Introduction

Neonicotinoid insecticides, including imidacloprid, thiacloprid, thiamethoxam, clothianidin and acetamiprid have been included in the extended “Watch” list of the European commission within the water framework directive since 2018, due to the confirmed risk and danger for the aquatic environment. The aim of this work was to develop modified TiO₂ photocatalysts and innovative designs of photocatalytic reactors for the decomposition of neonicotinoid insecticides under conditions of simulated solar irradiation. The surface functionalization of TiO₂ was performed to reduce the energy band gap (E₉₀) of the TiO₂ and to prepare a stable immobilized photocatalytic layer with acceptable mechanical and catalytic properties under different operating conditions and a flat-plate photoreactor equipped with two lamps was designed for degradation of imidacloprid, which was used as a representative of neonicotinoid insecticides.

Experimental

Catalysts:
- TiO₂ P25
- TiO₂ - UV-C susp.
- TiO₂ - UV-C
- TiO₂ - urea
- TiO₂ - plasma Ar
- TiO₂ - plasma N₂

Experimental conditions:
- Volume: 240 ml
- Flow: 30 - 300 ml/min
- Solar irradiation: Arcadia Sun light 8W; Solar GLO 125 W; Natural Sun
- pH: 3 - 9

Results

T1: Energy band gap (E₉₀)

<table>
<thead>
<tr>
<th>Sample</th>
<th>E₉₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ P25</td>
<td>3.20</td>
</tr>
<tr>
<td>TiO₂ - UV-C susp.</td>
<td>3.15</td>
</tr>
<tr>
<td>TiO₂ - UV-C</td>
<td>3.10</td>
</tr>
<tr>
<td>TiO₂ - urea</td>
<td>3.07</td>
</tr>
<tr>
<td>TiO₂ - plasma N₂</td>
<td>3.05</td>
</tr>
<tr>
<td>TiO₂ - plasma Ar</td>
<td>3.10</td>
</tr>
</tbody>
</table>

Conclusion

Photocatalytic degradation of imidacloprid was performed under the visible part of the solar spectrum to reduce the investment costs of the process in the real systems. Surface functionalization was performed, and TiO₂ energy band gap (E₉₀) was reduced as presented in table T1. Prepared stable immobilized layers of functionalized TiO₂ were used for photocatalytic degradation of imidacloprid, under same reaction conditions.

Results showed that although TiO₂ – plasma N₂ photocatalyst has lowest band gap (3.05 eV) it was not the most active tested photocatalyst (F2). TiO₂ – UV-C was the most active photocatalyst with energy band gap of 3.10 eV, which was functionalized using 2 UV-C lamps. The most active photocatalyst, TiO₂ – UV-C, was further tested using different reactant mixture flow rates (F3), pH of reaction mixture (F4) and different irradiation sources (F5). It was concluded that flow rates have minimal influence while pH and irradiation sources have great influence on photocatalytic degradation of imidacloprid in tested reaction system. The best results were achieved with pH = 5 and using natural sunlight as the irradiation source. Different functionalization methods can be used to reduce the energy band gap of the TiO₂, but this does not necessarily mean better photocatalytic degradation of imidacloprid can be achieved. Good results were obtained but further study is necessary for better understanding of the obtained results.