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Decomposition of acetaminophen (Ace) using TiO2/UVA/LED system

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ABSTRACT

For photocatalytic degradation of organic pharmaceutical pollutants in wastewater, an important limitation is low photonic efficiency. To solve this problem, using periodic illumination is a good option. However, due to the nature of widely applied traditional mercury lamp, which cannot be turned on and off efficiently, the study of periodic illumination was limited. In this research, ultraviolet-A/light emitting diode (UVA/LED) lamp was introduced and a TiO_2/UVA/LED photocatalytic system was setup for acetaminophen (Ace) degradation study. The background study was conducted, which included the effects of H_2O_2, humic acid and bicarbonate ion concentrations. Different periodic pulse frequencies were applied, results in this study shows that smallest duty cycle (0.2) and shortest cycle time (20 ms) gave the highest photonic efficiency for photocatalytic degradation of Ace in the studied range. The effect of additional H_2O_2 was also studied. H_2O_2 added into the heterogeneous reaction system enhanced both decomposition rate and photonic efficiency under both continuous illumination mode and periodic illumination mode. The enhancement effect of H_2O_2, however, was found more obvious for controlled periodic illumination, especially for small duty cycles and short cycle times. In addition, by the addition of H_2O_2, the mineralization of Ace was accelerated probably due to the increase of hydroxyl radical concentration.

1. Introduction

Photocatalytic process using TiO_2 as catalyst is an attractive advanced oxidation technology for decomposition of pharmaceutical pollutants nowadays due to its high efficiency and environmental friendly property [1–4]. A lot of advantages of photocatalytic process have been widely demonstrated, some of which were summarized by Chong et al. [5]. Such advantages as high degradation efficiency, small footprint make photocatalytic process a promising technology for the destruction of aquatic environmental pollutants. However, low photonic efficiency currently prevents the application of photocatalytic technology for large scale water treatment [3]. This is because during photocatalytic process, the photo-generated hole-electron pairs are very easy and fast to recombine instead of reacting with pollutants in the system [6,7]. To increase the photonic efficiency and degradation rate is an ongoing research problem in many parts of the world [8–13]. For example, some of the interests were focused on the control of operational conditions such as catalyst concentration, light intensity, pH value and temperature [8,14]. In addition, controlled periodic illumination (CPI) was also found a good method to improve photonic efficiency in photocatalytic process [15–18]. However, the practical application of CPI is limited owing to the intrinsic character of wildly applied traditional mercury lamp which needs time to warm up before it can give expected light output. Furthermore, mercury lamp is easy to burn out if it is turned on and off quickly and frequently. So to overcome this problem in studying CPI using mercury lamp, different system designs are generated. For example, a rotating disk reactor was reported [18]. This rotating disk reactor employed a pneumatic shutter to completely block the light or allow the light to illuminate the entire coated surface of the catalyst to generate CPI. In this case, even though CPI is generated, the mercury lamp is not turned off during the dark period, and light energy during dark period is wasted from this point of view. On the other hand, this mechanical design is difficult to realize as short as milliseconds or microseconds level frequency change.

Recently, ultraviolet-A/light emitting diode (UVA/LED) has been suggested to be a powerful and efficient light source for water treatment [3,19]. UVA/LED is more efficient in converting electricity into light by a process called electroluminescence which bases on the recombination of excessive electrons and holes. This lamp can generate high frequency CPI and it was reported more effective for photocatalysis than that emitted from xenon lamps controlled by mechanical shutters [20]. It can be driven by direct current flow and emit high-intensity UVA light in a specific narrow spectrum. Light output is in linear relationship with direct current applied

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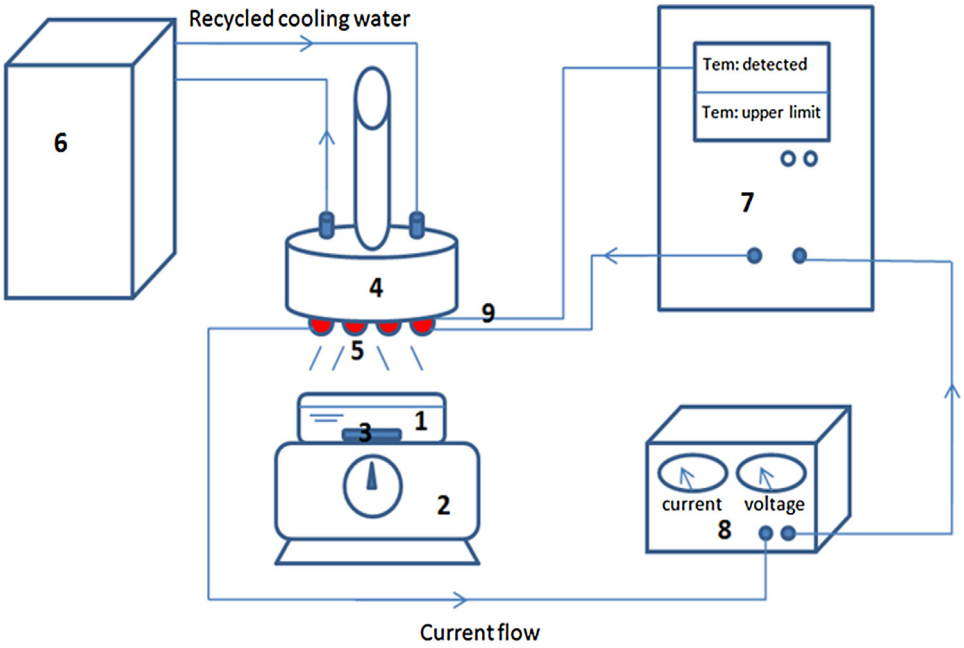

Fig. 1. Schematic diagram of experimental setup. 1: Crystallizing dish. 2: Magnetic stirrer. 3: Stir bar. 4: Hollowed aluminum cylinder. 5: UVA/LEDs. 6: Chiller with recycled cooling water. 7: Programmable logical controller (PLC). 8: DC power supplier. 9: Temperature detection head.

within the active region, so light output can be precisely adjusted to a precise value by only adjusting the forward current. In addition, compared to traditional mercury lamps, UVA/LED lamps are small, resistant to physical shock; they have a long life time (around 100,000 h) and do not generate mercury waste. Therefore, UVA/LED seems a promising light source to study the effect of periodic illumination. Furthermore, with the rapid development of LED industry, high power UVA/LED lamps are currently available in the market.

The main objective of this study is to explore the application of high power UVA/LED lamps for photocatalytic water treatment process. Acetaminophen (Ace, $C_8H_9NO_2$, pKa = 9.5) is a widely used over-the-counter analgesic and antipyretic and it is difficult to be completely degraded in conventional wastewater treatment processes. This compound had been detected in both wastewater treatment plant effluent and natural water bodies with concentrations from tens to hundreds ppb level [21,22]. It is the aim of this study to improve the degradation rate and photonic efficiency for Ace degradation by the UVA/LED/TiO_2 photocatalytic system by studying cycle time and duty cycle. In this particular scenario, CPI was two-dimensionally defined: specified by both cycle time ($\beta = \tau_L + \tau_D$) and duty cycle ($\gamma = \tau_L/(\tau_L + \tau_D)$). Cycle time controls one cycle light/dark time length and duty cycle controls the ratio of light time during one cycle. With this two-dimensional definition method, a specific CPI mode can be specified. With the help of a program controller in this study, light time (τ_L) and dark time (τ_D) were changed independently and this two factors were both studied in this research. In addition, in order to further improve the photonic efficiency and degradation rate, the effect of hydrogen peroxide addition was studied under both continuous illumination mode and CPI mode.

2. Materials and methods

2.1. Materials and experimental device

All pharmaceutical compounds were obtained from Sigma-Aldrich, Singapore and applied without further treatment. Non-porous titanium dioxide (Degusa-P25) was used as received from Aldrich, and the purity was reported greater than 99.5%. A Milli-Q water purification system (Millipore Synergy 185, US) provided the water used for all solutions and suspensions.

As shown in Fig. 1, high power UVA/LED lamps (peak wavelength 365 nm, SET, Inc, USA) were connected together to serve as a light source in this study. The radiation characteristic was measured by a spectrometer (USB4000, Ocean Optics, Inc. US) and it is shown in Fig. 2a. Eighteen lamps (three in series, six parallel groups) were connected to a direct-current (DC) power supply (ISO-TECH, IPS-2303, UK). The lamps were adhered with thermal grease to the lower surface of a hollowed aluminum cylinder (100 mm in diameter and 60 mm in height). Recycled cooling water at 25 °C was pumped through the center of aluminum cylinder to protect the lamps from overheating. For periodic illumination study, the light pulse frequency was controlled from 10 ms to 2000 ms by a programmable logic controller (PLC, Gama Automation Pte Ltd, Singapore). The light intensity was adjusted by changing the current of the DC power supply and measured by ILT1700 radiometer with a SED-033 probe (International light technologies, Inc, USA). Light intensity applied throughout this study was 5 mW/cm^2.

2.2. Experimental procedure and sample preparation

In this study, water samples were kept in a 10 cm diameter Pyrex® crystallizing dish (Aldrich, Singapore) which was located 2 cm under the UVA/LED lamps. The light beam fully illuminated the volume of the reaction sample. Magnetic stirrer provided proper mixing at arotational speed of 150 rpm. UV light intensity was kept constant at 5 mW/cm^2 and initial Ace concentration in reaction solution was 200 ppb (equivalent to 1.323×10^{-6}M) throughout this study. All experiments were conducted under room temperature(25 ± 2 °C). H_2O_2 concentration was determined by $KMnO_4$ titration method which was reported by Klassen [23]. The pH of water sample was adjusted to 5–6 by adding either sulfuric acid solution (0.01 M) or sodium hydroxide solution (0.02 M). To ensure good replication of experimental procedures, all experiments results were repeated three times and average results were reported.

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