DNP treatment with the TiO_2/AC-PET film is about two times larger than that with the AC-PET film. This implies that DNP is quickly attracted through the adsorption force of activated carbon and then decomposed when it passes through the porous structure of TiO_2 film. As a result, the lifetime of the activated carbon is prolonged. The TiO_2/AC-PET film saturated with DNP can efficiently be regenerated through its treatment at 60 °C for 24 h. The performances of TiO_2-PET and TiO_2/AC-PET films will be evaluated in more details through observation of the time courses of products (NO_3^-, NO_2^-, and CO_3^{2-}) in a subsequent paper.

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Legend

Fig. 1. Schematic of a batch-recirculation flow system equipped with an annular-flow reactor with a TiO_2-, AC-, or TiO_2/AC-PET film.

Fig. 2. SEM photographs of the AC-PET film surface magnified 100 times (A) and 2000 times (B) and the TiO_2/AC-PET film surface magnified 100 times (C) and 2000 times (D).

Fig. 3. Effect of flow rate on DNP decomposition in a batch-recirculation flow system equipped with an annular-flow reactor with a TiO_2/AC-PET film.

Fig. 4. Treatments of aqueous DNP solutions in a batch-recirculation flow system equipped with an annular flow reactor with a TiO_2-, AC-, or TiO_2/AC-PET film under UV irradiation.

Fig. 5. Treatments of aqueous DNP solutions in a batch-recirculation flow system equipped with an annular-flow reactor with a TiO_2-, AC-, or TiO_2/AC-PET film without UV irradiation.

Fig. 6. Treatment of aqueous DNP solutions in a batch-recirculation flow system equipped with an annular-flow reactor with a TiO_2/AC-PET film. The UV lamp was turned off until 150 min and turned on thereafter to start the photocatalytic reaction.

Fig. 7. Time courses of DNP concentrations in six runs for treatments of aqueous DNP solutions in a batch-recirculation flow system equipped with an annular flow reactor with an AC- or TiO_2/AC-PET film under UV irradiation.

Fig. 8. Variations in initial rates of DNP decomposition during six runs for treatments of aqueous DNP solutions in a batch-recirculation flow system equipped with an annular flow reactor with an AC- or TiO_2/AC-PET film under UV irradiation.

Fig. 9. Effect of solution temperature on DNP removal using a TiO_2/AC-PET film under UV irradiation.

Fig. 10. Regeneration of a DNP-saturated TiO_2/AC-PET film under uncontrolled solution temperature: (a) the time courses of DNP concentration and solution temperature during the regeneration; (b) time courses of DNP concentration in the decomposition of DNP at an initial

concentration of 10 g m^{-3} using the same TiO_2/AC-PET film under UV irradiation before and after the regeneration.

Fig. 11. Regeneration of a DNP-saturated TiO_2/AC-PET film under controlled solution temperature: (a) the time course of DNP concentration during the regeneration; (b) time courses of DNP concentration in the decomposition of DNP at an initial concentration of 10 g m^{-3} using the same TiO_2/AC-PET film under UV irradiation before and after the regeneration.

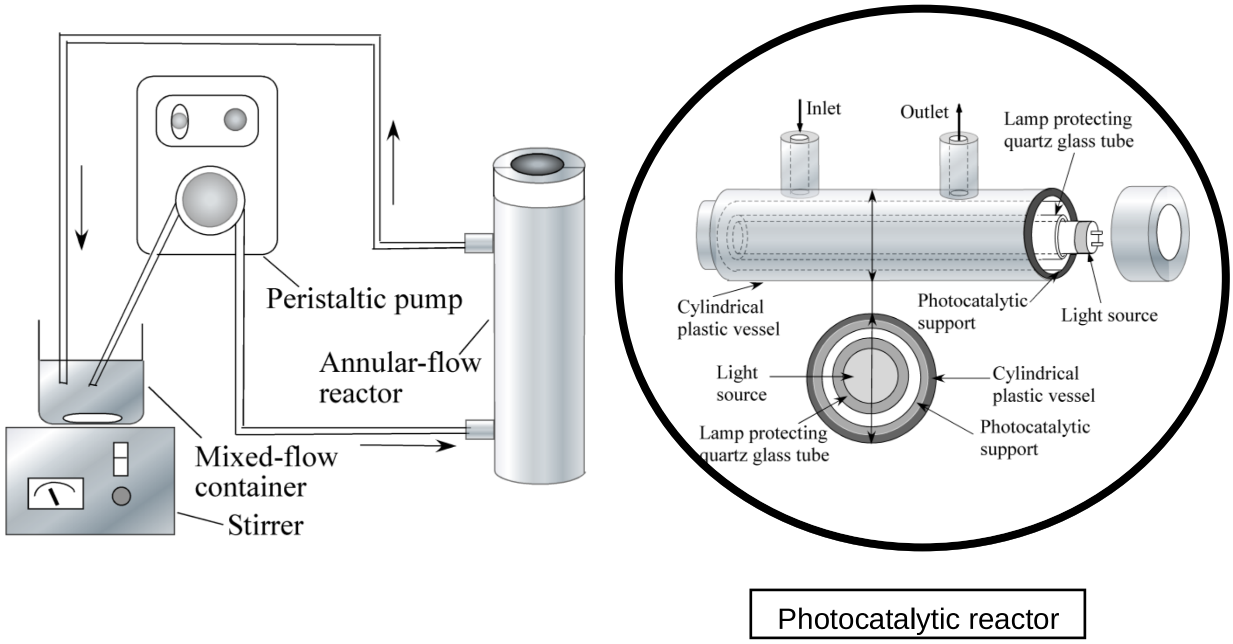


Fig. 1. Schematic of a batch-recirculation flow system equipped with an annular-flow reactor with a TiO_2-, AC-, or TiO_2/AC-PET film.

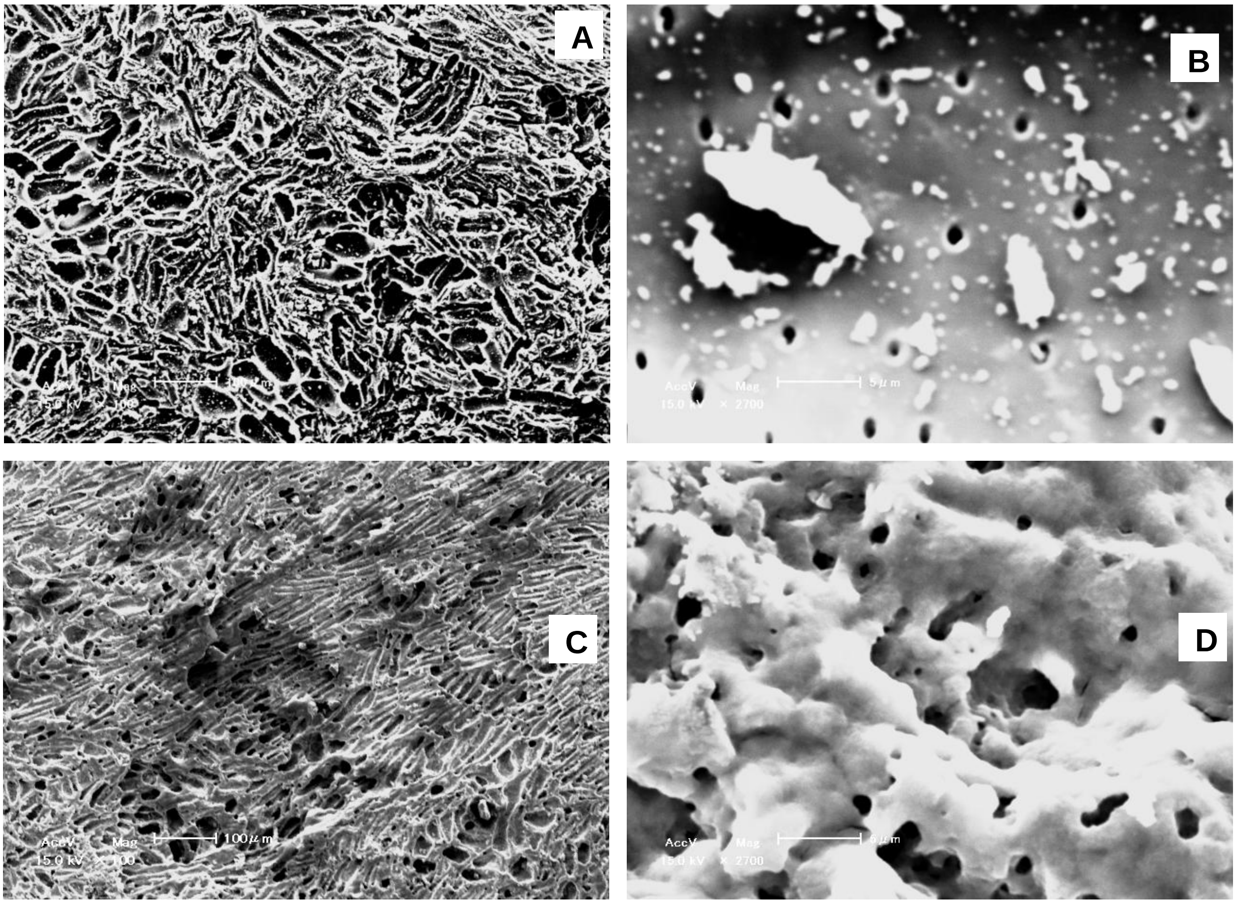

A
B
AccV Mag 5 μm
15.0 kV × 2700
C
AccV Mag 100 μm
15.0 kV × 100
D
AccV Mag 5 μm
15.0 kV × 2700

Fig. 2. SEM photographs of the AC-PET film surface magnified 100 times (A) and 2000 times (B) and the TiO_2/AC-PET film surface magnified 100 times (C) and 2000 times (D).

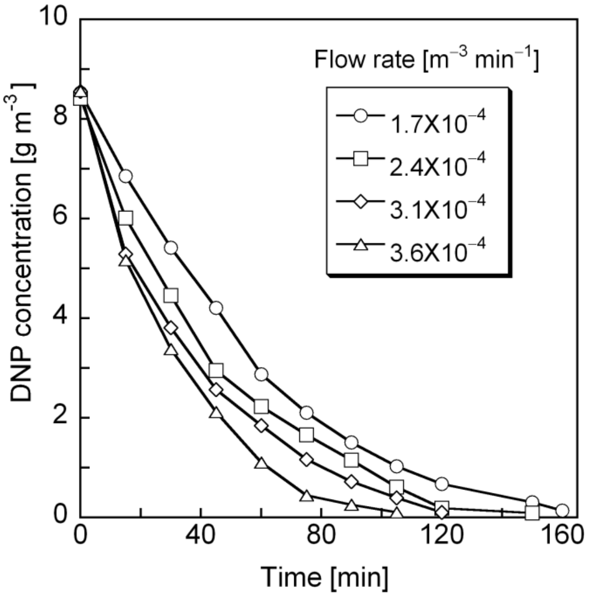


Fig. 3. Effect of flow rate on DNP decomposition in a batch-recirculation flow system equipped with an annular-flow reactor with a TiO_2/AC-PET film.

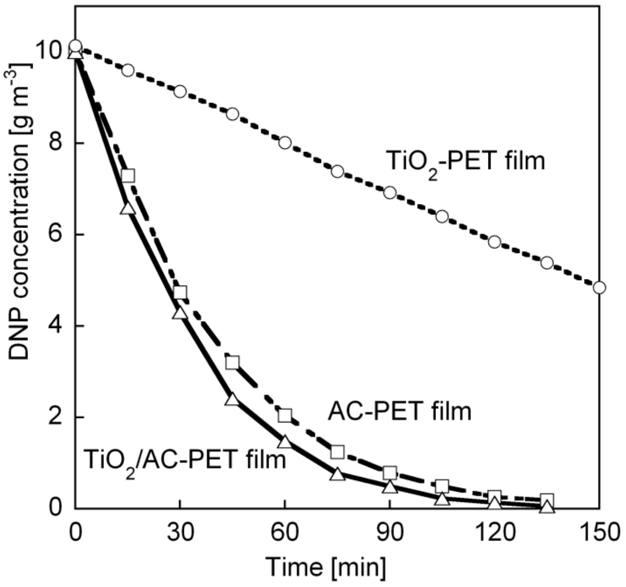
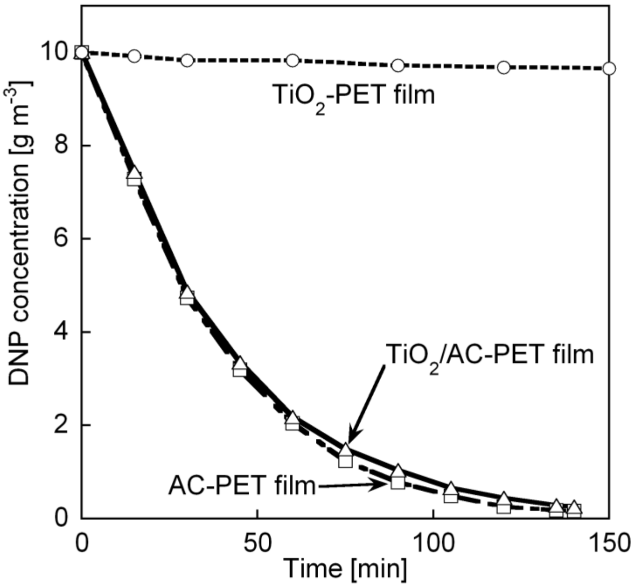


Fig. 4. Treatments of aqueous DNP solutions in a batch-recirculation flow system equipped with an annular flow reactor with a TiO_2-, AC-, or TiO_2/AC-PET film under UV irradiation.



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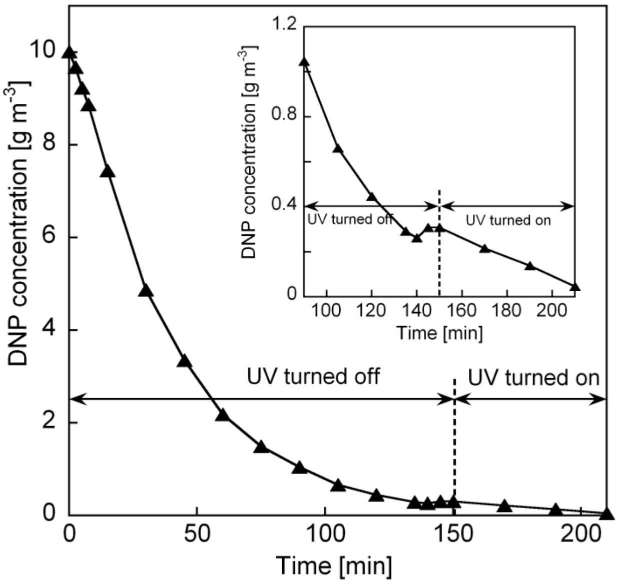

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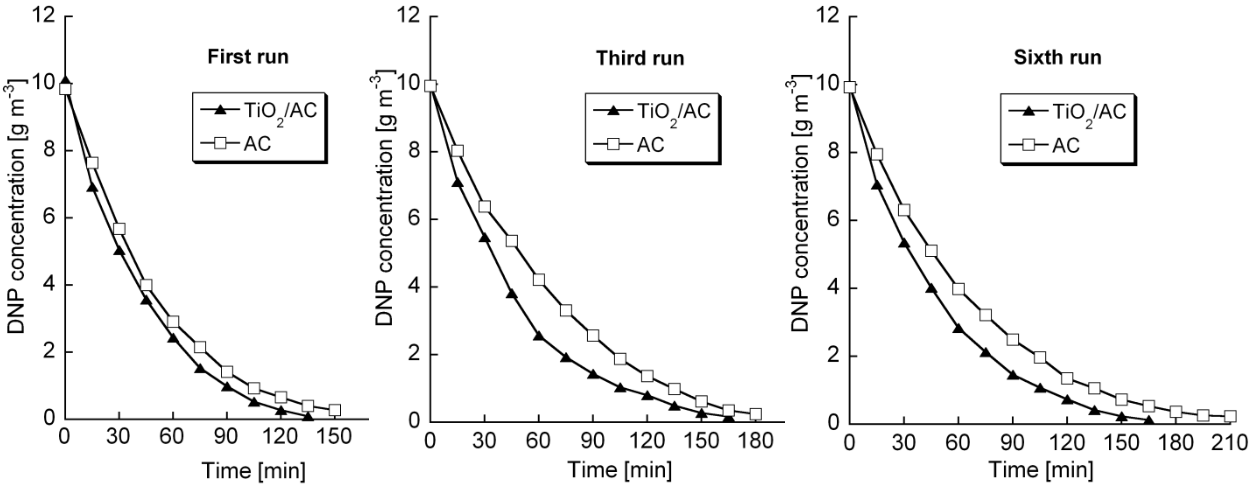


Fig. 7. Time courses of DNP concentrations in six runs for treatments of aqueous DNP solutions in a batch-recirculation flow system equipped with an annular flow reactor with an AC- or TiO_2/AC-PET film under UV irradiation.

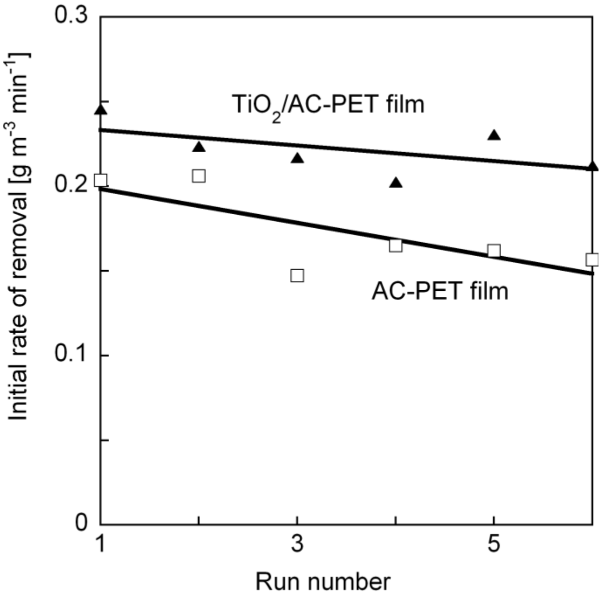


Fig. 8. Variations in initial rates of DNP decomposition during six runs for treatments of aqueous DNP solutions in a batch-recirculation flow system equipped with an annular flow reactor with an AC- or TiO_2/AC-PET film under UV irradiation.

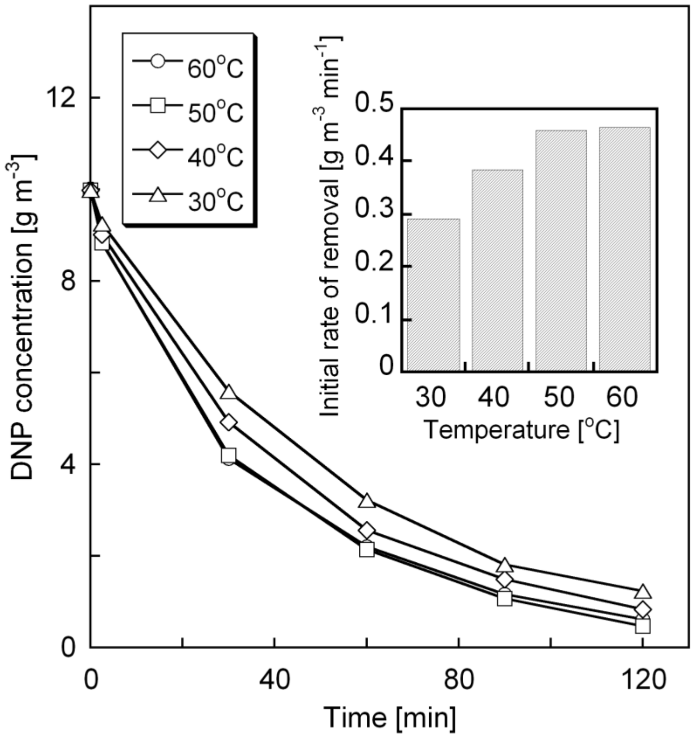
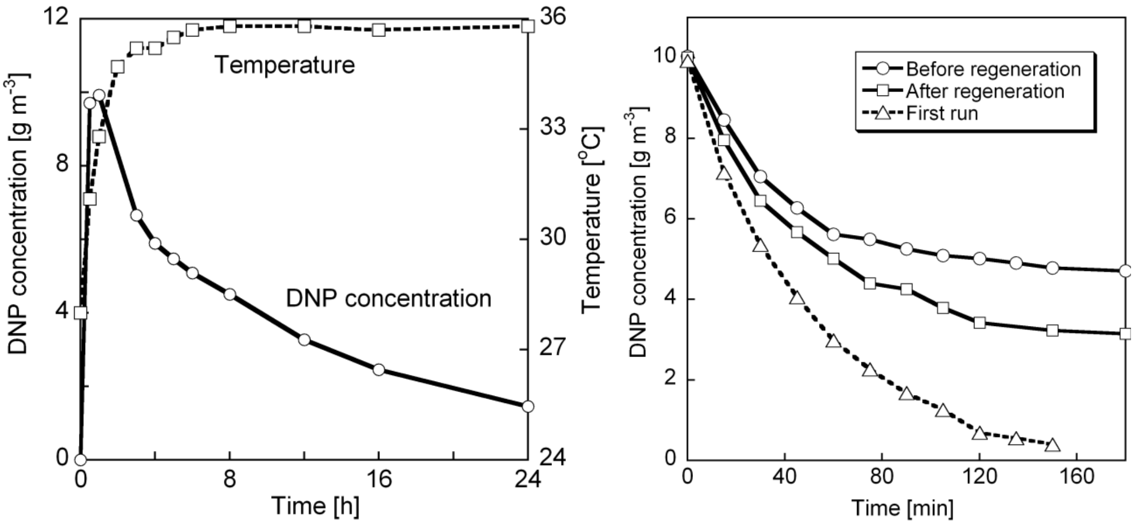


Fig. 9. Effect of solution temperature on DNP removal using a TiO_2/AC-PET film under UV irradiation.



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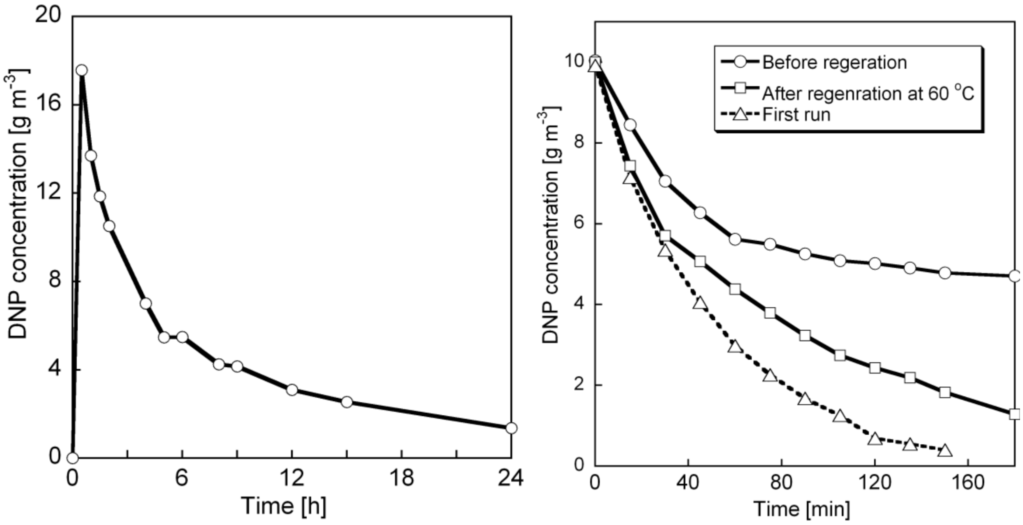

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Table 1 Comparisons of reactor performances for photocatalytic decomposition of 2,4-DNP

Reference	TiO_2 preparation	Liquid volume [L]	Initial DNP concentration [$g\ m^{-3}$]	[mM]	UV lamp	Reactivity [$mmol\ h^{-1}\ W^{-1}$]
[6]	1 $g\ L^{-1}$ TiO_2 suspension	1.0	32.2	0.175	125 W UV lamp (>290 nm)	1.44×10^{-3}
[9]	25 wt.% TiO_2/SiO_2	0.2	8	0.043	6 W blacklight lamp×4	6.00×10^{-4}
Present work	TiO_2/AC-PET	0.5	10	0.054	6 W backlight lamp	6.13×10^{-3}
	TiO_2-PET	0.5	10	0.054	6 W backlight lamp	9.01×10^{-4}