

Sunlight Photo-Assisted TiO₂-Based Pilot Plant Scale Remediation of (Simulated) Contaminated Aquatic Sites

Toshiyuki Oyama¹, Masashi Takeuchi¹, Ippei Yanagisawa¹, Takayoshi Koike¹, Nick Serpone² and Hisao Hidaka^{1*}

¹ Frontier Research Center for Global Environment Science, Meisei University (2-1-1 Hodokubo, Hino, Tokyo 191-8506, JAPAN)

² Gruppo Fotochimico, Dipartimento di Chimica Organica, Università di Pavia (Via Taramelli 10, Pavia 27100, ITALY)

Abstract: A tubular-type solar photoreactor system powered by commercial solar panels and consisting of six 20-tube modules (Pyrex glass) to mimic a pilot plant scale configuration was designed and constructed to examine the remediation of simulated wastewaters contaminated with various classes of organic pollutants such as endocrine disruptors (e.g. bisphenol A), anionic surfactants (sodium butylnaphthalenesulfonate and sodium dodecyl-benzenesulfonate), herbicides (e.g. 2,4-dichlorophenoxyacetic acid) and a commercial dishwasher detergent. Photo-oxidative processes followed first-order kinetics expressed in terms of the total light energy (in kJ) that impinged on the photoreactor. The influence of TiO₂ loading and circulation flow rate of the wastewaters on the dynamics of the photo-oxidation to mineralization (loss of total organic carbon, TOC, or formation of sulfate ions) was investigated. The optimal operational parameters were: TiO₂ loading, 2 g L⁻¹; circulation flow rate, 7.5 L min⁻¹. On a sunny day, near-quantitative mineralization of the contaminants was achieved after only 4 h of irradiation that corresponded to an accumulated energy of ca 1380 kJ.

Key words: photo-assisted oxidation, titanium dioxide, solar energy, water pollutants, advanced oxidation processes (AOP)

1 INTRODUCTION

Detergents, dyes, pesticides, herbicides and endocrine disruptors cause serious aquatic contamination resulting in harmful ecological problems to animals and plant life, since contaminants are but slowly and inefficiently biodegraded by microorganism consortia. Accordingly, alternative remediation technologies are needed to dispose of such organic pollutants. TiO₂-mediated photo-oxidative methods have been shown to be rather attractive in the remediation of wastewaters contaminated by various organic pollutants, although such advanced oxidation processes are still not economically practical in large scale owing to the relatively high costs of the photon energy. Sunlight is both an economically and ecologically sensible light source for the photon-mediated treatment of waterborne pollutants and should therefore prove beneficial in practical applications. Earlier laboratory-scale studies have demonstrated the feasibility of using sunlight and TiO₂ to photodegrade various organic pollutants¹⁻⁵ and thus represent a springboard from

which to explore sunlight-induced processes on a larger scale.

Over the last 15 years, two types of solar reactor have been developed and tested: (i) photoreactor systems that do not concentrate the sunlight and (ii) photoreactor units that concentrate the solar radiation either to a point (concave mirror concentrator) or to a line (parabolic mirror concentrator). Both types of solar photoreactors can be envisaged in wastewater remediation and both present certain advantages and disadvantages^{6, 7}. Non-concentrating photoreactors possess interesting characteristics such as (i) using low sunlight intensity, (ii) there is no need for a sunlight tracking device, and (iii) direct and diffuse sunlight can be harvested albeit at some cost for the entire photoreactor unit. By contrast, a photoreactor system that can concentrate solar radiation suffers (a) from losses of some of the sunlight through reflection by the parabolic or concave mirrors, (b) from rather relatively higher production costs, (c) from concentrating the sunlight radiation which leads

*Correspondence to: Hisao Hidaka, Frontier Research Center for Global Environment Science, Meisei University, 2-1-1 Hodokubo, Hino, Tokyo 191-8506, JAPAN

E-mail: Hidaka@epfc.meisei-u.ac.jp

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to very high irradiances impacting the reactor device, and (d) the need for a sunlight tracking device to harvest direct sunlight (not diffuse). Nonetheless, the capital costs of the photoreactor unit can be kept low. The state-of-the-art today is that concentrating collectors are not recommended for photocatalysis.

Herein we report the studies of a tubular-type photoreactor system designed specifically for sunlight-induced remediation of (simulated) wastewaters. The system consisted of a reactor composed of 120 Pyrex glass tubes (6 modules of 20 tubes each). Owing to a light receptive curved surface of the tubular reactor tubes, the reactor area facing the sunlight remained unchanged during the east-west movement of the Sun. The advantages of this system are similar to non-concentrating systems in that it can use both direct and diffuse solar radiation, the investment costs are low and the maintenance requirements are few. As the system used no reflecting mirror, there was no loss of UV-light photons that typically arises from the decrease of reflectivity of the mirrors caused by stains and dirt when such reflectors are exposed to the atmosphere. The photoreactor configuration enables circulation of the contaminants in the wastewaters in the reactor to occur at high flow rates with the added advantage that turbulent flow favors mass transfer and avoided possible catalyst sedimentation problems. To examine the efficacy of such a pilot plant scale photoreactor system, we investigated the photo-assisted TiO_2 -mediated remediation of simulated aquatic sites contaminated with such organic pollutants as the endocrine disruptor bisphenol A (BPA), the anionic surfactants sodium butylnaphthalenesulfonate (BNS) and sodium dodecylbenzenesulfonate (DBS), together with the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) and a representative commercial dishwasher detergent (henceforth referred to simply as the detergent). The solar photoreactor system included a feed tank containing 60 L of the wastewaters. Experimental factors (*e.g.* amount of loaded TiO_2 and flow rate) that impacted the dynamics of the photoredox processes were particularly examined to explore the optimal conditions that might lead to practical applications, especially where electrical power may be non-existent or is otherwise not available.

2 EXPERIMENTAL PROCEDURES

2.1 Chemicals

The endocrine disruptor BPA, and the anionic surfactants BNS and DBS were obtained from Tokyo Kasei Kogyo Co., whereas the herbicide 2,4-D was supplied by Wako Pure Chem. Co. and the detergent was from the Kao Co. of which the major ingredients were sodium alkylethersulfate, polyethoxyalkylether, alkylamineoxide, alkylhydroxysulfobetaine and alkylglycoside. All chemicals were employed as

received. Nanoparticulate TiO_2 was Degussa P-25 (surface area $\sim 50 \text{ m}^2 \text{ g}^{-1}$; mean diameter ca 30 nm; 87% anatase, 13% rutile), a generous gift from the Aerosil Nippon Co. Ion-exchanged water was used throughout to prepare the experimental solutions and dispersions. Unless noted otherwise, initial concentrations of each of the contaminants were 0.10 mM. For the liquid dishwasher detergent, the aqueous solution was diluted by four orders of magnitude. (Fig. 1)

2.2 The solar photoreactor system

Experience based on results obtained in earlier preliminary studies⁸⁾ led us to configure a photoreactor unit so as to treat a rather large volume of the contaminated wastewater(s)-60 L-which for the purpose used no less than six 20-tube modules connected in series. One of the 20-tube modules of the new solar photoreactor configuration is displayed schematically in Fig. 2a, whereas Fig. 2b shows an actual photograph of the photoreactor unit that consisted of 120 Pyrex glass tubes (inner diameter: 1.76 cm, length: 145 cm) along with the commercial solar panels that acted as the electrical power source. Twenty tubes of the six

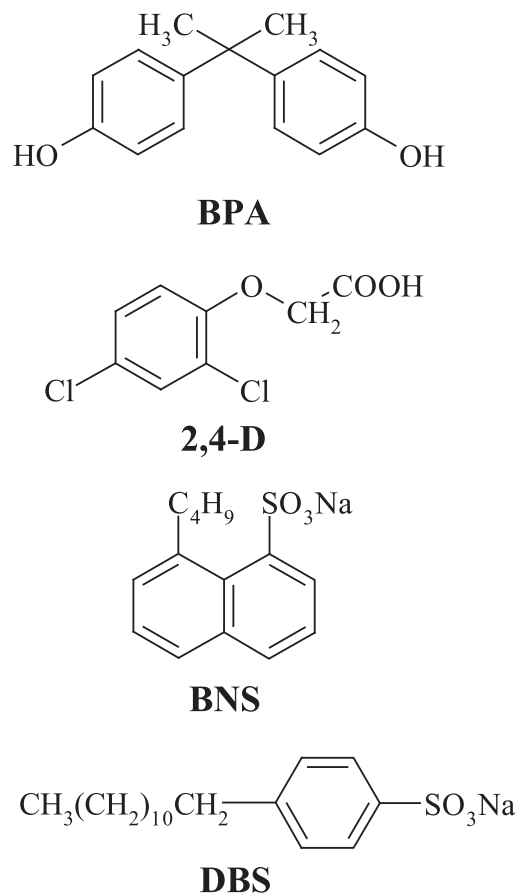


Fig. 1 Chemical structure of BPA, 2,4-D, BNS and DBS.

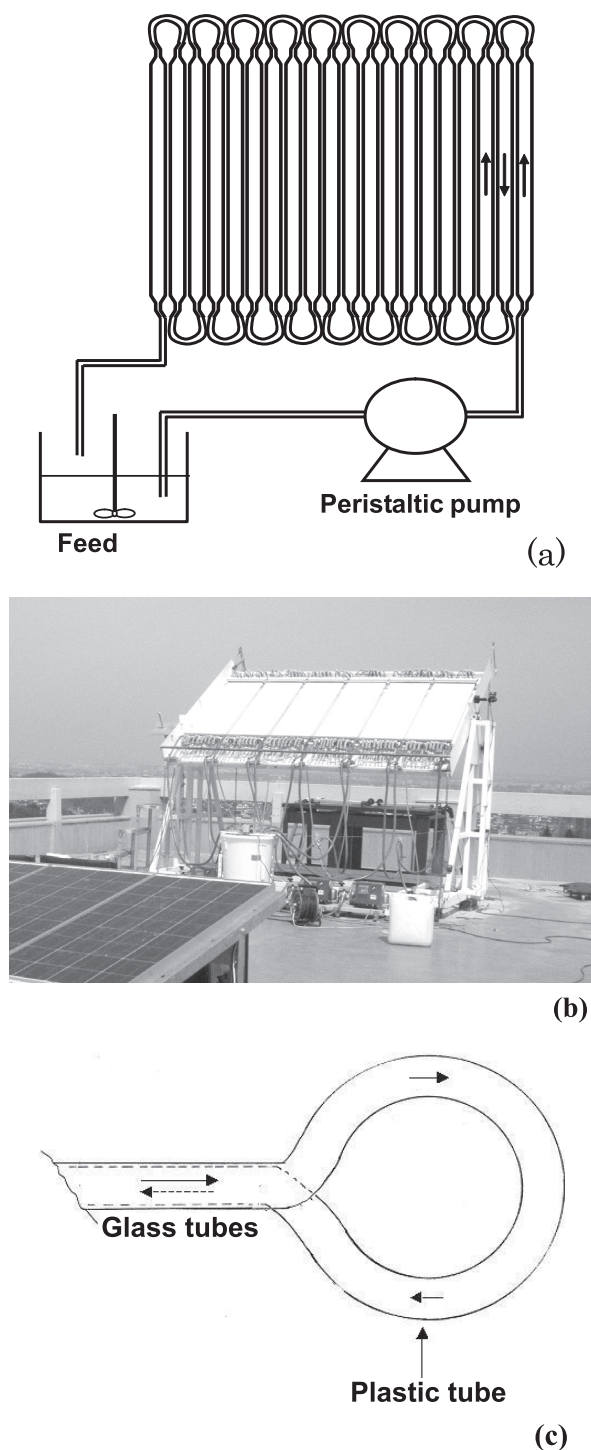


Fig. 2 (a) Schematic diagram of one of the 6 modules of the Pyrex glass photoreactor on the rooftop of the Chemistry Department's building of Meisei University (Tokyo). (b) Actual photograph of the experimental setup consisting of 6 modules connected in series (upper right) and the solar cell battery (lower left). (c) the plastic loop in the terminal joint.

modules were looped in series with plastic tubing at each end (Fig. 2c). This reactor design enabled the wastewater to flow through the photoreactor at rather high flow rates. Total volume of the photoreactor unit was 42.3 L and the light harvesting area was 3.06 m². This experimental device was thus used subsequently for the solar photo-assisted remediation, a process occurring in a closed-flow batch system for various wastewaters contaminated with the endocrine disruptor BPA, anionic DBS and BNS surfactants, the 2,4-D herbicide, and the commercial detergent.

No electrical power from a commercial network (domestic or otherwise) was used to power the various peripheral units of the system (*e.g.* computer, peristaltic pump, etc ...). Rather, electrical power was obtained from a solar driven photovoltaic battery system using conventional solar panels (Sharp Co. Ltd.). To the extent that this novel configuration approaches pilot plant scales, it was necessary to examine the parameters that affect process dynamics, namely flow rate and TiO₂ loading.

2.3 Procedures

A typical experiment was carried out as follows. A dispersion containing a 60-L solution of the substrate and TiO₂ nanoparticulate powder was prepared and placed in the feed tank. The aqueous TiO₂ dispersion was continuously introduced at the bottom of the photoreactor through plastic tubing combined with a peristaltic pump (PR-KV2, Furue Science Co.); the pump controlled the flow rate and maintained the reaction dispersion homogeneously mixed. The reaction dispersion was circulated continuously between the feed tank and the photoreactor, under solar exposure. Most of the solar experiments were performed at a flow rate of 7.5 L min⁻¹ (see below) to maintain the TiO₂ dispersion sufficiently stirred in the plastic tubes (turbulent flow), the feed tank and tubular reactor, and to maintain air saturation of the reactant solution with air oxygen supplied from the contact of the aqueous suspension with atmospheric air in the tank. The reactor was set up facing a southward direction and inclined by changing the angle of inclination with respect to the horizontal plane so as to maximize the solar radiation impinging on the photoreactor system. In all the experimental runs, various aliquots of degraded solution were collected at fixed time intervals as the photodegradation proceeded. After removing the TiO₂ from the collected samples, the levels of total organic carbon (TOC) remaining in the solar exposed dispersions were measured with a Shimadzu TOC-5000A analyzer. Decreases of substrate concentrations were monitored with a JASCO V-570 UV-visible spectro-photometer by measuring the absorption band of the benzenoid moieties in the substrates. The surface tension of the degraded solution was measured at ambient temperature with a Wilhelmy surface tensiometer (Kyowa Interface Science Co. Ltd., CBVPZ type). The solar light irradiance was measured with a radiometer

(UVR-36, Topcon Co.) at a wavelength of 360 nm and the data obtained per unit time (seconds) were integrated using a personal computer. The electrical power to drive the system, the pumps, the radiometer, and the computer was supplied entirely by the solar cell battery obtained from the Sharp Co. Ltd. In preliminary studies with various photoreactor configurations for outdoor applications under solar radiation, we were able to demonstrate that the optimal pH for the photo-oxidation treatment processes in the presence of the metal oxide TiO_2 ca $6-7^{(8)}$.

3 RESULTS

3.1 Degradation and mineralization of BPA with pilot plant scale photoreactor configuration

The photo-assisted decomposition of organic compounds in aqueous TiO_2 dispersions under constant UV light irradiance typically follows pseudo-first order kinetics. However, in solar experimental runs, sunlight intensity is continuously changing throughout the day. As such, to compare the results of different experimental runs obtained under different solar irradiation conditions or during different days, a kinetic analysis involving irradiation time is not appropriate as the variable parameter. Accordingly, the kinetic expression embodied in the following Eq. 1 proves useful in the analysis of the dynamics of photo-induced processes occurring in solar experiments^{9,10}:

$$\frac{C_t}{C_0} = e^{-k_{\text{obs}} E_{\text{tot}}} \quad (1)$$

where $E_{\text{tot}} = S \int E dt$; C_t is the time-dependent concentration changes; C_0 is the initial concentration of the reactant substrate; S is the area of the solar photoreactor; t is the irradiation time; E is the light irradiance (W cm^{-2}); k_{obs} is the observed rate constant; and $E_{\text{tot}} = S \int E dt$ represents the total accumulated light energy radiation (in J) that impinged on the photo-reactive system. Light energy was estimated using the light irradiance measured between 330 and 380 nm (maximal peak at 362 nm). On a sunny day, 1 h of UV light irradiation of 3 mW cm^{-2} irradiance impinging on the photoreactor corresponds to an incident light energy of 330 kJ.

Several experimental parameters can influence the dynamics of the photo-oxidation process and thus the corresponding efficiencies for a given sunlight irradiance that impinges upon the photoreactor unit. These are the rate of flow of the wastewater through the photoreactor unit, the quantity of the metal-oxide used to photo-assist the process (note that the process may or may not be photocatalytic¹¹⁻¹³), and the pH of the wastewater as this parameter affects the extent of adsorption of the contaminant onto the metal-oxide particle surface which may be positively, neutral or negatively charged as can be determined by zero-zeta potential measurements.

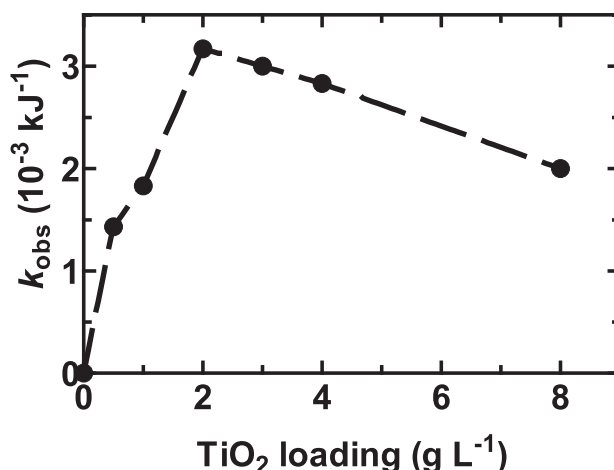


Fig. 3 Dependence of the observed dynamics on TiO_2 loading in the photodegradation of BPA.

Experimental conditions: initial concentration, 0.10 mM; volume of reactant solution, 60 L; circulation flow rate, 7.5 L min^{-1} ; six 20-tube modules connected in series configuration; pH 6.8.

3.2 Dependence of degradation dynamics on TiO_2 loading

The effects of the TiO_2 concentration on process kinetics (k_{obs}) are depicted in Fig. 3, which shows that the photodegradation dynamics of the endocrine disruptor BPA are greatest at ca 2 g L^{-1} TiO_2 loading under the conditions used.

The latter was subsequently used in all further experiments. Beyond this, the dynamics tended to decrease somewhat, likely the result of increased scattering of the sunlight radiation by the metal-oxide nanoparticles or otherwise the particulates masked others from being activated by the radiation, i.e. particles provided a pseudo-filtering effect on the rest of the dispersion. In this regard, it is relevant to note that the scattering coefficient of TiO_2 nanoparticles is significantly greater than the absorption coefficient in aqueous TiO_2 dispersions for a large range of wavelengths¹⁴.

3.3 Effect of circulation flow rates

The solar catalytic degradation of lower concentration of volatile organic compounds using reactor made of transparent inflatable tubes connected in parallel between two headers was carried out by Goswami¹⁵. The reactor tubes used in our experiment were made of Pyrex glass and connected in series. We investigated the role that the rate of flow of the dispersions in the pilot-scale photoreactor unit might play in the overall sunlight-assisted TiO_2 -mediated degradation dynamics for the BPA-contaminated wastewa-

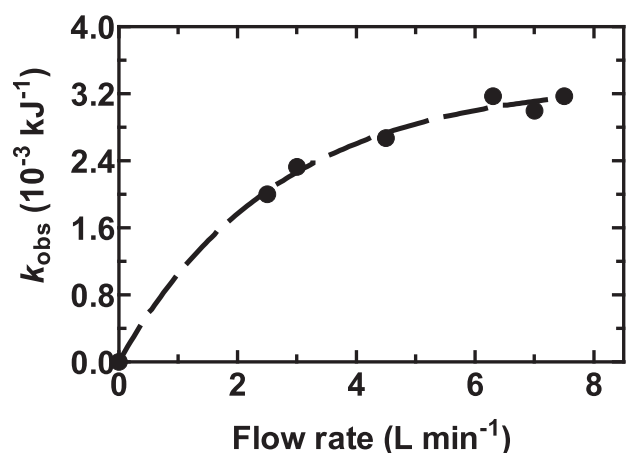


Fig. 4 Dependence of the observed reaction dynamics on circulation flow rate in the photodegradation of BPA.

Experimental conditions: initial concentration, 0.10 mM; volume of reactant wastewater, 60 L; TiO₂ loading, 2.0 g L⁻¹; six 20-tube modules connected in series; pH 6.8.

ter. Accordingly, we examined flow rates from 2.5 to 7.5 L min⁻¹. Observed first-order dynamics data are plotted against flow rates and are reported in Fig. 4.

The increase of flow rate of the dispersion through the sunlight-irradiated photoreactor enhanced the photo-degradation dynamics for BPA owing to the vigorous turbulent flow, which maintained the TiO₂ particulates and BPA solution well dispersed in a manner that optimized mass transfer of the substrate onto the TiO₂ nanoparticles and maximized aeration of the dispersion to introduce the essential reagent oxygen. We need not emphasize that air oxygen is an essential component in such heterogeneous photo-assisted reactions because it minimizes and may even suppress recombination of photogenerated electrons and holes on the sunlight-activated TiO₂ particulates. In all the outdoor experiments, the feed tank was constantly left open to the atmosphere as a means of introducing air oxygen into the aqueous TiO₂ dispersions. Flow rates greater than 6.3 L min⁻¹ appear to have no further effect on the photo-assisted degradation dynamics. From these results, all further solar experimental runs for the degradation and mineralization of the other pollutants were carried out with TiO₂ loadings of 2 g L⁻¹ and at the flow rate of 7.5 L min⁻¹.

3.4 Optimized degradation and mineralization of BPA

The first stage of the photodegradation process is cleavage of the aromatic ring in the substrates by attack of ·OH radicals generated on the surface of the metal-oxide nanoparticles under sunlight irradiation¹⁶. Using the optimized experimental parameters shows that the decrease of

BPA spectral features (Fig. 5a) occurs via first-order dynamics ($k_{obs} = 4.3 \pm 0.3 \times 10^{-3} \text{ kJ}^{-1}$) as a result of ring opening of the phenyl ring; the relevant data are plotted against accumulated incident sunlight energy and are displayed in Fig. 5b. The photo-assisted mineralization proceeded by further oxidative steps, also by, albeit slower, first-order dynamics ($k_{obs} = 2.6 \pm 0.2 \times 10^{-3} \text{ kJ}^{-1}$) via such intermediates as aldehyde and carboxylic acid derivatives that ultimately produced CO₂ as evidenced by the loss of TOC in the degraded aqueous suspension (Fig. 5b). The observed dynamics obtained by this procedure can be adopted to compare quantitatively the influencing effects of various

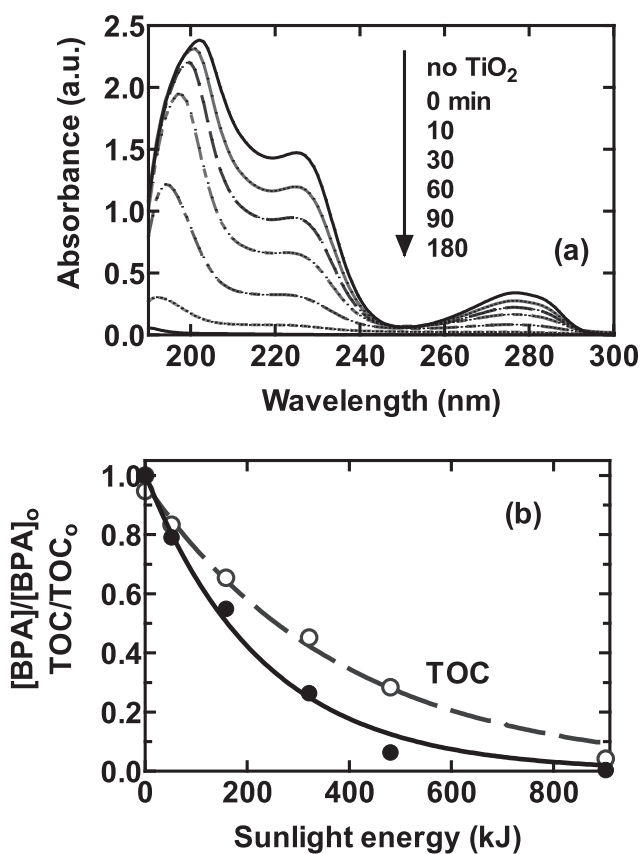


Fig. 5 (a) Absorption spectra during the photo-assisted degradation of BPA with and without TiO₂; (b) Dynamics of the photo-assisted degradation of BPA in aqueous TiO₂ dispersions under sunlight irradiation expressed against total sunlight energy that impinged on the photoreactor, and changes of loss of TOC in the dispersion during the mineralization of BPA under sunlight irradiation. Experimental conditions: initial concentration, 0.10 mM; volume of reactant suspension, 60 L; TiO₂ loading, 2.0 g L⁻¹; circulation flow rate, 7.5 L min⁻¹; pH 6.8; initial TOC, 18 ppm.

parameters under different experimental conditions during the photodegradation of substrates occurring under solar exposure.

3.5 Sunlight-assisted degradation/mineralization of pollutants in wastewaters containing TiO₂

Following the determination of the optimal metal-oxide loading and the optimal flow rate for the TiO₂/wastewater through the six 20-tube modules photoreactor configuration, we subsequently explored the degradation and mineralization (loss of TOC) for other contaminated model waste-

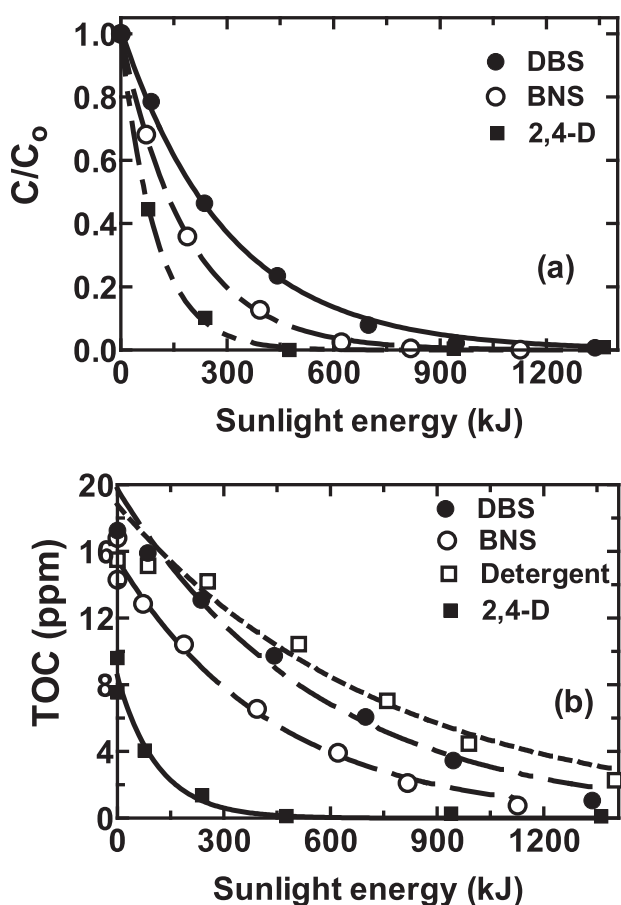


Fig. 6 (a) Photo-assisted degradation of the DBS, BNS and 2,4-D pollutants in aqueous TiO₂ dispersions under sunlight irradiation. (b) TOC loss in solution during the photomineralization of the DBS, BNS and 2,4-D pollutants together with the commercial detergent under sunlight irradiation. Experimental conditions: initial concentration, 0.10 mM; for the commercial detergent, the liquid was diluted by a factor of 1:10,000; volume of reactant suspensions, 60 L; TiO₂ loading, 2.0 g L⁻¹; pH 6.8; circulation flow rate, 7.5 L min⁻¹.

waters containing the anionic surfactants BNS and DBS, the herbicide 2,4-D and the dishwasher detergent. The decreased concentrations of the various aromatic substrates were the result of ring opening as evidenced by the loss of absorption spectral features pertinent to the presence of phenyl rings in the substrates. The quantitative results for the sunlight-assisted TiO₂-mediated degradation and mineralization of these organic contaminants are displayed in Figs. 6a and 6b. The relevant rate constants of degradation and that of mineralization are summarized in Table 1. Ratios of mineralization to degradation indicate slower mineralization of the substrates owing to the intervening intermediates produced prior to formation of carbon dioxide.

The sulfur-containing anionic surfactants yield SO₄²⁻ ions along the degradation/mineralization oxidative pathway. The levels of sulfate ions detected by ion chromatography are illustrated in Fig. 7 for DBS, BNS and the

Table 1

	DBS	BNS	2,4-D	Detergent
Degradation $k_{\text{obs}} (\times 10^{-3} \text{kJ}^{-1})$	3.4 ± 0.1	5.4 ± 0.1	10.2 ± 0.3	–
Mineralization $k_{\text{obs}} (\times 10^{-3} \text{kJ}^{-1})$	1.8 ± 0.2	2.3 ± 0.2	8.8 ± 1.7	1.3 ± 0.3
Ratios of mineralization to degradation	1.9	2.4	1.2	–

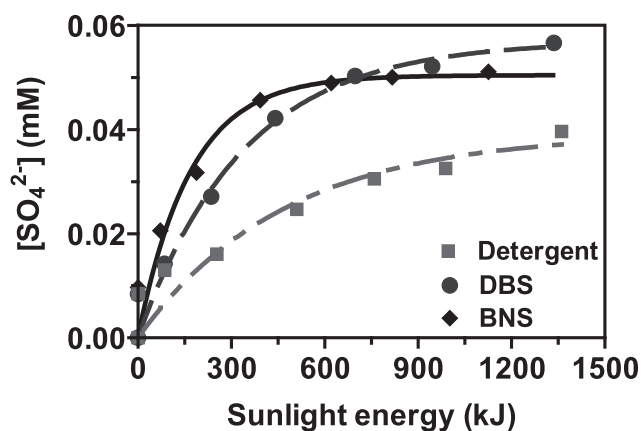


Fig. 7 Quantity of SO₄²⁻ ions detected during the mineralization of BNS, DBS and the commercial detergent under sunlight irradiation.

Experimental conditions: initial concentration, 0.10 mM for DBS and BNS; for the commercial detergent, the liquid was diluted by a factor of 1:10,000; volume of reactant suspensions, 60 L; TiO₂ loading, 2.0 g L⁻¹; pH 6.8; circulation flow rate, 7.5 L min⁻¹.

commercial detergent. The rate constants for the formation of SO₄²⁻ ions are shown in Table 2. The mineralization yields for sulfur detected as sulfate are nearly half those for carbon (60% for DBS and 50% for BNS), which we attribute to strong adsorption of the remaining sulfate anions on the positively charged metal-oxide surface under our conditions (note that mineralization of organic substrates typically cause the pH to become more acidic in aqueous media).

Figure 8 shows the temporal changes in the surface tension of the dispersions during the photodegradation of the commercial dishwasher detergent, and the anionic surfactants DBS and BNS. Where the surface tension of the starting stock solution before addition of TiO₂ catalyst was indicated as the points less than zero kJ of sunlight energy. The surface tension increased dramatically soon after the beginning of sunlight irradiation of the photoreactor unit. Indeed, the degraded solution gave the same degree of surface tension (about 72 mN m⁻¹) as that of water within 30 min of solar irradiance or after about 300 kJ of solar energy had fallen onto the photoreactor unit. Evidently the surfactant action of the sulfonated substrates terminated within the 30-min period that we attribute to the breakup of the aromatic ring within this time. The temperature of the solution increased to ca 45°C during the irradiation.

Table 2

	DBS	BNS	Detergent
$k_{\text{obs}} (\times 10^{-3} \text{kJ}^{-1})$	3.0 ± 0.5	6.0 ± 1.2	2.1 ± 0.8

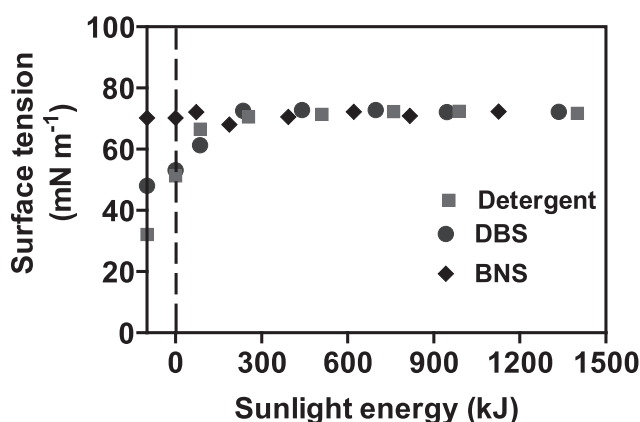


Fig. 8 Surface tension changes during the photo-assisted degradation of DBS, BNS and the commercial detergent.

Initial concentrations, 0.10 mM for DBS and BNS; for the commercial detergent, the liquid was diluted by a factor of 1:10,000; volume of reactant suspensions, 60 L; TiO₂ loading, 2.0 g L⁻¹; pH 6.8; circulation flow rate, 7.5 L min⁻¹.

4 CONCLUSION

The tubular type pilot plant scale photoreactor designed, constructed and located on the rooftop of our department (Tokyo) achieved significant degradation and mineralization of various wastewaters contaminated with surfactants, a herbicide and an endocrine disruptor, as well as with a commercial detergent using natural sunlight in the presence of TiO₂ under aerated conditions. Both the TiO₂ loading and the rate of flow of the wastewaters impacted on the dynamics of the degradation and mineralization processes. On a sunny day, sufficient mineralization of most of the pollutants was achieved within 4 h of sunlight irradiation (1380 kJ). A most interesting result of the present study is that an operating system for remediation of contaminated wastewaters and similar contaminated sites can be utilized at locations far from any domestic (or otherwise) electrical network since the electrical power needed to run the peristaltic pump, and other electrical/electronic apparatus could be supplied solely from the sunlight through the photovoltaic devices in the solar panels. Accordingly, the photoreactor system illustrated herein should prove ecologically friendly and favorable in terms of process economics. It should also be easily adaptable to treat domestic waters.

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