Persistent organic pollutants (POPs) degradation in natural waters using a V-UV/UV/TiO₂ reactor

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ABSTRACT

This paper presents the use of a V-UV/UV/TiO₂ reactor (M300 water purifier™) for the removal of sulfamethoxazole and atrazine from natural water. The efficiency of the different processes (photolysis, Vacuum UV (V-UV) and photocatalysis) within the photoreactor was investigated using para-chlorobenzoic acid (pCBA) which is a good probe for hydroxyl radicals. The effect of pH, dissolved organic carbon (DOC) and total inorganic carbon (TIC) was also studied. V-UV was found to be the most efficient process for pCBA degradation within this unit. No photocatalytic degradation was observed. The water quality largely affected the efficiency of the system. Indeed, both DOC and TIC lowered the hydroxyl radical concentration in the system, but DOC did it to a larger extent. Atrazine and sulfamethoxazole, were successfully degraded, and as for pCBA, V-UV was the most efficient process. Sulfamethoxazole displayed a better removal by photocatalysis than atrazine and pCBA. In addition, there was a larger contribution of photolysis during the degradation of sulfamethoxazole than of atrazine. The UV₂⁵₄ nm absorbance of the water affected the photolysis of sulfamethoxazole which has a high molar extinction coefficient and quantum yield at 254 nm, while the DOC is mainly competing with the pollutants for the hydroxyl radicals.

Key words | Micro-pollutants, natural waters, pCBA, photocatalysis, UV, vacuum UV

INTRODUCTION

There is a growing concern about the presence of emerging contaminants in different types of water. Persistent organic pollutants (POPs) have been identified as an increasing problem in our drinking water supplies (Eljarrat & Barceló 2003). Such substances can enter the water supply from various sources and are not effectively removed by conventional water treatment processes. Among the pollutants of concern, various pharmaceuticals, pesticides and herbicides can be found. Therefore there is a need for new technology and processes that can remove harmful compounds and POPs at low concentrations (Murray & Parsons 2004).

Advanced oxidation processes (AOP) are chemical oxidative processes, which can be applied to drinking water treatment to oxidize pollutants. AOPs are characterized by the generation of hydroxyl radicals (HO·), which is a very strong oxidant (2.8 V/ENH). It is able to oxidize and mineralize almost every organic molecule, yielding CO₂ and inorganic ions (Hoffmann et al. 1995). The UV/TiO₂ photocatalytic process is among the most studied AOPs and has been shown to have the potential for effectively treating many POPs (Hoffmann et al. 1995). Vacuum ultraviolet (V-UV) permits the photolysis of water and is a very interesting and powerful source of hydroxyl radicals, and consequently represents a considerable application potential (Gonzalez et al. 2004). Combining V-UV and photocatalysis have shown to be very efficient (Han et al. 2004). Thus, in this work we have used a commercial unit with immobilized TiO₂ (to avoid a separation step) irradiated with a low pressure mercury lamp emitting at two wavelength 254 nm and 185 nm for the treatment of two POPs, sulfamethoxazole (bacteriostatic antibiotic) and atrazine (herbicide used in agriculture). These two
compounds have been selected because they are frequently found as water pollutant and are widely studied (Pelizzetti et al. 1990; McMurray et al. 2006; Canonica et al. 2008). They have very stable chemical structures which allow them to remain in the environment for a long time. Their presence is considered dangerous in both low and high concentrations. In addition, para-chlorobenzoic acid (pCBA) has been used as a model pollutant since it has been reported to be an ideal compound for UV based AOP studies because it displays slow reaction rates with photolysis but rapid oxidation kinetics with the hydroxyl radicals ($k = 5 \times 10^9 \text{M}^{-1}\text{s}^{-1}$) (Rosenfeldt et al. 2006), consequently it is a good probe for hydroxyl radicals formation. pCBA has been used to investigate the water quality effect as well as the efficiency of the different processes involved within our test unit.

### METHODS

#### Reagents

Parachlorobenzoic acid (purity >97%), atrazine (purity >98%) and sulfamethoxazole (purity >98%) were used as received from Sigma-Aldrich-Fluka. Table 1 shows the different compounds studied with their pKa. Sodium bicarbonate (purity 100%), ortho-phosphoric acid (assay (acidimetric): 85%) and HPLC reagent gradient grade acetonitrile were from VWR.

#### Experimental setup

Experiments were conducted in batch mode using an annular reactor (M300 water purifier<sup>®</sup>) provided by Wallenius Water AB. The photoreactor was 330 mm high, with an inner diameter of 44 mm and the lamp placed in the centre of the photoreactor with a quartz tube protection (diameter 22 mm). In order to investigate the importance of the different processes (photolysis, photocatalysis and V-UV photolysis of water) involved during the degradation of the pollutants by this system, different configurations were used. Two types of reactors (with or without immobilized TiO<sub>2</sub>) and two types of 15 W low pressure mercury lamps (emitting only at 254 nm or both at 254 nm and 185 nm) were combined. The two lamps had an approximate photon flux of $(1.2 \pm 0.1) \times 10^{-5} \text{mole s}^{-1}$ at 254 nm. The available water volume of the photoreactor was 0.34 L and the total volume of the batch was 10 L.

The solution was continuously re-circulating through the photoreactor using a pump at a flow rate of 800 L/h corresponding to a turbulent flow regime ($Re \sim 18000$), which allowed an efficient transport of the pollutant towards the oxidation sites. A schematic sketch of the reactor and the complete system set-up is shown in Figure 1.

### Water qualities used

Different types of water were used during this work. The synthetic waters used, were composed of distilled water (DW) and buffered to desired pH with a 10 mM phosphate buffer and to desired total inorganic carbon (TIC) content by adding NaHCO<sub>3</sub>. In addition, natural waters were used, either from Lake Jonsvatnet (LW) or from a well in France. Their compositions are shown in Table 2. These natural waters were filtered, buffered and adjusted to desired pH and TIC by the same procedure as for the synthetic waters.
Analyses

The different micro-pollutants (atrazine and sulfamethoxazole) and the pCBA were analyzed using reverse-phase liquid chromatography with a DAD detector in a HPLC-UV Chromatograph (Agilent, series 1200) and a C-18 column (column Zorbax Eclipse XDB-C18 3.5 μm, 4.6 x 150 mm from Agilent). An eluent consisting of 50%:50% acetonitrile: H2O adjusted to the correct pH with H3PO4 (pH 2 for pCBA, pH 3 for sulfamethoxazole, and pH 7 for atrazine) was used with a flow of 0.7 mL min⁻¹, and the UV detector was set to the relevant wavelength for the measurement of the different compounds (240 nm for pCBA, 223 nm for atrazine, and 254 nm for sulfamethoxazole).

Turbidity was measured using HACH 2100N Turbidity meter. Color (number representing the platinum concentration (mg Pt/l) in a platinum cobalt chloride solution that has the same absorbance at 410 nm as the sample) and UV254 nm (absorbance at the wavelength 254 nm) were measured using Hitachi U-3000 Spectrophotometer. Prior to the measurements the samples were adjusted to pH 7 and then filtered through 0.45 μm Millipore membrane filters. Alkalinity and pH were analyzed using Metrohm Titrprocessor 726 equipped with sample changer 717 and Dosimat 685. Total organic carbon (TOC) and dissolved organic carbon (DOC) were analyzed using Tekmar Dohrmann Apollo 9000 total organic carbon analyzer. In the case of the DOC analysis, the sample was filtered using 0.45 μm Millipore membrane filters prior to analysis.

Description of the processes

The unit used combines a lamp emitting at 185 nm and 254 nm and a reactor with immobilized TiO2 internal surface. Under such experimental conditions, three different processes can occur in order to degrade the organic compounds contained in the water: UV photolysis and two AOPs: TiO2 photocatalysis and V-UV water photolysis.

Direct UV photolysis

The micro-pollutants structures contain chromophores that are capable of absorbing electromagnetic radiations and consequently a direct photolysis of pollutants by the irradiation at 254 nm could occur. At 185 nm the water is absorbing all the irradiation not permitting any photolysis of the pollutant at this wavelength.

V-UV photolysis of water

Since 185 nm irradiation is in the V-UV region, photolysis of water occurs and leads to the formation of hydroxyl radical with a quantum yield of 0.33 (Equation 1) (Getoff & Schenck 1968). Consequently, generated hydroxyl radicals could oxidize the organic compounds, but only in a layer close to the quartz sleeve of the lamp due to the high absorption of 185 nm irradiation by the water (1.8 cm⁻¹) (Weeks & Rabani 1966). This means that 99% of the irradiation is absorbed in a 10 mm pathway of water, and almost no V-UV irradiation is reaching the TiO2 surface.

\[ \text{H}_2\text{O} + h\nu(\text{V–UV}) \rightarrow \text{HO}^+ + \text{H}^- \]  

### Table 2 | Main characteristics of the natural waters investigated

<table>
<thead>
<tr>
<th>Water origin</th>
<th>pH</th>
<th>Alkalinity</th>
<th>Turbidity</th>
<th>TOC</th>
<th>UV254 nm 5 cm cuvette</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artesian Well, Maisons-Laffitte, France</td>
<td>8</td>
<td>2.5</td>
<td>&lt;0.5</td>
<td>0.9</td>
<td>0.11</td>
</tr>
<tr>
<td>Lake Jonsvatnet, Trondheim, Norway</td>
<td>8</td>
<td>0.3</td>
<td>0.1</td>
<td>3</td>
<td>0.55</td>
</tr>
</tbody>
</table>
UV/TiO\textsubscript{2} photocatalysis

During excitation, the energy is transferred to the semiconductor (TiO\textsubscript{2}) through UV-light and an electron can pass from the valence band (VB) to the conduction band (CB) leading to creation of positive holes (h\textsuperscript{+}) in the VB and liberation of electrons (e\textsuperscript{-}) in the CB (Equation 2). On the TiO\textsubscript{2} surface, the holes (h\textsuperscript{+}) react with H\textsubscript{2}O or OH\textsuperscript{-} leading to the formation of hydroxyl radicals (Equation 3 and 4). At the same time the electrons transferred into the CB, can react with oxygen and form superoxide anions (O\textsuperscript{2-}) (Equation 5). The superoxide ion can further react with water giving additional hydroxyl radicals, hydroxide ions, and oxides (Equation 6 and 7). OH\textsuperscript{-} from the last reaction can react further with holes in the VB creating even more hydroxyl radicals (Equation 4) (Herrmann 1999).

\[
\text{TiO}_2 + h\nu(\lambda \leq 380 \text{ nm}) \rightarrow h^+(\text{VB}) + e^-(\text{CB}) (2)
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^+ (3)
\]

\[
h^+ + \text{OH}^- \rightarrow \text{OH} (4)
\]

\[
e^- + \text{O}_2 \rightarrow \text{O}_2^- (5)
\]

\[
2\text{O}_2^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- + \text{O}_2 (6)
\]

\[
\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \text{OH} (7)
\]

In order to determine the importance of each process different configurations of photoreactors have been used in this study. These configurations and resulting processes occurring are summarized in Table 3.

RESULTS AND DISCUSSION

pCBA degradation

The main goal of the experiments with pCBA was to investigate the formation of hydroxyl radicals at different water qualities and in different configurations of the photoreactor.

Degradation kinetics

In general the photocatalytic degradation can be well described by the Langmuir-Hinshelwood kinetic model, in which the reaction rate (r) varies proportionally with the surface coverage (θ) and is a function of the concentration C (Equation 8) (Herrmann 1999):

\[
r = \frac{\frac{dC}{dt} = kr\theta}{1 + kC} (8)
\]

Where C is the concentration of pollutant (mole L\textsuperscript{-1}), t is the irradiation time (s), k\textsubscript{r} is the Langmuir-Hinshelwood photocatalytic rate constant (mole L\textsuperscript{-1} s\textsuperscript{-1}), and K is the adsorption constant (L mole\textsuperscript{-1}). However, according to Herrmann (1999) at low concentration (C < 10\textsuperscript{-3} M), the product KC is negligible in relation to unity and Equation (8) can be described as a first order kinetics as follows (Equation 9):

\[
r = k_rKC = k_{\text{photocatalysis}}C (9)
\]

The results in Figure 2 show that the two other processes (photolysis and V-UV) follow a pseudo-first order reaction kinetic as well. Consequently, when the complete process (V-UV/UV/TiO\textsubscript{2}) is considered for the degradation of a pollutant, a pseudo-first order reaction

<table>
<thead>
<tr>
<th>Lam emission</th>
<th>Reactor</th>
<th>Process occurring</th>
</tr>
</thead>
<tbody>
<tr>
<td>185 nm + 254 nm</td>
<td>With TiO\textsubscript{2}</td>
<td>Photocatalysis + Photolysis + Vacuum UV photolysis of water</td>
</tr>
<tr>
<td>254 nm</td>
<td>With TiO\textsubscript{2}</td>
<td>Photocatalysis + Photolysis</td>
</tr>
<tr>
<td>185 nm + 254 nm</td>
<td>Without TiO\textsubscript{2}</td>
<td>Photolysis + Vacuum UV photolysis of water</td>
</tr>
<tr>
<td>254 nm</td>
<td>Without TiO\textsubscript{2}</td>
<td>Photolysis</td>
</tr>
</tbody>
</table>
kinetic can be employed (Equation 10): 

\[
r = \frac{dC}{dt} = -(k_{\text{Photocatalysis}} + k_{\text{Photolysis}} + k_{\text{V-UV}})C = -k_{\text{app}}C
\]  

(10)

Where \(k_{\text{Photocatalysis}}\) is the rate constant for the photocatalysis (min\(^{-1}\)), \(k_{\text{Photolysis}}\) is the rate constant for the photolysis (min\(^{-1}\)), \(k_{\text{V-UV}}\) is the rate constant for the Vacuum UV (min\(^{-1}\)), and \(k_{\text{app}}\) is the apparent rate constant (min\(^{-1}\)) for the complete process. Thus the concentration at a given time can be described by Equation (11):

\[
C_t = C_0e^{-k_{\text{app}}t}
\]  

(11)

As can be seen from Figure 2, which includes a number of experiments using the different configurations described in Table 3, all the degradations are well described by the pseudo-first order kinetic model. According to Equation (10) the apparent rate constant is the sum of the rate constants for the different processes involved. From this the rate constants for each of the processes is calculated and reported in Table 4.

From Figure 2 and Table 4 it is obvious that the most efficient process for the pCBA removal in this unit is the V-UV process which represents 91.4% of the total removal efficiency at a given time. The photolysis contributes considerably less to the pCBA degradation (8.5%) and there are no significant differences between the data obtained for the photocatalysis + photolysis and photolysis, meaning that the photocatalysis is not significant. Thus, the main process generating the hydroxyl radicals responsible for the pCBA removal is the V-UV process. This also shows that there is a large potential for improvement of the system by increasing the surface area of TiO\(_2\) in order to utilize the photons produced by the lamp (improve the photocatalysis). Indeed, the M300 water purifier uses a very small surface area of TiO\(_2\).

**Effect of dissolved organic carbon**

Figure 3 shows the apparent rate constants of pCBA obtained using distilled water (DW) free in DOC and lake water (LW) with a DOC of 5 mg/L at two different pHs and TIC concentrations. The results show that there is a decrease in the rate constants when the water contains DOC. The dissolved organic carbon (DOC), which in this case mainly consists of natural organic matter (NOM), can affect the removal efficiency of the pollutant by many ways. The NOM is an organic matter which will behave as the pollutant being oxidized, and therefore consume oxidants, which according to the results in Figure 3 also would be the main reason for the decrease in the rate constant. In addition, the NOM are conjugated olefinic, aromatic, phenolic-semiquinone-quinone structures containing macromolecules of humic acid with a wide spectrum of functional groups (\(- \text{C} =\text{O}, -\text{COOH}, -\text{OH}, -\text{NH}_2, -\text{N} =\) ) and chromophores that may be capable of absorbing electromagnetic radiations (Uyguner & Bekbolet 2005). Consequently, and according to the UV\(_{254\text{nm}}\) absorbance of

<table>
<thead>
<tr>
<th>UV 254 photolysis</th>
<th>V-UV</th>
<th>Photocatalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{\text{app}})</td>
<td>(3.5 \times 10^{-3}) min(^{-1})</td>
<td>(3.72 \times 10^{-2}) min(^{-1})</td>
</tr>
</tbody>
</table>

**Figure 2** | Experimental and calculated concentration of pCBA (\(C_0 = 1\) mM) versus irradiation time, in lake water (pH 7; DOC: 3 mg/L; TIC: 1 mM) for different configuration of reactors.

**Figure 3** | Effect of DOC on the apparent degradation rate constants of pCBA (\(C_0 = 1\) mM) in distilled water (DW) and lake water (LW) at different alkalinities and pHs.
the water from Lake Jonsvatnet, the NOM is able to limit the transmission of the 254 nm irradiation to the TiO\textsubscript{2} surface, and to limit the pollutant photolysis.

**Effect of pH and TIC**

Figure 4 shows the apparent rate constants of pCBA obtained using lake water (LW) with a DOC of 3 mg/L and different levels of TIC and pH values. Although the degradation rates and therefore the hydroxyl radical formation should increase with the pH of the solution according to the Equation (12), the results show a decrease (Figure 4):

\[
\text{OH}^- + hv(185\text{nm}) \rightarrow \text{OH} + e^{\text{(solvated)}} \quad (12)
\]

Carbonate and bicarbonate are known to be radical scavengers, and since CO\textsubscript{3}\textsuperscript{2-} (1.78 V/ENH) is much less reactive than hydroxyl radical (2.8 V/ENH), inhibition by carbonate influence the degradation (Legrini et al. 1993). The apparent effect of pH and TIC in Figure 4 is caused by TIC and the distribution of TIC species as a function of pH. The relative distribution of TIC species as shown in Table 5, and the fact that CO\textsubscript{3}\textsuperscript{2-} is a more efficient hydroxyl radical scavenger than HCO\textsubscript{3}\textsuperscript{-}, which is illustrated by the faster reaction of the hydroxyl radical with carbonate than with bicarbonate (Equation 13 and 14) (Weeks & Rabani 1966), results in a decrease in the rate constant as pH is increased in TIC containing water (Figure 4).

\[
\text{HCO}_3^- + \cdot\text{OH} \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow k_1 = 8.5 \times 10^8 \text{M}^{-1}\text{s}^{-1}
\]

(13)

\[
\text{CO}_3^{2-} + \cdot\text{OH} \rightarrow \text{CO}_3^{3-} + \text{OH}^- \rightarrow k_2 = 5.8 \times 10^8 \text{M}^{-1}\text{s}^{-1}
\]

(14)

Hence, the presence of carbonate species in the water can result in a significant reduction in the removal efficiency of micro-pollutants. In order to avoid such a reduction, the pH in high carbonate water (high TIC) should be low to convert carbonate and bicarbonate to bicarbonate and carbonic acid, respectively. However, in low carbonate water it is beneficial with a high pH.

**Micro-pollutants removal**

As for pCBA, different reactor configurations have been used to evaluate the efficiency of each process within the full system (V-UV/UV/TiO\textsubscript{2}) for the degradation of sulfamethoxazole and atrazine. All the degradation kinetics followed a pseudo-first order kinetic model and are reported in Table 6. The results (Table 6) show that the

<table>
<thead>
<tr>
<th>Percentage of carbonate species formed at different pHs at 25°C</th>
<th>pH 5</th>
<th>pH 7</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>% H\textsubscript{2}CO\textsubscript{3}</td>
<td>95.2</td>
<td>16.6</td>
<td>1.9</td>
</tr>
<tr>
<td>% HCO\textsubscript{3}</td>
<td>4.8</td>
<td>83.4</td>
<td>97.6</td>
</tr>
<tr>
<td>% CO\textsubscript{3}\textsuperscript{-}</td>
<td>0.00001</td>
<td>0.01</td>
<td>0.5</td>
</tr>
</tbody>
</table>
V-UV is the dominant degradation process for sulfamethoxazole and atrazine as well. Nevertheless, sulfamethoxazole displays a better removal by photocatalysis, probably due to better adsorption ability on the TiO$_2$ surface, than atrazine and pCBA. In addition, there was a larger contribution of photolysis during degradation of sulfamethoxazole than of atrazine, which in turn was much larger than of pCBA. This is caused by a higher absorptivity and quantum yield at 254 nm for sulfamethoxazole than for atrazine (Table 6) and pCBA ($\epsilon = 2,553$ M$^{-1}$ cm$^{-1}$ and $\phi = 0.026$ Mole Einstein$^{-1}$ (Rosenfeldt et al. 2006)).

As it has been shown for pCBA, the water quality also has a large impact on the removal efficiency of sulfamethoxazole and atrazine by the system. The water from Maison Laffite has considerable lower DOC and UV$_{254}$ absorbance than Lake Jonsvatnet. Thus, the degradation rate constant for both pollutants has been found to be higher in water from Maison Laffite than in the water from Lake Jonsvatnet (Table 7). In addition, one can see that even if the Maison Laffite’s water has a higher TIC than Lake Jonsvatnet, the rate constants are still higher, which means that DOC is affecting the rate constants more than TIC, which also was confirmed by the results obtained for pCBA.

| Table 6 | Molar extinction coefficient, apparent degradation rate constants and % contribution of each process within the photoreactor, for atrazine and sulfamethoxazole in water from Lake Jonsvatnet (pH 7; DOC: 3 mg/L; TIC: 1 mM) |
|---|---|---|
| $\epsilon$ for $\lambda = 254$ nm and quantum yield, $\phi$ | Rate constant in min$^{-1}$ | % of the total rate constant within the full system |
| Atrazine | $\epsilon = 3,860$ M$^{-1}$ cm$^{-1}$ | $k_{total} = 3.9 \times 10^{-2}$ | V-UV: 73.2% |
| | $\phi = 0.046$ Mole Einstein$^{-1}$ (Hessler et al. 1995) | $k_{V-UV + Photolysis} = 3.9 \times 10^{-2}$ | UV$\_$(photolysis): 28.8% |
| | $\epsilon = 11,936$ M$^{-1}$ cm$^{-1}$ | $k_{V-UV + Photolysis} = 1.1 \times 10^{-2}$ | Photocatalysis: 0% |
| Sulfamethoxazole | $\phi = 0.046$ Mole Einstein$^{-1}$ (Canonica et al. 2008) | $k_{total} = 1.00 \times 10^{-1}$ | V-UV: 48% |
| | | $k_{photolysis + photocatalysis} = 8 \times 10^{-2}$ | UV$\_$(photolysis): 32% |
| | | $k_{photolysis} = 3.2 \times 10^{-2}$ | Photocatalysis: 20% |

Table 7 | Apparent degradation rate constants for atrazine and sulfamethoxazole in natural waters

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Artesian well, Maisons-Laffite (pH 7)</th>
<th>Lake Jonsvatnet (pH 7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>$7.5 \times 10^{-2}$ min$^{-1}$</td>
<td>$3.9 \times 10^{-2}$ min$^{-1}$</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>$2.15 \times 10^{-1}$ min$^{-1}$</td>
<td>$1.00 \times 10^{-1}$ min$^{-1}$</td>
</tr>
</tbody>
</table>

CONCLUSION

The M300 water purifier which is a V-UV/UV/TiO$_2$ reactor has been investigated for the removal of different pollutants in different water qualities.

- For the pollutants investigated, it has been shown that within this unit, the V-UV is the most efficient process.
- The water quality was found to largely affect the efficiency of the system, where both DOC and total inorganic carbon lowered the hydroxyl radical concentration.
- Two micro-pollutants, atrazine and sulfamethoxazole, were successfully degraded in the system. However, their removal efficiency was very dependent on the water quality. The UV$_{254}$ absorbance of the water affects the photolysis of the sulfamethoxazole which has a high molar extinction coefficient and quantum yield at 254 nm, while the DOC is mainly competing with the pollutants for the hydroxyl radicals.

The results have shown that the system is able to remove micro-pollutants. However, the efficiency can be improved considerably by, in particular, increasing the TiO$_2$ surface area in order to benefit from the photocatalytic effect, or by adding H$_2$O$_2$ to increase the hydroxyl radical concentration.
ACKNOWLEDGEMENTS

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