Kinetics of photocatalytic removal of imidacloprid from water by advanced oxidation processes with respect to nanotechnology
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ABSTRACT

In this study, the kinetics of photocatalytic removal of imidacloprid, a systemic chloronicotinoid insecticide, from water using two advanced oxidation systems (ZnO(normal)/H₂O₂/artificial sunlight and ZnO(nano)/H₂O₂/artificial sunlight) were investigated. Moreover, the effects of pH, insecticide concentration, catalyst concentration, catalyst particle size, and water type on the photocatalytic removal of imidacloprid were evaluated. Furthermore, total mineralization of imidacloprid under these advanced oxidation systems was evaluated by monitoring the decreases in dissolved organic carbon (DOC) concentrations and formation rate of inorganic ions (Cl⁻ and NO₂⁻) with irradiation time using total organic carbon (TOC) analysis and ion chromatography to confirm the complete detoxification of imidacloprid in water. The degradation rate of imidacloprid was faster under the ZnO(nano)/H₂O₂/artificial sunlight system than the ZnO(normal)/artificial sunlight system in both pure and river water. The photocatalytic degradation of imidacloprid under both advanced oxidation systems was affected by pH, catalyst concentration, imidacloprid concentration, and water type. Almost complete mineralization of imidacloprid was only achieved in the ZnO(nano)/H₂O₂/artificial sunlight oxidation system. The photogeneration rate of hydroxyl radicals was higher under the ZnO(nano)/H₂O₂/artificial sunlight system than the ZnO(normal)/H₂O₂/artificial sunlight system. Advanced oxidation processes, particularly those using nanosized zinc oxide, can be regarded as an effective photocatalytic method for imidacloprid removal from water.

Key words | hydroxyl radical, imidacloprid, mineralization, nanocatalyst, removal, water

INTRODUCTION

Pesticides are widely used in agriculture to reduce the loss of production caused by pests; however, they also contribute to pollution of the environment (Derbalah et al. 2013, 2014, 2016). The presence of pesticide residues in water poses a risk to aquatic organisms as well as to human health (Sathiyanarayanan et al. 2009). The United Nations has reported that less than 1% of applied pesticides reach their target pests, while the remainder become distributed in different environmental components such as soil, air, and water (Readman et al. 1993; Kopling et al. 1996; Meyer & Thurman 1996). Because organic pesticides are generally toxic, persistent and difficult to destroy biologically, their
presence in aquatic environments leads to unexpected hazards (Hayo 1996; Hilz & Vermeer 2012). Therefore, the process of treating contaminated water with pesticides is a major concern because pesticides are toxic and sometimes carcinogenic, resulting in significant health risks (Derbalah et al. 2004, 2016).

Imidacloprid is a neonicotinoid insecticide registered in more than 140 countries to control many of the sucking insects that affect field crops such as rice, wheat, and cotton. Imidacloprid is also used to control pests in crops grown in greenhouses. This pesticide can be applied as a systemic insecticide to soil and seeds, or by spraying on crops (Jeschke & Nauen 2008; Morrissey et al. 2015; Lewis et al. 2016). Imidacloprid is also used as a topical treatment for fleas on domestic pets. Owing to the intensive use of this pesticide, imidacloprid commonly enters water either by spray drift or runoff after application. Because of the high solubility of imidacloprid, it may have adverse effects on aquatic organisms and human health (Armbrust & Peeler 2002; Hilz & Vermeer 2012).

In order to minimize the residues of pesticides in water to levels established by the World Health Organization and the US Environmental Protection Organization, which do not have harmful health effects on humans and the environment, as well as to meet the standards of water quality of pesticides to protect human health, methods of removal of pesticide residues from water must be more effective and highly sensitive. Therefore, the ideal procedures for removing pesticide residues from water are non-selective methods that achieve the rapid and complete destruction of organic pesticides to non-toxic inorganic products that are effective in small-scale remediation units (Blanco & Malato 2001; Derbalah et al. 2004, 2013, 2014, 2016).

Multiple techniques such as advanced oxidation processes, adsorption and biological methods are used for the removal of pesticide residues from water. The elimination of many toxic agrochemicals, including pesticides in water, using advanced oxidation processes such as (Fe2O3(nano)/H2O2/UV), ZnO/H2O2/UV, (Fe6(nano)/H2O2/UV), (TiO2/UV-A), and (Fe3+/H2O2/UV-A or vis) has been studied with promising results. In addition, studies have shown the possibility for complete or partial removal of pesticides from natural water (Huston & Pignatello 1999; Blake 2001; Blanco & Malato 2001; Konstantinou & Albanis 2003; Ishiki et al. 2005; Toepfer et al. 2006; Derbalah & Ismail 2012; Derbalah et al. 2013, 2014, 2016).

The photocatalysts created by nanotechnology are unique and differ in their morphology and characteristics when compared with the same materials prepared without nanotechnology; thus, they represent an important step in improving the efficiency of the photocatalytic removal of pesticides from water. Metal oxides that are synthesized using nanotechnology like zinc oxide and titanium dioxide can take different forms, such as nanoparticles, nanorods, nanowires, nanotubes, nanosheets, and nanoflowers. The reduction of metal oxides particle size to the nanoscale increases their surface area, and subsequently their active sites on the surface for oxidation and degradation of pesticides (Colon et al. 2007; Derbalah et al. 2014, 2016).

Zinc oxide is a semi-conductive material that can be fabricated with various morphological forms in normal and nanoscale sizes (Kumari et al. 2010). Zinc oxide is environmentally friendly and does not have harmful effects on living organisms (Ismail et al. 2015). Fabrication of ZnO in nanostructure can change its properties. Light absorption of ZnO as a photocatalyst in the visible region is limited because of its wide band gap. Therefore, its optical properties must be modified using nanotechnology to enable the economic use of zinc oxide in advanced oxidation systems for removal of pesticide residues from water in the presence of sunlight. Additionally, zinc oxide created by nanotechnology can be used very efficiently to eliminate pesticide residues from water depending on the used fabrication methods (Baruah et al. 2012).

In this study, the photocatalytic removal of imidacloprid from water using two advanced oxidation systems (ZnO(normal)/H2O2 and ZnO(nano)/H2O2) was investigated. Artificial sunlight (solar simulator) was used in this study to examine the photocatalytic removal of imidacloprid since the sunlight advanced oxidation system is not much studied, compared with the UV light advanced oxidation system. Moreover, the effects of pH, catalyst concentration, insecticide concentration, and water type on the photocatalytic removal of imidacloprid were evaluated. Furthermore, the complete mineralization of imidacloprid in water to CO2 and H2O, as well as inorganic ions, was evaluated using a total organic carbon (TOC) analyzer and ion chromatography to confirm the complete detoxification of imidacloprid in water. To interpret the differences in the degradation rate of imidacloprid under both oxidation systems, the photoformation rates of hydroxyl radicals were determined.
METHODS

Chemicals

Imidacloprid technical standard (99% purity) was obtained from Sigma-Aldrich, USA, as were zinc oxide nanopowder (<100 nm with a specific surface area of 15–25 m²/g) and zinc oxide powder with a purity of 99.99%. Benzene, acetonitrile, and phenol (99.5% purity) were obtained from Nacalai Tesque, Japan, and methanol was obtained from Wako Chemical Company, Japan. For TOC analysis, imidacloprid was dissolved directly in Milli-Q water to avoid the influence of methanol on dissolved organic carbon (DOC) levels. Acetonitrile (HPLC grade) was obtained from Kanto Chemical Company, Japan.

Zinc oxide nanoparticles

Zinc oxide nanopowder (with a particle size 80 nm and specific surface area of 15–25 m²/g) and zinc oxide powder with a purity of 99.99% (particle size 130 nm and surface area of 5–10 m²/g) were obtained from Sigma Aldrich Company, USA. Fabrication of ZnO oxide nanopowder as reported by the company was conducted by the physical vapor synthesis (PVS) method to produce ZnO nanoparticles with unique characteristics.

Photocatalytic degradation of imidacloprid in water

This experiment was designed to assess the efficiency of the advanced oxidation process using zinc oxide nanopowder (synthesized) and normal-sized zinc oxide (commercial) to remove imidacloprid (Figure 1) from water. River water samples of the chemical composition given in Table 1 were collected from the Yamato River (a Japanese class A river in the Kansai region, Japan) in May of 2018. Water samples were filtered through a glass fiber filter (GC-50, diameter: 47 mm, nominal rating: 0.5 μm, Advantec) before use.

Irradiation of water samples was conducted using a solar simulator (Oriel, Model 81160-1000) unit equipped with a 300 W Xenon lamp (O₃ free) with special glass filters (Oriel, AM0, and AM1.0) that restricted the transmission of wavelengths below 300 nm. The solar simulator provides illumination approximating natural sunlight at the Earth’s surface, and thus the emitted light has been shown to be equivalent to natural sunlight when conducting photodegradation of pesticides in the aquatic environment (Durand et al. 1994). Experimental data from all the photo-irradiation equipment were normalized to a 2-nitrobenzaldehyde degradation rate (J₂NB) of 0.0093 s⁻¹ which was determined at noon under clear sky conditions in Higashi-Hiroshima city (34°25’N) on May 1, 1998 (Arakaki et al. 1999).

For photocatalytic removal of imidacloprid, a water solution containing imidacloprid (1 mg/L) and zinc oxide (1,000 mg/L) in normal or nanosize was stirred for 15 min. This was done in the dark to attain equilibrium while taking the loss of imidacloprid caused by adsorption into account. Hydrogen peroxide was then added at a concentration of 20 mM and the final volume of the solution in the beaker was diluted to 100 mL with Milli-Q water. The pH of the solution was subsequently adjusted to 7, which was the optimum pH for the zinc oxide catalyst, using a Jenway pH/mV/temperature meter, Model 3510 (Derbalah 2009). During irradiation, the solution in the quartz glass cell (60 mL) was mixed well with a stir bar while the temperature was kept constant at 20 °C. After irradiation started, the

| Chemical composition of river water used in photocatalytic degradation of imidacloprid | Concentration (μM) |
|---|---|
| Cl⁻ | 1,135.79 ± 10.25 |
| NO₂⁻ | 6.49 ± 0.21 |
| NO₃⁻ | 203.42 ± 2.45 |
| SO₄²⁻ | 211.78 ± 5.47 |
| Na⁺ | 1,361.60 ± 15.24 |
| NH₄⁺ | 7.42 ± 0.54 |
| K⁺ | 142.16 ± 1.23 |
| Mg²⁺ | 193.05 ± 2.45 |
| Ca²⁺ | 622.94 ± 3.87 |
| pH | 7.70 ± 1.78 |
| DOC | 3.09 ± 0.28 (mg/L) |
solutions from the irradiated samples were removed at regular intervals for HPLC analysis. All experiments were conducted in triplicate and the average values were reported.

To evaluate the effects of catalyst concentration on the degradation rate of imidacloprid, different initial concentrations of ZnO were used (100, 500, and 1,000 mg/L). To investigate the effects of pH on the degradation process, different pH values were employed (5, 7, and 9). The effects of imidacloprid concentration on its degradation rate were investigated using different initial concentrations (100, 500, and 1,000 μg/L). Finally, the effects of water type on the degradation rate of imidacloprid were evaluated in river and Milli-Q water.

The efficacy of H2O2 alone without catalyst in the presence of solar light for the degradation of imidacloprid at different initial concentrations (100, 500, and 1,000 μg/L) was evaluated in Milli-Q water spiked with H2O2 (20 mM) at the optimum pH value (7). The efficacy of H2O2 (20 mM) alone without catalyst in the presence of solar light for the degradation of imidacloprid (1,000 μg/L) at pH value of 7 in river water was also evaluated. A blank experiment under the ZnO (nano)/H2O2 system was conducted with the tested insecticide at the optimum pH under dark conditions to assess the abiotic loss of the tested insecticide (imidacloprid) (Derbalah et al. 2004). Direct photolysis of imidacloprid under solar simulator without ZnO or hydrogen peroxide was also examined.

**HPLC analysis**

The treated water samples were analyzed directly using an HPLC system with a mixture of acetonitrile and Milli-Q water (30:70) as the mobile phase. The flow rate was maintained at 1.0 ml min⁻¹ and the UV detector wavelength was 270 nm (Dewangan et al. 2016). The detection and quantification limit of imidacloprid in water were 1.2 and 3 μg/L, respectively. The degradation rate constant (k) and half-life (t_{1/2}) were calculated as described by Bondarenko et al. (2004) and Evgenidou et al. (2007). The photodegradation rate constants were normalized as described by Arakaki et al. (1999).

**Mineralization experiments**

To evaluate the mineralization rate of imidacloprid in Milli-Q water by the two tested oxidation systems, losses in DOC and formation rate of inorganic ions (Cl⁻ and NO₂⁻) under irradiation using the solar simulator described above in this study were measured using a TOC analyzer and ion chromatography, respectively. For the loss of DOC with different times of solar light exposure (0, 2, 4, 6, and 8 h) a concentration of 3 mg C/L of imidacloprid was used. After exposure to solar light, the water samples were acidified using HCl and injected directly into a TOC analyzer that had been calibrated using standard solutions of potassium hydrogen phthalate. To monitor the process of imidacloprid (7 mg/L) mineralization to its inorganic ions, the yield of the selected major ions of chloride (Cl⁻) and nitrite (NO₂⁻) were measured using ion chromatography (IC) Dionex ICS-1600 system (Dionex Corporation, Sunnyvale, USA). The water samples were irradiated at different interval times (0, 2, 4, 6, and 8 hours) for both TOC and ion chromatography analysis. The mineralization data were normalized as mentioned earlier in this study.

**Photo-formation rate of hydroxyl radical (•OH) under both oxidation systems**

•OH production from an irradiated solution containing H2O2 (20 mM) and ZnO (1 mg/L) was determined using benzene as a chemical probe. Benzene reacts with •OH to form phenol with a high reaction rate constant of 7.8 × 10⁹ M⁻¹ s⁻¹. The solution was spiked with 1.2 mM benzene (final concentration) and irradiated under a solar simulator (Takeda et al. 2004; Nakatani et al. 2007). A detailed description of the solar simulator is provided in Nakatani et al. (2007). Samples were irradiated for 10 min, during which time aliquots were obtained at various intervals for phenol analysis using HPLC. The HPLC system consisted of a pump (LC-10A, Shimadzu, Kyoto, Japan) that delivered eluent (acetonitrile: MQ (60:40)) at a flow rate of 1 mL/min. An injection port equipped with a 50 μL sample loop was used to inject samples into the system. Phenol was separated on a C₁₈ column (Cosmosil, MS-II, 250 mm × 4.6 mm, 5 μm), then analyzed using a fluorescence detector (RF-10AXL, Shimadzu, Kyoto, Japan) set at excitation/emission wavelengths of 270/298 nm. The initial rate of phenol production was obtained and applied in Equation (1) to determine the rate of •OH photoformation (R_{OH}) (Mopper...
& Zhou 1990):

$$R_{OH} = \frac{R_{phenol}}{Y_{phenol} \times F_{benzene-OH}}$$ (1)

where $R_{phenol}$ is the photoformation rate of phenol in each irradiated sample; $Y_{phenol}$ is the yield of phenol formed in the reaction between benzene and OH, and $F_{benzene-OH}$ is the fraction of OH that reacts with benzene. A $Y_{phenol}$ of 0.75 reported by Arakaki & Faust (1992) was utilized. The $F_{benzene-OH}$ obtained in both samples (containing normal and nano ZnO) was 0.9.

Data analysis

For analysis of variance (ANOVA) of obtained data, XLSTAT PRO statistical analysis software (Addinsoft) was used. Fisher’s least significant difference (LSD) test was used to separate the mean of each treatment. All analyses were performed at a significance value of $P \leq 0.05$.

RESULTS

Kinetics of photocatalytic removal of imidacloprid in water

Photocatalytic degradation of imidacloprid in water using two advanced oxidation systems (ZnO(nano)/H$_2$O$_2$/artificial sunlight and ZnO(normal)/H$_2$O$_2$/artificial sunlight) was investigated. The effects of imidacloprid concentration, ZnO concentration, solution pH, catalyst particle size (nano and normal), and water type (Milli-Q and river waters) were evaluated to identify the optimum conditions for photocatalytic removal of imidacloprid in water.

Effect of imidacloprid concentration

The effects of imidacloprid initial concentration (100, 500, and 1,000 μg/L) on its degradation rate were evaluated. As shown in Table 2, the degradation rate of imidacloprid decreased as its concentration increased in the examined advanced oxidation systems (ZnO(nano)/H$_2$O$_2$/artificial sunlight, ZnO(normal)/H$_2$O$_2$/artificial sunlight and H$_2$O$_2$/artificial sunlight). The half-lives of imidacloprid were 41.68, 83.36, and 85.89 min for imidacloprid at concentrations of 100, 500, and 1,000 μg/l, respectively, when normal sized zinc oxide was used (Table 2). However, when using nanosized zinc oxide, the half-lives of imidacloprid were 26.24, 50.61, 72.68 min at concentrations of 100, 500, and 1,000 μg/l, respectively (Table 2). The half-lives of imidacloprid were 77.4,116.1, and 135.2 min for imidacloprid at concentrations of 100, 500, and 1,000 μg/l, respectively, when H$_2$O$_2$/artificial sunlight only was used.

Effect of catalyst concentration

The effects of zinc oxide (normal and nanosized) initial concentration (100, 500, and 1,000 mg/L) on the degradation

| Process                        | Concentration of imidacloprid | Degradation rate constant, k, (min$^{-1}$) | Half-life $t_{1/2}$ (min) |
|-------------------------------|-------------------------------|---------------------------------------------|----------------------------|
| ZnO(normal)/H$_2$O$_2$/artificial sunlight | 100 μg/L                      | 0.0166 ± 0.0001                            | 41.68 ± 0.18$^b$          |
|                               | 500 μg/L                      | 0.0083 ± 0.00001                           | 83.36 ± 0.56$^{de}$       |
|                               | 1,000 μg/L                    | 0.0081 ± 0.0001                            | 85.89 ± 0.34$^{ef}$       |
| ZnO(nano)/H$_2$O$_2$/artificial sunlight | 100 μg/L                      | 0.0264 ± 0.0002                            | 26.24 ± 0.39$^a$          |
|                               | 500 μg/L                      | 0.0137 ± 0.0002                            | 50.61 ± 0.42$^{c}$        |
|                               | 1,000 μg/L                    | 0.0095 ± 0.0001                            | 72.68 ± 0.68$^{ef}$       |
| H$_2$O$_2$/artificial sunlight | 100 μg/L                      | 0.0090 ± 0.0001                            | 77.4 ± 0.88$^{d}$         |
|                               | 500 μg/L                      | 0.0060 ± 0.0001                            | 116.1 ± 1.20$^{d}$        |
|                               | 1,000 μg/L                    | 0.0051 ± 0.0001                            | 135.2 ± 2.60$^{f}$        |

Statistical comparisons were made among treatments within a single column. The different letters represent significant differences using Fisher’s LSD test at $P \leq 0.05$. Data presented in mean value (three replicates) ± standard deviation.
rate of imidacloprid were evaluated. As shown in Table 3, the degradation rate of imidacloprid increased with increasing catalyst concentration following treatment with both normal and nanosized zinc oxide. Moreover, the half-lives of imidacloprid were 149.18, 94.48, and 85.89 min following treatment with normal sized zinc oxide at 100, 500, and 1,000 mg/l, respectively (Table 3). However, treatment with nanosized zinc oxide at 100, 500, and 1,000 mg/l resulted in imidacloprid half-lives of 97.41, 91.43, and 72.68 min, respectively (Table 3).

Effect of pH

Photocatalytic degradation of imidacloprid by the two advanced oxidation systems (ZnO(nano)/H2O2/artificial sunlight and ZnO(normal)/H2O2/artificial sunlight) under different pH values (5, 7, and 9) was conducted to evaluate the effects of pH on degradation efficiency. As shown in Table 4, the highest degradation rate of imidacloprid was recorded under a pH of 7 followed by 9 and 5, respectively, in both advanced oxidation systems. In the normal advanced oxidation system (ZnO(normal)/H2O2/artificial sunlight), the half-lives of imidacloprid were 85.89, 141.72, and 123.23 min under pH values of 5, 7, and 9, respectively. However, in the nano advanced oxidation system (ZnO(nano)/H2O2/artificial sunlight), the half-lives of imidacloprid were 72.68, 88.57, and 83.36 min under pH values of 5, 7, and 9, respectively.

Effect of water type on degradation process

River and Milli-Q water were used to evaluate the effects of water type on the photocatalytic degradation of imidacloprid under examined advanced oxidation systems (H2O2/UV-Vis, ZnO(normal)/H2O2/artificial sunlight and ZnO(nano)/H2O2/artificial sunlight) at a pH of 7. As shown in Table 5, the degradation rate of imidacloprid in Milli-Q water was faster than that of river water in both examined systems. For the normal oxidation system (ZnO(normal)/H2O2/artificial sunlight), imidacloprid half-lives of 85.89 and 123.23 min were observed in Milli-Q and river water, respectively. However, in nano oxidation systems

### Table 3 | Degradation rate and half-lives of imidacloprid (1 mg/L) at different concentrations of ZnO and H2O2 concentration of 20 mM at pH 7

| Process                              | Concentration of ZnO | Degradation rate constant, k, (min⁻¹) | Half-life t₁/₂ (min) |
|--------------------------------------|----------------------|--------------------------------------|----------------------|
| ZnO(normal)/H2O2/artificial sunlight | 100 mg/L             | 0.0046 ± 0.0001                      | 149.18 ± 1.25⁵       |
|                                      | 500 mg/L             | 0.0073 ± 0.00002                     | 94.48 ± 1.34⁶        |
|                                      | 1,000 mg/L           | 0.0080 ± 0.00003                     | 85.89 ± 2.65⁷        |
| ZnO(nano)/H2O2/artificial sunlight   | 100 mg/L             | 0.0071 ± 0.00004                     | 97.41 ± 3.17⁸        |
|                                      | 500 mg/L             | 0.0076 ± 0.00001                     | 91.43 ± 1.87⁹        |
|                                      | 1,000 mg/L           | 0.0095 ± 0.00001                     | 72.68 ± 2.35⁹        |

Statistical comparisons were made among treatments within a single column. The different letters represent significant differences using Fisher’s LSD test at P ≤ 0.05. Data presented in mean value (three replicates) ± standard deviation.

### Table 4 | Degradation rate and half-lives of imidacloprid (1 mg/L) at different pH values with ZnO and H2O2 concentration of 1,000 mg/l and 20 mM, respectively

| Process                              | pH value | Degradation rate constant, k, (min⁻¹) | Half-life t₁/₂ (min) |
|--------------------------------------|----------|--------------------------------------|----------------------|
| ZnO(normal)/H2O2/artificial sunlight | pH 5     | 0.0081 ± 0.0001                      | 141.72 ± 2.45⁶       |
|                                      | pH 7     | 0.0048 ± 0.00002                     | 85.89 ± 2.63¹        |
|                                      | pH 9     | 0.0056 ± 0.00002                     | 123.25 ± 1.68²       |
| ZnO(nano)/H2O2/artificial sunlight   | pH 5     | 0.0095 ± 0.0001                      | 88.57 ± 2.41³        |
|                                      | pH 7     | 0.0078 ± 0.0001                      | 72.68 ± 2.35⁴        |
|                                      | pH 9     | 0.0083 ± 0.00001                     | 83.36 ± 0.56⁴        |

Statistical comparisons were made among treatments within a single column. The different letters represent significant differences using Fisher’s LSD test at P ≤ 0.05. Data presented in mean value (three replicates) ± standard deviation.
The effects of zinc oxide particle size (normal and nanosized) on the photocatalytic degradation of imidacloprid in Milli-Q and river water were investigated. The results showed that the particle size of zinc oxide catalyst significantly influenced the photocatalytic degradation rate of imidacloprid, with nanosized zinc oxide resulting in faster degradation than normal sized zinc oxide (Table 5). As shown in Table 5, the half-lives for imidacloprid were 85.89 and 72.68 min in Milli-Q water when normal and nano sized zinc oxide were used, respectively. However, for river water, the half-lives of imidacloprid were 123.23 and 88.57 min using normal and nanosized zinc oxide, respectively.

### Effect of catalyst particle size

The effects of zinc oxide particle size (normal and nanosized) on the photocatalytic degradation of imidacloprid in Milli-Q and river water were investigated. The results showed that the particle size of zinc oxide catalyst significantly influenced the photocatalytic degradation rate of imidacloprid, with nanosized zinc oxide resulting in faster degradation than normal sized zinc oxide (Table 5). As shown in Table 5, the half-lives for imidacloprid were 85.89 and 72.68 min in Milli-Q water when normal and nano sized zinc oxide were used, respectively. However, for river water, the half-lives of imidacloprid were 123.23 and 88.57 min using normal and nanosized zinc oxide, respectively.

### Total mineralization of imidacloprid

The total mineralization of imidacloprid in water was confirmed by the decline in DOC and the yield of inorganic ions (Cl⁻ and NO₂⁻) with irradiation time under both examined advanced oxidation systems. The mineralization of imidacloprid to CO₂ and H₂O was expressed as a reduction in DOC with irradiation time. As shown in Figure 2, the ZnO(nano)/H₂O₂/artificial sunlight system was an effective method for mineralization of imidacloprid, with more than 97% of imidacloprid being mineralized within 8 hours of irradiation. In comparison, around 72% of imidacloprid was mineralized within the same irradiation time using the ZnO(normal)/H₂O₂/artificial sunlight system.

Moreover, the total mineralization of imidacloprid to its inorganic ions (Cl⁻ and NO₂⁻) was expressed by the yield of chloride and nitrite ions with irradiation time. As shown in Figures 3(a) and 3(b), the mineralization rate of imidacloprid to its inorganic ions (Cl⁻ and NO₂⁻) was higher by irradiation using a ZnO(nano)/H₂O₂/artificial sunlight compared with the ZnO(normal)/H₂O₂/artificial sunlight system. Based on molecular weight ratio, the

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**Table 5**  Degradation rate and half-lives of imidacloprid (1 mg/L) in different water matrix at pH value of 7 and ZnO and H₂O₂ concentration of 1,000 mg/L and 20 mM, respectively

| Process                                | Water matrix  | Degradation rate constant, k, (min⁻¹) | Half-life t₁/₂ (min) |
|----------------------------------------|---------------|--------------------------------------|---------------------|
| ZnO(normal)/H₂O₂/artificial sunlight   | Milli-Q water | 0.0081 ± 0.00001                     | 88.57 ± 2.41b       |
|                                        | River water   | 0.0056 ± 0.0002                      | 123.25 ± 1.68a      |
| ZnO(nano)/H₂O₂/artificial sunlight     | Milli-Q water | 0.0095 ± 0.0001                      | 72.68 ± 2.35a       |
|                                        | River water   | 0.0078 ± 0.0001                      | 88.57 ± 2.41a       |
| H₂O₂/artificial sunlight               | Milli-Q water | 0.0051 ± 0.0001                      | 135.2 ± 2.60a       |
|                                        | River water   | 0.0045 ± 0.0001                      | 154.8 ± 2.41a       |
| Direct photolysis                       | Imidacloprid only | 0.0029 ± 0.00001                 | 236.20 ± 3.25       |

Statistical comparisons were made among treatments within a single column. The different letters represent significant differences using Fisher’s LSD test at P ≤ 0.05. Data presented in mean value (three replicates) ± standard deviation.

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*(ZnO(nano)/H₂O₂/ artificial sunlight), the imidacloprid half-lives were 72.68 and 88.57 min in Milli-Q and river water, respectively. In the case of H₂O₂/artificial sunlight system, imidacloprid half-lives of 135.2 and 154.8 min were observed in Milli-Q and river water, respectively.*
mineralization percentages of Cl\(^{-}\) and NO\(_2\) were 97.5 and 79% under irradiation using ZnO(nano)/H\(_2\)O\(_2\)/artificial sunlight while under ZnO(normal)/H\(_2\)O\(_2\)/artificial sunlight system the mineralization percentages were 76 and 54%, respectively. The results showed that the yield of Cl\(^{-}\) was greater than that of NO\(_2\) under both examined systems. Therefore, imidacloprid was almost completely de-chlorinated by the end of the irradiation time.

**Photoformation of OH under examined oxidation systems**

The photoformation of OH for the two examined oxidation systems that were used for imidacloprid photocatalytic removal besides H\(_2\)O\(_2\) alone without the catalyst are presented in Table 6. The data indicate that the rate of OH formation under the ZnO(nano)/H\(_2\)O\(_2\)/artificial sunlight system (13.8 \(\times\) 10\(^{-8}\) M s\(^{-1}\)) was higher than that generated under the ZnO(normal)/H\(_2\)O\(_2\)/artificial sunlight system (12.8 \(\times\) 10\(^{-8}\) M s\(^{-1}\)). Moreover, the rate of OH formation under both examined oxidation systems was significantly enhanced compared with when H\(_2\)O\(_2\) alone was used without the catalyst in the presence of solar light (10.1 \(\times\) 10\(^{-8}\) M s\(^{-1}\)).

**DISCUSSION**

In this study, significant degradation of imidacloprid with a short half-life (41.68 and 26.24) was observed under the examined advanced oxidation systems, ZnO(normal)/H\(_2\)O\(_2\)/artificial sunlight and ZnO(nano)/H\(_2\)O\(_2\)/artificial sunlight, respectively. The effective degradation of imidacloprid by the two examined advanced oxidation systems was due to the high generation rate of highly reactive OH under both oxidation systems. The high generation rate of OH under both oxidation systems can be explained as follows: ZnO semiconductors act as sensitizers in the presence of light; thus, when the light energy irradiating the conduction band is greater than the band gap, valence band electrons are promoted to the conduction band, leaving a hole behind (Equation (2)). These electron (e\(_{-}\ cb\))-hole (h\(_{+}\ vb\)) pairs can either recombine again (Equation (3)) or react in a separate way with other chemical species. It is possible that adsorbed H\(_2\)O or OH\(^{-}\) can be oxidized by the holes in the ZnO valence band and generate OH radicals (Equation (4)). Moreover, as described in Equation (5), O\(_2\) can be reduced to superoxide radical (O\(_2\)\(^{-}\)) by conduction band electrons on the ZnO surface. The O\(_2\)\(^{-}\) can then produce H\(_2\)O\(_2\) or -OOH as described in Equations (6) and (7). H\(_2\)O\(_2\) can produce ‘OH radicals as described in Equations (8) and (9) (Plank et al. 2009). Imidacloprid degradation or mineralization may be induced by the generated ‘OH, which are highly reactive and attack imidacloprid to form intermediate products. These intermediates subsequently react with more hydroxyl radicals until imidacloprid is mineralized to CO\(_2\).
and H\textsubscript{2}O (Equation (10)) (Hoffmann et al. 1995; Kaneco et al. 2007) and other inorganic ions.

\begin{align*}
\text{ZnO} + \text{h}_\circ \rightarrow \text{ZnO} (e_{-cb}/h_{+vb}) & \rightarrow e_{-cb} + h_{+vb} \\
 e_{-cb} + h_{+vb} & \rightarrow \text{heat} \\
 h_{+vb} + \text{OH}^- (\text{or H}_2\text{O})_{ads} & \rightarrow \bullet \text{OH}(+\text{H}^+) \\
 e_{-cb} + \text{O}_2 & \rightarrow \text{O}_2^- \\
 \text{O}_2^- + \text{H}_2\text{O} + \text{H}^+ & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
 \text{H}_2\text{O}_2 + \text{hv} & \rightarrow 2\text{OH} \\
 \text{H}_2\text{O}_2 + \text{O}_2^- & \rightarrow \text{OH}^- + ^* \text{OH} \\
 ^*\text{OH}(\text{or } \bullet \text{OOH}) + \text{imidacloprid} & \rightarrow \text{Oxidative products} + \text{CO}_2 + \text{H}_2\text{O} + \text{Cl} + \text{NO}_2 \\
\end{align*}

Investigation of the effects of the initial concentration of imidacloprid on the rate of its degradation using the tested oxidation systems showed that the imidacloprid degradation rate decreased in response to increasing the primary imidacloprid concentration. The observed decrease in the pesticide degradation rate with an increase in its initial concentration may have occurred because a higher concentration of pollutants reduces the rate of hydroxyl radicals formation and thus decreases the rate of degradation in the solution (Patil et al. 2014). Also, in a previous study, Patil & Gogate (2012) found a similar trend in the degradation of methyl parathion.

The results revealed that the photocatalytic degradation rate of imidacloprid increased with increasing concentration of ZnO catalyst either at nano or normal size. This may have occurred because the increase in ZnO concentration led to an increase in its surface area (an increase of active sites) that became available for photocatalytic reaction (Eissa et al. 2015), which led to increased generation of \text{OH} and subsequently faster degradation of imidacloprid. These results are in agreement with those reported by Changgen et al. (2013), who found the degradation of imidacloprid significantly increased with increasing catalyst dose.

The results of this study showed that pH is an important factor affecting the photocatalytic degradation of imidacloprid in water, which is consistent with the results reported by Thuyet et al. (2013), who explained that changes in pH in water play an important role in pesticide destruction. Furthermore, analysis of the imidacloprid degradation rate as a function of water solution pH indicated that increases in pH increased the photodegradation rate. This may have occurred because increasing the hydroxyl ion by elevating pH could enhance the rate of \text{OH} generation through photo-oxidation via holes in the ZnO valence band. These holes may react with surface-bound H\textsubscript{2}O or OH\textsuperscript{−} to generate \text{OH} (Equation (4)) (Chu & Wong 2004). Moreover, the \text{OH} are likely the dominant oxidizing species in the photocatalytic process (Chu & Wong 2004; Eissa et al. 2015).

The degradation rate of imidacloprid in Milli-Q water was faster than that in river water under both advanced oxidation systems, which agrees with the findings reported by Muhamad (2010a) and Fadaei et al. (2012b), who demonstrated that the order of the catalytic photodegradation rate was distilled water > river water > drainage water.

The low degradation rate of imidacloprid in river water relative to that in Milli-Q water was likely due to the presence of \text{OH} scavengers such as dissolved organic matter (DOM), Cl\textsuperscript{−} and CO\textsubscript{3}\textsuperscript{2−} in river water which will compete for the generated \text{OH} (Pare et al. 2008; Derbalah 2009). This will reduce the concentration of \text{OH} available for degradation of imidacloprid in river water compared to Milli-Q water where such scavengers are absent. A typical example of how Cl\textsuperscript{−} may scavenge \text{OH} is shown in Equation (11). Moreover, the common inorganic anions in river water such as Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, and SO\textsubscript{4}\textsuperscript{2−} can be competitively adsorbed on the surface of the photocatalyst and decrease the photodegradation rate of organic compounds (Chládková et al. 2015). As a result, this reduction in the rate of hydroxyl radical generation in river water slows the degradation rate of imidacloprid. In addition, DOC, which is present in river water, absorbs most of the emitted photons, thereby slowing the degradation of imidacloprid (Konstantinou et al. 2006).

\begin{equation}
\text{Cl}^{-} + ^{*}\text{OH} \rightarrow \text{Cl}^{*} + \text{OH}^{-} \tag{11}
\end{equation}

As shown in Table 5, there was considerable degradation of imidacloprid in Milli-Q water by direct photolysis, with a half-life of 236.2 min; however, the degradation of imidacloprid under dark conditions using both oxidation systems...
was negligible. These findings are in agreement with the results reported by Changgen et al. (2013). The negligible degradation of imidacloprid in the dark could have been caused by hydrolysis and volatilization (Thuyet et al. 2013).

The degradation of imidacloprid under H2O2/artificial sunlight system without the catalyst was lower than that of using ZnO catalyst either in normal or nano size and this may be due to the high generation rate of hydroxyl radical in both catalyst systems compared to hydrogen peroxide only, as shown in Table 6. This also implies the necessity of using ZnO catalyst for removal of imidacloprid in water. This is in agreement with the findings of El-Saharty & Hassan (2014), who reported that the degradation of carbendazim and metalaxyl was much faster under ZnO /H2O2/UV compared to H2O2/UV.

In this study, the degradation and mineralization rates of imidacloprid were enhanced by irradiation under the ZnO(nano)/H2O2/artificial sunlight system relative to the ZnO(normal)/H2O2/artificial sunlight system. This may have been because the zinc oxide nanocatalyst used in the nano oxidation system had a small particle size that offered much greater surface area and reactivity, leading to a higher rate of ·OH generation relative to the normal particles of zinc oxide catalyst (Dhal et al. 2015), and a subsequently higher degradation rate of organic pollutants (Dhal et al. 2015). Moreover, the higher formation rate of ·OH under the ZnO(nano)/H2O2/artificial sunlight system than the ZnO(normal)/H2O2/artificial sunlight system (Table 3) supports this trend. The higher formation rate of ·OH in irradiated H2O2 solutions in the presence of ZnO compared with H2O2 only reflects the significant role of ZnO catalyst in enhancing the formation rate of ·OH.

A strong and clear index of the success of an advanced oxidation process is the complete mineralization of toxic intermediates in addition to the parent compound itself. Based on this criterion, the current study has been successful (Huston & Pignatello 1999; Derbalah et al. 2004). The reduction in DOC concentration (Figure 2) and the yield of inorganic ions (Figure 3) indicate significant mineralization of imidacloprid. Moreover, the faster degradation and mineralization rates of imidacloprid expressed in a reduction in DOC and the formation of Cl− and NO2− ions under the ZnO(nano)/H2O2/artificial sunlight system compared with the ZnO/H2O2/artificial sunlight system may have been because of the high rate of ·OH generation under the ZnO(nano)/H2O2/artificial sunlight system compared with the ZnO/H2O2/artificial sunlight system. The fabrication of nano-sized ZnO increased its surface area and subsequently its reactivity to produce ·OH compared with normal-sized ZnO, as shown in Table 6. This high generation rate of ·OH under the nano oxidation system led to faster mineralization of imidacloprid compared with normal oxidation systems. The low formation rate of nitrite ion under both oxidation systems compared to chloride may be due to the fact that part of nitrite is oxidized to nitrate by ·OH (Son et al. 2011).

CONCLUSIONS

The degradation rate of imidacloprid using the ZnO(nano)/H2O2/artificial sunlight oxidation system was faster than that of the ZnO(normal)/H2O2/artificial sunlight oxidation system in Milli-Q or river water. The photoformation rate of ·OH using ZnO (nano)/H2O2/artificial sunlight was higher than that of the ZnO (normal)/H2O2/artificial sunlight system. Some parameters such as water type, pH, catalyst, and pesticide concentration as well as the catalyst particle size significantly affect the efficacy of advanced oxidation processes during imidacloprid removal from water. Total mineralization of imidacloprid was only achieved by using the ZnO(nano)/H2O2/artificial sunlight oxidation system, which confirms the complete detoxification of imidacloprid in treated water. Advanced oxidation processes, particularly with zinc oxide nanocatalyst, can be regarded as an effective photocatalytic method for imidacloprid removal from water.

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REFERENCES

Arakaki, T. & Faust, B. C. 1998 Sources, sinks, and mechanisms of hydroxyl radical (·OH) photoproduction and consumption in acidic authentic continental cloud waters from Whiteface Mountain, New York: the role of the Fe(r) (r = II, III) photochemical cycle. *Journal of Geophysical Research* 103 (D3), 3487–3504.

Arakaki, T., Miyake, T., Shibata, M. & Sakugawa, H. 1999 Photochemical formation and scavenging of hydroxyl radical in rain and dew water. *Nippon Kagaku Kaishi* 1999 (5), 335–340.

Armbrust, K. L. & Peeler, H. B. 2002 Effects of formulation on the run-off of imidacloprid from turf. *Pest Management Science* 58 (7), 702–706.

Baruah, S., Pal, S. K. & Dutta, J. 2012 Nanostructured zinc oxide for water treatment. *Nanoscience Nanotechnology Asia* 2, 90–102.

Blake, D. 2001 Bibliographic Work on the Heterogeneous Photocatalytic Removal of Hazardous Compounds From Water and air. Technical Report, NREL/TP-510-31319, National Renewable Energy Laboratory, Golden, CO, USA.

Blanco, J. & Malato, S. 2001 Solar Detoxification. Natural Sciences, World Solar Programme 1996–2005 (chapter 2), UNESCO, Harare. http://www.unesco.org/science/wsp

Bondarenko, S., Gan, J., Haver, D. L. & Kabashima, J. N. 2004 Persistence of selected organophosphate and carbamate insecticides in waters from a coastal watershed. *Environmental Toxicology Chemistry* 23, 2649–2654.

Changgen, F., Gang, X. & Xia, L. 2013 Photocatalytic degradation of imidacloprid by composite catalysts H3PW12O40/La2O3. *Journal of Rare Earths* 31, 44–48.

Chládková, B., Evgénidou, E., Kvitk, L., Panáček, A., Zboril, R., Kovář, P. & Lambropoulou, D. 2015 Adsorption and photocatalysis of nanocrystalline TiO2 particles for reactive red 195 removal: effect of humic acids, anions and scavengers. *Environmental Science Pollution Research* 22, 16514–16524.

Chu, W. & Wong, C. C. 2004 The photocatalytic degradation of dicamba in TiO2 suspensions with the help of hydrogen peroxide by different near UV irradiations. *Water Research* 38 (4), 1037–1043.

Colón, G., Belver, C. & Fernandez-García, M. 2007 Nanostructured oxides in photocatalysis. In: Synthesis, Properties and Applications of Solid Oxides (J. A. Rodriguez & M. Fernandez-García, eds). Wiley, New York, USA, pp. 491–592.

Derbalah, A. S. 2009 Chemical remediation of carbofuran insecticide in aquatic system by advanced oxidation processes. *Journal of Agriculture Research Kafr El-Sheikh University* 35, 308–327.

Derbalah, A. S. & Ismail, A. A. 2012 Efficiency of different remediation technologies for fenitrothion and dimethoate removal in the aquatic system. *Agrochimica Journal* 56 (2), 234–246.

Derbalah, A. S., Nakatani, N. & Sakugawa, H. 2004 Photocatalytic removal of fenitrothion in pure and natural waters by photo-Fenton reaction. *Chemosphere* 57, 635–644.

Derbalah, A. S., Ismail, A. A. & Shaheen, S. M. 2013 Monitoring of organophosphorus pesticides and remediation technologies of the frequently detected compound (chlorpyrifos) in drinking water. *Polish Journal of Chemical Technology* 15 (3), 25–34.

Derbalah, A. S., Ismail, A. A., Hamza, A. M. & Shaheen, S. M. 2014 Monitoring and remediation of organochlorine residues in water. *Water Environment Research* 86 (7), 584–593.

Derbalah, A. S., Ismail, A. A. & Shaheen, S. M. 2016 The presence of organophosphorus pesticides in wastewater and its remediation technologies. *Environmental Engineering and Management Journal* 15 (8), 1777–1787.

Dewangan, G., Mishra, A. & Manda, T. K. 2016 A simple RP-HPLC method for determining imidacloprid residues in goat tissues. *Biomedical Research* 27 (1), 11–15.

Dhal, J. P., Mishra, B. G. & Hota, G. 2015 Hydrothermal synthesis and enhanced photocatalytic activity of ternary Fe2O3/ZnFe2O4/ZnO nanocomposite through cascade electron transfer. *RSC Advances* 5, 58072–58083.

Durand, G., De Bertrand, N. & Barcelo, D. 1991 Applications of thermospray liquid chromatography-mass spectrometry in photochemical studies of pesticides in water. *Journal of Chromatography A* 554 (1–2), 233–250.

Eissa, F., Zidan, N. & Sakugawa, H. 2015 Photodegradation of the herbicide diuron in water under simulated sunlight. *Geochimical Journal* 49 (3), 309–318.

El-Saharty, A. & Hassan, I. A. 2014 Photochemical purification of wastewater from the fungicides and pesticides using advanced oxidation processes. *Australian Journal of Basic and Applied Sciences* 8 (1), 434–441.

Evgenidou, E., Konstantinou, I., Fytianoska, K. & Poulios, I. 2007 Oxidation of two organophosphorus insecticides by the photo-assisted fenton reaction. *Water Research* 41, 2015–2027.

Fadaei, A. M., Dehghani, M. H., Mahvi, A. H., Nasseri, S., Rastkari, N. & Shayeghi, M. 2012b Degradation of organophosphorus pesticides in water during UV/H2O2 treatment: role of sulphate and bicarbonate ions. *E-Journal of Chemistry* 9, 2015–2022.

Hayo, M. G. 1996 Assessing the impact of pesticides on the environment. *Agriculture Ecosystem Environment* 60, 81–96.

Hilz, B. E. & Vermeer, A. W. P. 2012 Effects of formulation on spray drift: a case study for commercial imidacloprid products. *Aspects of Applied Biology* 114, 445–450.

Hoffmann, M. R., Martin, S. T., Choi, W. & Bahnmann, D. W. 1995 Environmental applications of semiconductor photocatalysis. *Chemical Reviews* 95 (1), 69–96.
Huston, P. L. & Pignatello, J. J. 1999 Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. Water Research 33, 1238–1246.

Ishiki, R. R., Ishiki, H. M. & Takashima, K. 2005 Photocatalytic degradation of imazethapyr herbicide at TiO2/H2O interface. Chemosphere 58, 1461–1469.

Ismaïl, A. A., Derbalah, A. S. & Shaheen, S. M. 2015 Monitoring and remediation technologies of organochlorine pesticides in wastewater. Polish Journal of Chemical Technology 17, 115–122.

Jeschke, P. & Nauen, R. 2008 Neonicotinoids—from zero to hero in insecticide chemistry. Pest Management Science 64, 1084–1098.

Kaneco, S., Katsumata, H., Suzuki, T., Funasaka, T. & Kiyohisa, K. 2007 Solar photocatalytic degradation of endocrine disruptor di-n-butyl phthalate in aqueous solution using zinc oxide. Bulletin of the Catalysis Society of India 6, 22–33.

Konstantinou, I. K. & Albanis, T. A. 2005 Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways. Applied Catalysis B 42, 319–335.

Konstantinou, I. K., Hela, D. G. & Albanis, T. A. 2006 The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. Environment Pollution 141, 555–570.

Kopling, D. W., Thurman, E. M. & Goosby, D. A. 1996 Occurrence of selected pesticides and their metabolites in near-surface aquifers of the Midwestern United States. Environmental Science Technology 30, 335–340.

Kumari, L., Li, W. Z., Vannoy, C. H., Leblanc, R. M. & Wan, D. Z. 2010 Zinc oxide micro- and nanoparticles: synthesis, structure and optical properties. Materials Research Bulletin 45, 190–196.

Lewis, K. A., Tzilivikas, J., Warner, D. J. & Green, A. 2016 An international database for pesticide risk assessments and management. Human Ecological Risk Assessment 22, 1050–1064.

Meyer, M. T. & Thurman, E. M. 1996 Herbicide Metabolites in Surface Water and Ground Water. ACS Symposium Series 630, American Chemical Society, Washington, DC, USA.

Mopper, K. & Zhou, X. 1990 Hydroxyl radical photo production in the sea and its potential impact on marine processes. Science 250, 661–664.

Morrissey, C. A., Mineau, P., Devries, J. H., Sanchez-Bayo, F., Liess, M., Cavallaro, M. C. & Liber, K. 2015 Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: a review. Environmental International 74, 291–303.

Muhammad, S. G. 2010a Kinetic studies of catalytic photodegradation of chlorpyrifos insecticide in various natural waters. Arabian Journal of Chemistry 3, 127–133.

Nakatani, N., Hashimoto, N., Shindo, H., Yamamoto, M., Kikkawa, M. & Sakugawa, H. 2007 Determination of photoformation rates and scavenging rate constants of hydroxyl radicals in natural waters using an automatic light irradiation and injection system. Analystica Chimica Acta 581 (2), 260–267.

Pankaj, N. P., Sayli, D. B. & Parag, R. G. 2014 Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation. Ultrasonics Sonochemistry 21 (5), 1770–1777.

Pare, B. P., Singh, S. & Jonnalagadda, B. 2008 Visible light induced heterogeneous advanced oxidation process to degrade pararos anilin dye in aqueous suspension of ZnO. Indian Journal of Chemistry 4, 830–835.

Patil, P. N. & Gogate, P. R. 2012 Degradation of methyl parathion using hydrodynamic cavitation: effect of operating parameters and intensification using additives. Separation Purification Technology 95, 172–179.

Patil, P. N., Bote, S. D. & Gogate, P. R. 2014 Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation. Ultrasonics Sonochemistry 21 (5), 1770–1777.

Plank, N. O. V., Howard, I., Rao, A., Wilson, M. W. B., Duacti, C., Mane, R. S., Bandall, J. S., Louca, R. R. M., Greenham, N. C., Miura, H., Friend, R. H., Snaith, H. J. & Welland, M. E. 2009 Zno nanowire slide-state dye-sensitized solar cells using organic dyes and nanostructures. Journal of Physical Chemistry C 113, 18515–18522.

Readman, J. W., Albanis, T., Barcelo, D., Galassi, S., Tronczynski, J. & Gabrielides, G. 1993 Herbicide contamination of Mediterranean estuarine waters. Marine Pollution Bulletin 26, 613–619.

Sathiyanarayanan, S. P., Ravji, E. & Ramesh, A. 2009 Applications of zinc oxide nanorods as photocatalyst for the decontamination of imidacloprid and spirotetratram residues in water. The Open Catalysis Journal 2, 24–32.

Son, H., Ahammad, A. J. S., Rahman, M. M., Noh, K. M. & Lee, J. 2011 Effect of nitrate and nitrite as the source of OH radical in the O3/UV process with or without benzene. Bulletin of the Korean Chemical Society 32, 3039–3044.

Takeda, K., Takedoi, H., Yamaji, S., Ohita, K. & Sakugawa, H. 2004 Determination of hydroxyl radical photoproduction rates in natural waters. Analytical Science 20 (1), 153–158.

Thuyet, D. Q., Watanabe, H. & Ok, J. 2013 Effect of pH on the degradation of imidacloprid and fipronil in paddy water. Journal of Pesticide Science 38 (4), 223–227.

Toepfer, B., Gora, A. & Li Puma, G. 2006 Photocatalytic oxidation of multicomponent solutions of herbicides: reaction kinetics analysis with explicit photon absorption effects. Applied Catalysis B 68, 171–180.