Intensification of the O$_3$/TiO$_2$/UV advanced oxidation process using a modified flotation cell


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Support information

S.1: Water properties of the city of Cali

Table S.1 Water properties of the city of Cali

<table>
<thead>
<tr>
<th>DO (%)</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>EC (µS/L)</th>
<th>TDS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100.77</td>
<td>7.15</td>
<td>8</td>
<td>164.9</td>
</tr>
</tbody>
</table>

* Dissolved Oxygen, b Chemical Oxygen Demand, c Electrical Conductivity, d Total Dissolved Solids

S.2. Spectrum of the Repti Glo 5.0 lamps

Figure S. 1. Spectrum of the Repti Glo 5.0 lamp.

S.3. Results of experimental control

S.3.1. Adsorption of DCF on TiO₂ surface

Adsorption tests were carried out under complete darkness for 24 hours at catalyst concentration of 0.3 and 0.8 g L⁻¹, room temperature and neutral pH. The amount of diclofenac adsorbed was calculated using the equation S.1 and the percentage of contaminant adsorbed on the catalyst surface was calculated by the difference between initial and final concentrations of the solutions i.e., before adding the catalyst and after recovering it by filtration. Table S.2 summarizes the results obtained.

Table S.2 Adsorption of DCF on catalyst surface at pH = 7.

<table>
<thead>
<tr>
<th>Concentration of TiO₂ (g L⁻¹)</th>
<th>Time of adsorption</th>
<th>DCF initial concentration (mg L⁻¹)</th>
<th>DCF adsorbed on TiO₂ (mg L⁻¹)</th>
<th>q mg DCF/g TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>40 min</td>
<td>27.96</td>
<td>2.04</td>
<td>6.68</td>
</tr>
<tr>
<td>0.8</td>
<td>40 min</td>
<td>25.91</td>
<td>4.09</td>
<td>5.11</td>
</tr>
</tbody>
</table>

\[ q = \frac{V}{m}(C_i - C_f) \]
%DCF adsorbed on TiO₂ = 100 \cdot \left(\frac{C_i - C_f}{C_i}\right)

Where: \(V\) is volume (4.5 L), \(m\) is mas of TiO₂ (1.35 or 3.6 g), \(C_i\) is DCF initial concentration and \(C_f\) is DCF concentration in solution after 40 minutes of adsorption.

S.3.2. Photolysis test

Photolysis test was carried out in the flotation cell for a time of 40 minutes using two Repti Glo 5.0 lamps. A percentage lower to 7% of diclofenac degradation was obtained.

S.3.3. Photocatalysis tests

Photocatalysis tests were performance in the flotation cell for catalyst concentration of 0.3 g L\(^{-1}\) and 0.8 g L\(^{-1}\). The results of degradation and mineralization of DFC are shown in Table 3 of the article.

S.3.4. Effect of the temperature on ozone production

In order to determine the ozone production of the equipment A2Z Model 5GLAB as a function of temperature, the ozone concentration was quantified at 29 \(\pm\) 1 and 34 \(\pm\) 1°C. The initial conditions were 2 L min\(^{-1}\) of oxygen and 220 milliAmperes.

Figure S.2. shows the ozone generation profiles as a function of time for both temperatures. It was found that the ozone production below 30°C is more stable and had an average production of 7.4 g m\(^{-3}\) of ozone, while at 34°C the average production was of 5.8 g m-3, being very unstable with a fall of 0.1 g m-3 per minute of operation. This behavior can be caused by overheating of the electrodes of the ozonator, so in this work the temperature was maintained constant at 29\(\pm\)1°C.

Figure S.2. Effect of temperature on ozone production
S.4. Hatta number calculation

A gas-liquid reaction is occurring in the flotation cell, mass transfer and chemical reaction must be considered to study the kinetics. The dimensionless number of Hatta (Ha) establishes the relative importance of the chemical reaction and the rates of mass transfer, and allows to classify the kinetic regime of ozonation and is defined as (Journal of Hazardous Materials 163 (2009) 768–776):

\[
Ha = \sqrt[3]{\frac{k D_{O_3} C_{DCF}}{k_L}}
\]  

(5.3)

Where \( k \) is the rate constant of the direct reaction between ozone and the DCF, \( D_{O_3} \) is the diffusivity of ozone in water, \( C_{DCF} \) diclofenac concentration and \( k_L \) the mass transfer coefficient for the liquid phase. For the calculation of Hatta number the following data previously reported in the literature (Water Res., 2014, 50, 189–199) were used: ozone diffusivity (\( D_{O_3} = 1.3 \times 10^{-9} \) m\(^2\) s\(^{-1}\)), transfer mass coefficient (\( k_L = 5 \times 10^{-5} \) m s\(^{-1}\)) and the rate constant of the direct reaction of ozone-diclofenac (\( k = 10^6 \) M s\(^{-1}\)) at pH 7. The initial concentration of DCF was 30 ppm (\( C_{DCF} = 10^{-4} \) M).