Degradation of acetaminophen in aqueous solution by UV and UV-activated sludge processes

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ABSTRACT

Acetaminophen (N-acetyl-p-aminophenol, APAP) is one of the most common antipyretic analgesics used to treat common ailments throughout the world. Recently, APAP has been frequently detected in wastewater effluent and groundwater, resulting in potential risks to the environment. Current methods for eliminating APAP are complicated and cost-prohibitive. This study examined APAP degradation by ultraviolet-C (UV-C) and UV-C irradiation combined with activated sludge (UV/AS) to evaluate potential applications in wastewater treatment. The results of this study indicate that UV-C irradiation reached an APAP degradation efficiency of more than 52% and a degradation rate of 0.0012–0.0013 min⁻¹ during 720 min of exposure, while the initial APAP concentration exhibited only a nominal effect on the degradation rate. However, the UV/AS treatment demonstrated an APAP degradation rate that was 9.6 times the rate of the UV-C-only treatment, with a degradation efficiency of 99% over the same UV irradiation period. The results further indicated that APAP photolysis efficiency was more effective when applied to sterilized AS than when applied to unsterilized AS. Finally, excessive dosage of both AS and humic acid inhibited APAP photolysis efficiency.

Key words | acetaminophen, pharmaceuticals and personal care products, photolysis, ultraviolet/activated sludge, ultraviolet-C

INTRODUCTION

As one of the most prevalent pharmaceuticals and personal care products (PPCPs), acetaminophen (N-acetyl-p-aminophenol, APAP) is a common antipyretic analgesic that is often used to treat colds, fever, arthralgia, neuralgia, migraine headaches, and post-operative pain. Due to its oral administration and extensive usage, APAP and its metabolites have been discharged into wastewater effluent and groundwater for more than 50 years. In recent years, a number of studies have detected APAP in groundwater at levels ranging from ng/L to μg/L (Boix et al. 2015; Fairbairn et al. 2016; Paiga & Delerue-Matos 2016; Ma et al. 2017). This has given rise to concerns regarding the potential threat of APAP to environmental health and safety because its molecular structure includes a phenol ring, which makes APAP stable and hard to degrade (Figure 1). Although APAP’s toxic effects have only recently been clarified (Li et al. 2017), the toxicity of one of its metabolites (N-acetyl-p-benzoquinoneimine (NAPQI)) has been well-established. From a toxicity perspective, APAP is now considered to be the leading cause of acute liver failure in the United States (Larson et al. 2005) and it has also been designated as a Category 3 carcinogen by the World Health Organization’s International Agency for Research on Cancer (IARC) (China Food and Drug Administration 2017). While the long-term health effects of low levels of APAP exposure are still not completely understood, the identification of cost-effective methods to eliminate APAP and other pharmaceuticals from wastewater is important for the purpose of countering any currently unknown risks.

Ultraviolet (UV) irradiation is an effective method for treating pollutants with benzene and phenol rings that are common in PPCP molecular structures (Kurniawan et al. 2017). Among the various UV wavelengths available, UV-C (254nm) is one of the wavelengths that can effectively degrade organic substances due to its strong absorption properties for benzene and phenol rings. Therefore, this study aimed to investigate the effects of ultraviolet-C (UV-C) irradiation on the degradation of acetaminophen (APAP) in aqueous solution. In addition, the study also examined the effects of ultraviolet-C irradiation combined with activated sludge (UV/AS) on the degradation of acetaminophen (APAP) in aqueous solution.
To enhance photolysis efficiency, UV irradiation reaction systems typically incorporate oxidants and catalysts that increase treatment cost, such as H₂O₂, Fe(OH)₂, and TiO₂ (de Vidas et al. 2015; Lutterbeck et al. 2015; Zhang et al. 2015). Although these substances are very effective at eliminating an extensive range of pharmaceuticals from water and wastewater, they can introduce new contaminants to the waste stream that then also need to be treated, such as used TiO₂. Moreover, the reaction intermediates may exhibit their own toxicity risks when the reaction conditions cannot be controlled well, and this may introduce extra risks to the environment (Yuan et al. 2011; Lai et al. 2015). Therefore, if there was a substance that could help UV treatment reduce cost and waste, UV treatment is promising.

In practice, activated sludge (AS) processes constitute the dominant technology in large-scale wastewater treatment, and excess AS contributes significantly to solid waste. As a result, much research has been devoted to AS recycling and minimization. Coagulation–flocculation enhancement, phosphorus extraction, and dye absorption (Kuroda et al. 2002; Djafer et al. 2017; Singh et al. 2017) have been the conventional methods of recycling excess AS. To the best of our knowledge, studies regarding the cooperation of UV and AS for PPCPs are rare. Common combinations of these approaches made use of AS as a pretreatment followed by UV for further degradation in sequence (De la Cruz et al. 2012), and made use of UV for the disinfection of microorganisms in AS treatment plants (Neto et al. 2006). Since UV treatment has a high cost, it could provide a valuable option for excess AS utilization and lower photolysis cost only if the cooperation of UV and AS is able to reach efficiencies closer to the APAP degradation efficiency of UV/H₂O₂ or UV/TiO₂ systems.

In this work, photolysis of APAP in aqueous solution using UV irradiation was studied to determine optimal removal conditions. Previous research indicated that UV-A (315–400 nm) and UV-B (280–315 nm) are not able to degrade APAP (Xie et al. 2016), so UV-C (i.e. UV₂₅₄) was selected due to its shorter wavelength and proven photolysis performance. Considering the potential benefits of a UV and AS combination, the efficiency of APAP degradation by UV irradiation coupled with AS (UV/AS) was also examined. Furthermore, as humic acid (HA) is one of the main components of AS, the effect of a UV/HA system on APAP removal efficiency was evaluated.

**MATERIALS AND METHODS**

**Preparation of the aqueous APAP solution**

APAP stock solution (1 g/L) was prepared by dissolving 0.1 g of APAP in 100 mL of ultrapure water. This solution was further diluted 100 times to obtain a 10 mg/L APAP solution.

**Preparation of the AS**

The AS was obtained in sediment stage from a stable-running cyclic activated sludge system (CASS) reactor located in our laboratory. After vacuum filtration, the AS was cleaned three times with distilled water, and was then freeze-dried and filtered through a 50-mesh screen. Finally, a portion of the meshed AS was sterilized at 121°C for 20 min.

**Measurement of APAP concentrations**

Samples were filtered using a 0.45-μm membrane before analysis. The APAP water concentration was quantified by reverse-phase high performance liquid chromatography (HPLC) (Elite P230II, China) with a SinoChrom ODS-BP column (4.6 mm × 150 mm × 5 μm, Elite, China) and a UV-vis detector (Elite, UV230II) at 243 nm. The mobile phase was comprised of methanol and water (20/80, volume ratio) with a flow rate of 1.0 mL/min.

**UV-C experimental conditions**

**Initial APAP concentration**

A 100-mL diluted solution was kept in a glass beaker covered with a colorless, transparent fresh-keeping film, and was placed at the center of the platform of a UV-C reactor (ZF1, Qiwei instrument company, China) with a SinoChrom ODS-BP column (4.6 mm × 150 mm × 5 μm, Elite, China) and a UV-vis detector (Elite, UV230II) at 243 nm. The mobile phase was comprised of methanol and water (20/80, volume ratio) with a flow rate of 1.0 mL/min.
in the residue. A maximum of 11 sample times were observed for each solution. To evaluate the effect on the initial APAP concentration, 0.8, 1.6, 2, 4, and 6 mg/L samples of the APAP solution were irradiated individually under UV-C for 720 min, and the changes in the APAP concentration were determined during irradiation as described above.

UV-C exposure surface area

To evaluate the effect of the exposure surface area, 10 mL samples of 10 mg/L APAP solution were placed in a culture dish (90 mm diameter), a 100-mL beaker (58 mm diameter), and a test tube (15 mm diameter). After UV-C irradiation for 720 min, the residue APAP concentration in each sample was determined as described above.

UV/AS experimental conditions

AS activity

Five types of samples containing 10 mL of 10 mg/L APAP solution were used for these experiments, the experimental conditions of which are listed in Table 1. The supernatants of the samples were filtered twice using a 0.45-μm membrane, and the APAP concentrations were determined as described above.

Dosage of AS and HA

The sterilized AS samples with dry weights of 0–0.20 g and 0–10 mg C/L of HA were added to 10 mL of the 10 mg/L APAP solutions. HA (CAS: 1415-93-6, black powder, technical grade) was supplied by Sigma-Aldrich, and was prepared following previously published methods (Li & Hu 2010). HA contents were determined using a total organic carbon (TOC) analyzer (Shimadzu, TOC-VWP). The residual APAP concentrations were measured following the procedures described in the section ‘Measurement of APAP concentrations’. This experiment was run in triplicate, and the data appear as averages in the figure.

RESULTS AND DISCUSSION

Influence of the initial APAP concentration on the degradation process

After 720 min of UV-C exposure, samples with different initial APAP concentrations displayed degradation efficiencies that ranged from 52.91% to 55.68% (Figure 2). Previous research reported an APAP degradation efficiency of 40% after 96 h of UV-C irradiation (Kawabata et al. 2013), which is lower than the results of this study. It is also notable that the catalyzed Vis-TiO2 and Vis-β-Bi2O3 nanospheres visible light irradiation pathways degraded APAP more slowly than the UV-C-only process that was utilized in this study (Xiao et al. 2013; de Luna et al. 2016).

To determine the reaction rate, the Langmuir–Hinshelwood (L–H) kinetic model (Equation (1)) was calculated according to Dimitrakopoulou et al. (2012):

\[ r_0 = \frac{K C_{eq}}{1 + K C_{eq}} \]

\[ r_0 = \frac{1}{k_r K C_{eq} + \frac{1}{k_r}} \]

(1)

where \( r_0 \) is the initial reaction rate, \( C_{eq} \) is the equilibrium concentration, \( K \) is the adsorption constant onto the substance surface, and \( k_r \) is the intrinsic reaction rate constant. For cases when there was no adsorbent, \( K \) is set to 0. The \( r_0 \) was computed from the data in Figure 2 for

Table 1 | Experimental condition of five sample types

<table>
<thead>
<tr>
<th>Sample</th>
<th>AS weight (g)</th>
<th>AS condition</th>
<th>Irradiation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>–</td>
<td>–</td>
<td>720 min</td>
</tr>
<tr>
<td>AS1 (under irradiation)</td>
<td>0.05</td>
<td>Unsterilized</td>
<td>720 min</td>
</tr>
<tr>
<td>AS2 (under irradiation)</td>
<td>0.05</td>
<td>Sterilized</td>
<td>720 min</td>
</tr>
<tr>
<td>AS1 (in dark)</td>
<td>0.05</td>
<td>Unsterilized</td>
<td>–</td>
</tr>
<tr>
<td>AS2 (in dark)</td>
<td>0.05</td>
<td>Sterilized</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 2 | Degradation processes of APAP at different initial APAP concentration. Insert graph: the L–H kinetic model for APAP degradation.
the first 300 min of reaction, with $C_{eq}$ taken as $C_0$. Data fit the L–H model well ($R^2 = 0.997$), and the intercept indicated that $k_r$ was 7.29 mg/(L·min).

The photolysis kinetics of APAP on UV-C exposure time was expressed by Equation (2), and this is depicted in Figure 3. Since the slopes of each kinetic line were similar, kinetic figures were divided into five panels to avoid confusion.

$$\ln\left(\frac{C_t}{C_0}\right) = k_{APAP}t$$

(2)

where $C_0$ and $C_t$ are the reactant concentrations at times $t = 0$ and $t = t$, respectively, and $k_{APAP}$ (min$^{-1}$) is the apparent reaction rate constant determined by a plot of $\ln(C_t/C_0)$ vs. the reaction time ($t$).

The results indicated that the reaction kinetics of all of the samples were well-fitted by the pseudo first-order rate model with high correlation coefficients ($R^2 > 0.90$) (Lin et al. 2016; Xie et al. 2016), as depicted in Figure 3. The $k_{APAP}$ ranged from 0.0012 to 0.0013 min$^{-1}$, which is approximately 25% of the $k_{APAP}$ associated with UV/TiO$_2$ systems (Yang et al. 2008). As depicted in Table 2, the relatively small $k_{APAP}$ range indicated that the influence of the initial APAP concentration on the photolysis process is nominal. This result differs from that of previous studies that found that the photolysis rates decreased as the APAP concentrations increased in UV/TiO$_2$ and UV/H$_2$O$_2$ systems (Tan et al. 2014). In common, under the same irradiation conditions, lower pollutant concentrations would increase the degradation rate. However, the results of this study indicated that the APAP degradation rate was constant for different initial APAP concentrations. For the UV/H$_2$O$_2$ and UV/TiO$_2$ systems, -OH was determined to be a limiting factor in the degradation process (Tan et al. 2014), and as the APAP concentration increased, the average -OH decreased, resulting in slower degradation rates. In the UV-C-only system, however, no limiting factors except for photons were needed to drive the degradation process, and there was less competition. Given the potential

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>Degradation rate (%)</th>
<th>Reaction constant (min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>55.68</td>
<td>0.0012</td>
<td>0.954</td>
</tr>
<tr>
<td>4</td>
<td>55.38</td>
<td>0.0013</td>
<td>0.946</td>
</tr>
<tr>
<td>2</td>
<td>55.61</td>
<td>0.0013</td>
<td>0.954</td>
</tr>
<tr>
<td>1.6</td>
<td>52.91</td>
<td>0.0012</td>
<td>0.949</td>
</tr>
<tr>
<td>0.8</td>
<td>53.48</td>
<td>0.0012</td>
<td>0.907</td>
</tr>
</tbody>
</table>
limitations of the UV/H₂O₂ and UV/TiO₂ systems, UV-C-only treatment may offer more stable and predictable characteristics than these photocatalytic systems.

Influence of the UV exposure surface area on APAP degradation

The degradation efficiencies of APAP in the three differently-shaped containers with different exposure surface areas were measured and the results are shown in Figure 4. While previous studies found that higher photon fluence rates resulted in higher treatment efficiency (Yuan et al. 2011), the current study found that, for the same UV-C exposure time of 12 h, a lower photon fluence rate (0.05 × 10⁻⁶ E/(s·cm²)) resulted in a high APAP degradation efficiency (62.77%) and a higher photon fluence rate (1.81 × 10⁻⁶ E/(s·cm²)) resulted in a lower APAP degradation efficiency (22.28%). For each 10-mL sample, the path length that the photons needed to pass through lengthened as the exposure surface area decreased. Accordingly, photons attenuated more quickly and lowered the efficiency.

In photocatalysis research, the large surface area of TiO₂ powders in reaction media have been reported to be favorable for high photocatalytic performance (Tryba et al. 2005), suggesting that the larger reaction area between the TiO₂ and the target pollutant resulted in better treatment efficiency. Therefore, it was speculated that the reaction area between catalyst and pollutant as well as between the UV photons and the solution could affect the treatment process. Since we found no studies on the effect of different solution surface areas at similar volumes on UV irradiation efficiencies, we hypothesized that a larger exposure surface area/volume ratio would improve the APAP degradation process, and that this ratio might also affect other UV irradiation efficiencies. According to our findings, for a set UV power, a treatment system that is designed to have a large exposure surface area/volume ratio may be more efficient than a system with a smaller exposure surface area/volume ratio.

Influence of sludge activity on APAP degradation by UV irradiation

To evaluate the manner in which the AS activity affected the photolysis of APAP, both sterilized sludge (AS1) and unsterilized sludge (AS2) were utilized. Both types of AS were added to separate APAP solutions, and their influence on the photolysis process was evaluated, as depicted in Figure 5. Since both AS1 and AS2 displayed low rates of APAP reduction after 720 min in darkness (4% and 2.7%, respectively), the effect of sludge activity under UV/AS conditions can likely be attributed to chemical reaction rather than adsorption.

The irradiated AS2 sample achieved a degradation efficiency of 99% and a degradation rate of 0.0096 min⁻¹, which was 9.6 times higher than that of the control sample (Table 3). This degradation rate was similar to a catalyst reaction process that uses Fe₃O₄ magnetic nanoparticles/peroxymonosulfate (Tan et al. 2014), faster than the zero-valent iron/persulfate process (Deng et al. 2014), and slower than the UV/H₂O₂ photocatalytic process. It is worth noting that the AS1 sample only degraded 13.80% of the APAP, which was much lower than the 49.20% of APAP that was degraded in the control sample.

![Figure 4](http:// iwaponline.com/wst/article-pdf/78/10/2088/516632/wst078102088.pdf)  
Figure 4 | Influence of exposure surface area on APAP degradation efficiency.

![Figure 5](http://iwaponline.com/wst/article-pdf/78/10/2088/516632/wst078102088.pdf)  
Figure 5 | Influences of AS activity on APAP degradation processes. Insert graph: the pseudo first-order kinetic model for control, AS1 (under irradiation) and AS2 (under irradiation) sample.
Natural organic matter (NOM) was observed to play a dominant role in APAP photolysis (Li et al. 2017), and previous studies indicated that the enhancement of APAP degradation was due to the suppression of APAP self-coupling in the presence of dissolved NOM, which was likely caused by the cross-coupling between dissolved NOM and APAP (Lu & Huang 2018). Since the AS utilized in this study was cleaned three times using distilled water to eliminate the adsorbed NOM and other impurities, the NOM present in the experiments most likely came from the AS itself. The high-temperature and high-pressure (HTHP) environment likely forced the microbial cells to break and release NOM that could combine with APAP to elevate the APAP irradiation efficiency. AS1 was not subjected to the HTHP condition; therefore, most of the available NOM remained isolated within the microbial cells. While AS1 absorbed a portion of the UV-C instead of supplying NOM, it could not contribute to the APAP photolysis process, and instead made it an inhibitor of this process.

In addition to NOM, the residual HA in AS was exposed to the UV-C during the generation of additional -OH (Wu 2017; Zhang et al. 2017), and this led to the accelerated photolysis of benzene rings, phenol rings, and side chains of APAP.

### Effect of AS dosage and HA on APAP degradation by UV irradiation

As depicted in Figure 6(a), the APAP degradation efficiency in the 0.10 g AS2 sample was 82.83% of that in the 0.05 g AS2 sample. As more AS2 was added, the APAP degradation efficiency decreased. Furthermore, 0.20 g of the AS2 sample performed 22.65% less than that of the control sample. Since it was speculated that the NOM in AS was responsible for the treatment differences, HA was used in this study to simulate NOM and verify this influence of NOM on APAP degradation. Consistent with Wu (2012), who reported that HA had the ability to both enhance and decrease the photolysis rate, Figure 6(b) illustrates a similar tendency. The highest degradation efficiency was 83.10% for the 6 mg/L HA condition, which was 35.5% higher than the blank sample. Similarly, when HA was dosed at >6 mg/L, the degradation of APAP reduced rapidly by 12.59% and 49.48% at HA concentrations of 8 mg/L and 10 mg/L, respectively. A similar phenomenon occurred in the UV/peroxymonosulfate degradation of the anatoxin-a process (Verma et al. 2010). HA acted as an -OH generator as well as an -OH scavenger in the UV system (Ma & Graham 1999), and Verma et al. (2010) suggested that the reason for the reduced degradation at high concentrations of HA was the competition between anatoxin-a and HA for the oxidative radicals.

Besides oxidative radical competition, UV radiation competition between HA and APAP also existed. HA itself was the degradation target of UV-C (Doll & Frimmel 2003). When HA was present in relatively low concentrations similar to those used in this study (<6 mg/L), the available photons were sufficient to treat both HA and APAP. When the concentration of HA was increased further, competition for available photons occurred between HA and APAP. Since HA photolysis was faster than -OH generation, a reverse effect occurred and the degradation efficiency of APAP was lower than the blank sample.

### CONCLUSIONS

UV and UV/AS systems were evaluated for their efficiencies during the APAP treatment process. Sterilized AS was observed to accelerate the APAP irradiation efficiency, and the addition of HA produced similar results with different AS dosages in the APAP photolysis process. The performance of the UV/AS system was close to and even...
exceeded the performance of many of the existing photolysis systems. Experiments indicated that the initial APAP concentration did not influence the treatment process; however, the AS dosage was a key component of the UV/AS system. This UV/AS system may provide a new path for surplus sludge treatment by reducing the addition of external substances and the treatment cost.

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