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# Impact of Reaction Parameters and Water Matrices on the Removal of Organic Pollutants by $TiO_2$/LED and ZnO/LED Heterogeneous Photocatalysis Using 365 and 398 nm Radiation

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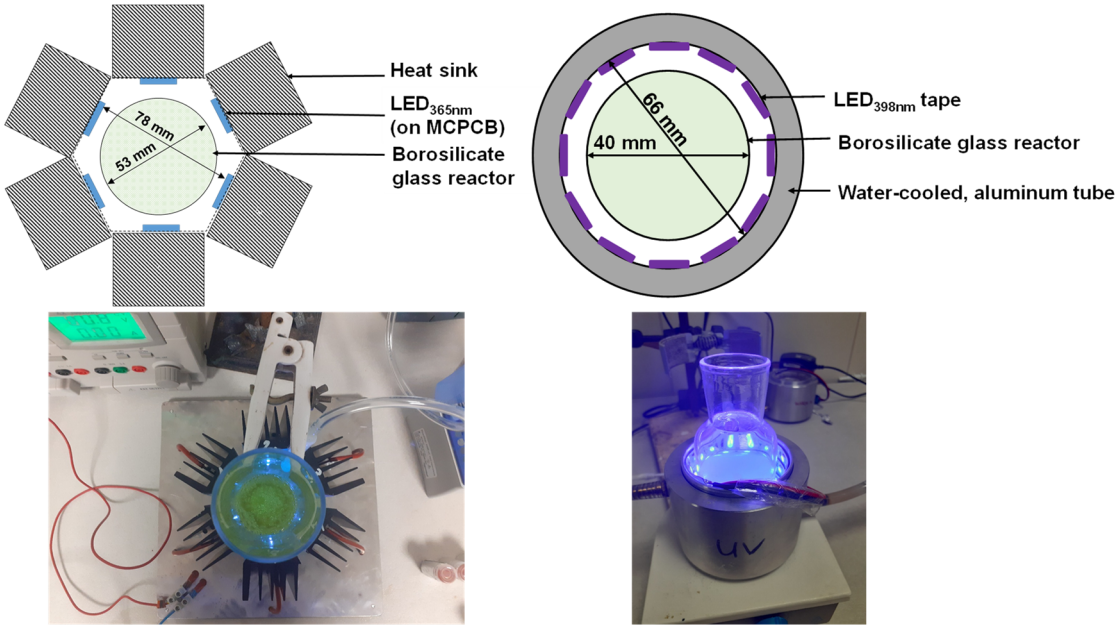


**Figure S1.** The schematic figures and photos of the photoreactors (**left**: $LED_{365nm}$, **right**: $LED_{398nm}$).

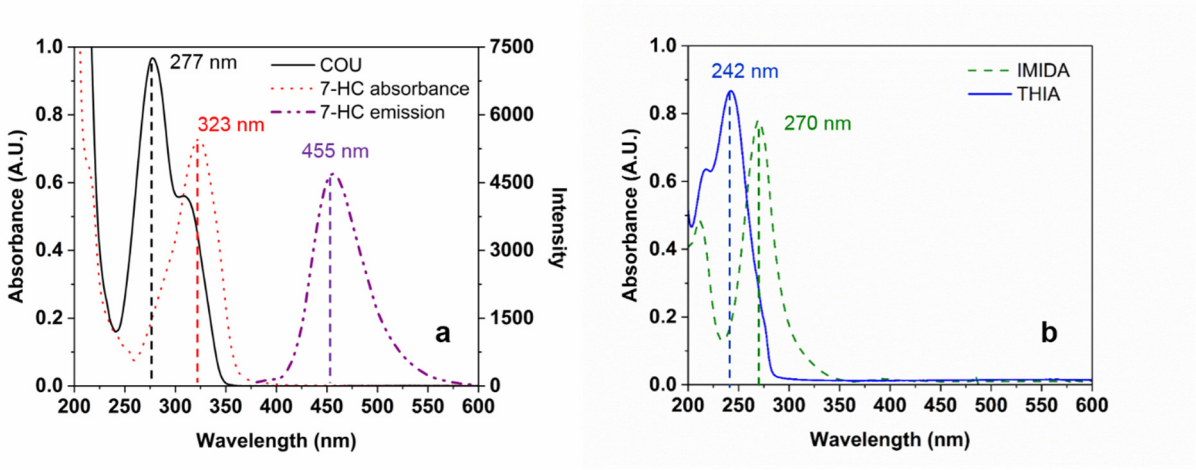


**Figure S2.** UV-Vis absorption and emission spectra of COU and 7-HC (**a**), and the UV-Vis absorption spectra of IMIDA and THIA (**b**).

**Table S1.** The list of used chemicals, their distributors and purity.

| Chemical | Distributor | Purity |
|---|---|---|
| coumarin | Sigma Aldrich (St.Louis, USA) | 99% |
| 7-hydroxycoumarin | Sigma Aldrich (St.Louis, USA) | 99% |
| imidacloprid | VWR (Radnor, USA) | 98% |
| thiacloprid | Sigma Aldric h(St.Louis, USA) | 99% |
| NaCl | VWR (Radnor, USA) | 99% |
| $NaHCO_3^-$ | VWR (Radnor, USA) | 99% |
| HCl | Sigma Aldrich (St.Louis, USA) | 98% |
| NaOH | VWR (Radnor, USA) | 99% |
| Catalase (bovine liver) | Sigma Aldrich (St.Louis, USA) | >55% protein content |
| $Fe_2(SO_4)_3 \times nH_2O$ | VWR (Radnor, USA) | 98% |
| $K_2C_2O_4$ | Reanal (Budapest, Hungary) | 98% |
| 1,4-phenantroline | Sigma Aldrich (St.Louis, USA) | 99% |
| $TiO_2$ | Acros Organics (Geel, Belgium) | 99.5% |
| ZnO | Sigma Aldrich (St.Louis, USA) | 80% |
| $N_2$ | Messer Hungary (Budapest, Hungary) | 99.995% |
| Synthetic air | Messer Hungary (Budapest, Hungary) | Medical grade |
| MeOH | VWR (Radnor, USA) | 99.8% |
| $H_2O$ | Merck-Millipore (Burlington, USA) | ultrapure |

**Table S2.** The parameters of the matrices.

| Parameter | Tap Water | Biologically Treated Domestic Wastewater |
|---|---|---|
| pH | 7.4 | 7.8 |
| Conductivity (μS $cm^{-1}$) | 627 | 1258 |
| COD (mg $dm^{-3}$) | 4.2 | 24.4 |
| $NH_4^+$–N (mg $dm^{-3}$) | <0.4 | <0.4 |
| $NO_3^-$ (mg $dm^{-3}$) | <0.7 | 3.37 |
| $Cl^-$ (mg $dm^{-3}$) | 8.75 | 120 |
| TOC (mg $dm^{-3}$) | 0.79 | 6.9 |
| Inorganic carbon * (mg $dm^{-3}$) | 73.4 | 103.4 |

* Dissolved $CO_2$, $HCO_3^-$ and $CO_3^{2-}$.

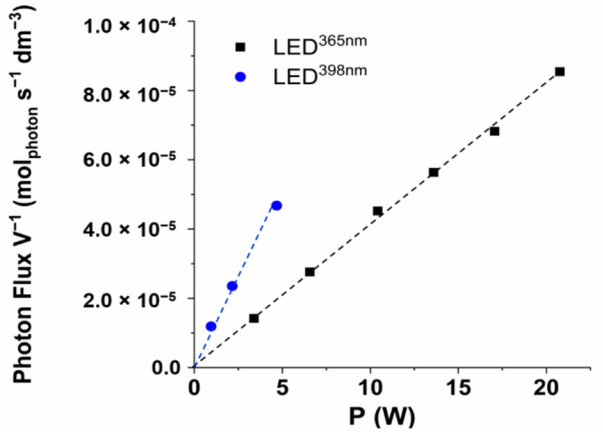


**Figure S3.** The photon flux of the LEDs as a function of electric power input.

**Table S3.** The photon flux of the light sources and the calculated electric efficiencies.

| Light Source | Photon Flux ($mol_{photon}$ $s^{-1}$) | $P_{electric}$ (W) | $E_{photon}$ * (eV) | $P_{radiant}$ (W) | Electric Efficiency $P_{radiant}/P_{electric}$ |
|---|---|---|---|---|---|
| $LED_{365nm}$ | $2.83\times10^{-6}$ | 3.39 | 3.38 | 0.93 | 0.27 |
| | $5.52\times10^{-6}$ | 6.56 | 3.38 | 1.80 | 0.27 |
| | $1.13\times10^{-5}$ | 13.60 | 3.38 | 3.67 | 0.27 |
| | $1.71\times10^{-5}$ | 20.77 | 3.38 | 5.58 | 0.27 |
| $LED_{398nm}$ | $1.19\times10^{-6}$ | 0.96 | 3.12 | 0.36 | 0.37 |
| | $2.35\times10^{-6}$ | 2.16 | 3.12 | 0.71 | 0.33 |
| | $4.68\times10^{-6}$ | 4.68 | 3.12 | 1.41 | 0.30 |

* Nominal value calculated for $\lambda_{max}$.

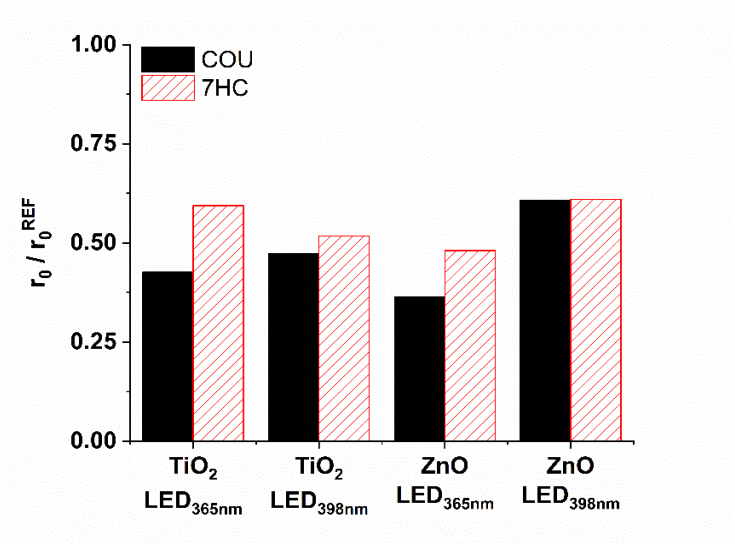


**Figure S4.** The effect of $5.0 \times 10^{-3}$ M MeOH on the transformation rate of COU and the formation rate of 7-HC.

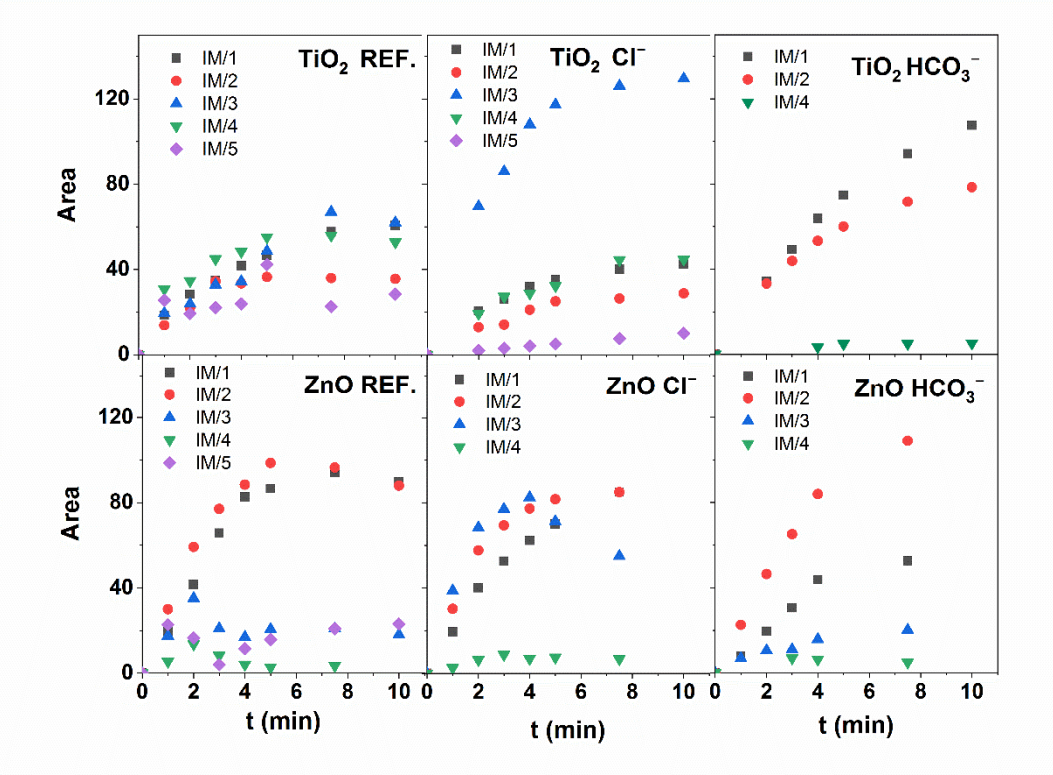


**Figure S5.** The effect of inorganic ions on the products of IMIDA detected by HPLC-DAD during treatment using $LED_{365nm}$.

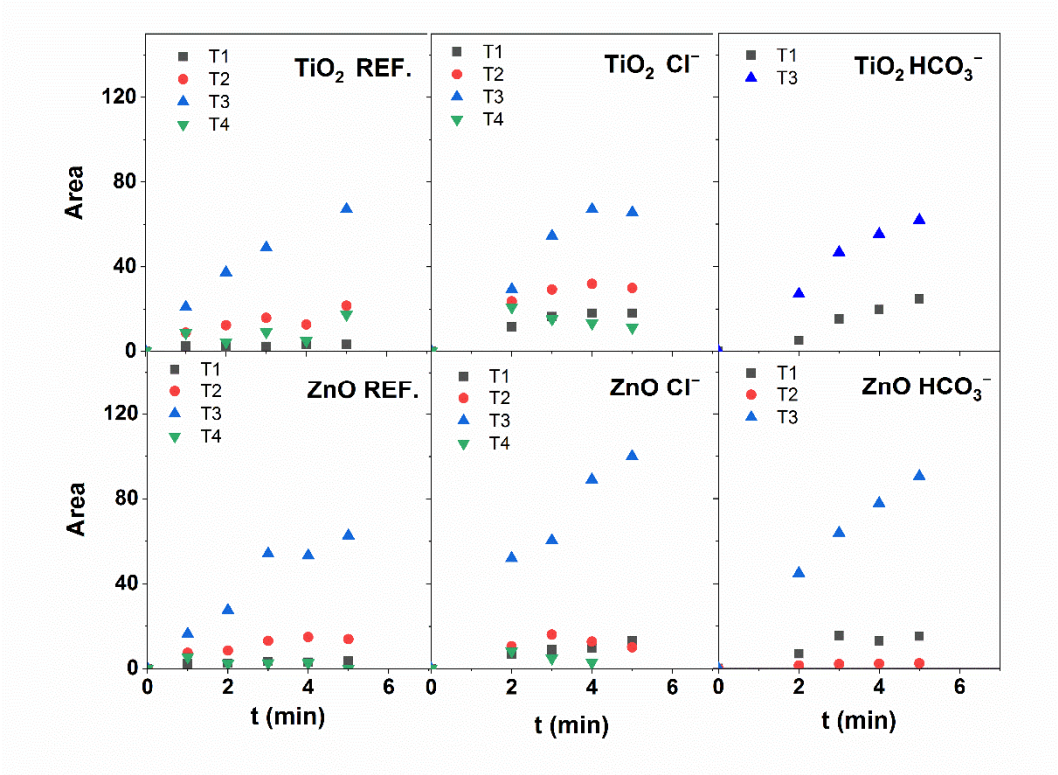


**Figure S6.** The effect of inorganic ions on the products of THIA detected by HPLC-DAD during treatment using $LED_{365nm}$.

**Table S4.** The inorganic standard electrode potentials of the ions and radical ions [105].

| Half Reaction | Electrode Potential/V |
|---|---|
| $O_2(aq) + e^- \rightarrow O_2^{\bullet}$ | −0.18 |
| $O_2(aq) + H^+ + e^- \rightarrow HO_2^{\bullet}$ | +0.10 |
| $HO_2^{\bullet} + H^+ + e^- \rightarrow H_2O_2$ | +1.46 |
| $HO^{\bullet} + e^- + H^+ \rightarrow H_2O$ | +2.730 |
| $HO^{\bullet} + e^- \rightarrow OH^-$ | +1.902 |
| $Cl^{\bullet} + e^- \rightarrow Cl^-$ | +2.432 |
| $Cl_2^{\bullet -} + e^- \rightarrow 2\ Cl^-$ | +2.126 |
| $HOCl + e^- \rightarrow ClOH^{\bullet -}$ | +0.25 |
| $ClOH^{\bullet -} + e^- \rightarrow Cl^- + OH^-$ | +1.912 |
| $ClOH^{\bullet -} + e^- + H^+ \rightarrow Cl^- + H_2O$ | +2.740 |
| $NO_3^{\bullet} + e^- \rightarrow NO_3^-$ | +2.466 |
| $NO_2^{\bullet} + e^- \rightarrow NO_2^-$ | +1.04 |
| $CO_2^{\bullet -} + H^+ + e^- \rightarrow CO_3^{2-}$ | +1.52 |
| $CO_3^{\bullet -} + e^- \rightarrow HCO_2^-$ | +1.57 |