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HETEROGENEOUS PHOTOCATALYSIS OF IMIDACLOPRID – EFFECT OF REACTION PARAMETERS, MINERALIZATION AND MATRICES

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Abstract

The photocatalytic removal of imidacloprid, a neonicotinoid insecticide with serious environmental effects, has been investigated. Photocatalytic treatment using TiO_2 photocatalyst was effective at the complete transformation of imidacloprid over 30 minutes. The mineralization was also investigated, and the reduction of total organic carbon and chemical oxygen demand was inhibited after the transformation of imidacloprid, indicating the accumulation of degradation products resistant to HO•. The dechlorination of the organic content was complete, but only 25 % of total nitrogen content was transformed into NO_3^-, indicating that the accumulated products are nitrogen containing organic compounds. The effect of two light matrices, drinking water and purified industrial wastewater was also investigated. The low organic content of the wastewater only slightly reduced the transformation rate of imidacloprid, but the high ionic content of drinking water significantly reduced the effectiveness by increasing the aggreagation of TiO_2.

Introduction

Pesticides are one of the most widespread pollutants of agricultural wastewaters, and they have been detected in trace amounts in natural and drinking water too. Neonicotinoid pesticides have been investigated in the last decade due to their harmful effect on pollinators and aquatic life, especially imidacloprid, which has the highest toxicity to honeybees (LD50 5-70 ng). [1] It has been banned in open-field use by the European Union in 2018, and several researches have been conducted for their removal from water and wastewater. Advanced Oxidation Processes (AOPs) have been investigated for the removal of imidacloprid, and heterogeneous photocatalysis is a promising method for its degradation. [2,3]

The most widespread photocatalyst is TiO_2. When it absorbs photons with an energy higher than its band gap, a separation of charges occur, forming a conduction band electron (e_{cb}^-), and a valence band hole (h_{vb}^+). [4] These charge carriers may react with O_2 and H_2O/HO^- and through a series of reactions, hydroxyl radical (HO•) form. The photogenerated charges may also react with adsorbed organic compounds in direct charge transfer reactions. [5] Heterogeneous photocatalysis is well known for the high mineralization rates, as the degradation of the target compounds and its intermediates happens at the same time due to the reactions with non-selective HO•.

The aim of this study was to investigate the transformation and mineralization of imidacloprid using commercial TiO_2 photocatalyst. The transformation and mineralization were characterized by the change of the concentration of chemical oxygen demand (COD), total organic carbon (TOC) content, concentration of adsorbable organic halogen content (AOX), NO_3^- concentration and the concentration of H_2O_2. For the practical reasons, the effect of two light matrices (drinking water from Szeged, and a purified industrial wastewater) were investigated on the effectiveness of the degradation process at two pesticide concentrations.

Experimental

All experiments were performed in a thermostated (at 25 °C) glass reactor. 1.0 g dm^{-3} TiO_2 Aeroxide P25® (Acros Organics) suspensions were recirculated, bubbled with air, and stirred during the experiment. 250 cm^3 imidacloprid (0.1 and 0.025 mM) was dissolved in either Milli-Q (MQ) water, drinking water or purified wastewater. The samples were centrifuged and filtered with 0.22 µm PVDF-L syringe filters before analysis. The concentration of imidacloprid was measured using HPLC-DAD, using an Agilent 1100 with a Licrosphere 100 RP-18 column. The eluent contained 40 % methanol and 60 % water, its flow rate was 1.0 ml min^{-1}. The detection wavelength was 270 nm. The TOC content was measured using an Analytik Jena N/C 3100. The COD measurements were performed using LCK1414 (Hach) colorimetric cuvette test with a 5.0-60.0 mg dm^{-3} measuring range. The digestion was performed in a HT200S thermostate, the COD values were measured using a DR2800 spectrophotometer. The concentration of H_2O_2 was measured with a cuvette test by Merck, with a 0.015-6.00 mg dm^{-3} measuring range. The NO_3^- concentration was also measured with a cuvette test provided by Merck, with a 0.4-111 mg dm^{-3} measuring range. The H_2O_2 and NO_3^- tests were measured using a Spectroquant Multy (Merck) spectrophotometer. The AOX measurements were performed using an Analytik Jena Multi X 2500 instrument. Before the measurements 15 cm^3 sample was adsorbed on 100 mg high purity activated carbon adsorbent. Drinking water from Szeged (Hungary), and industrial wastewater (purified with reverse osmosis) were used to investigate the matrix effect. The main analytical parameters for both matrices are presented in Table 1.

Table 1. Parameters of the matrices

Parameters	Drinking water	Purified wastewater
pH	7.3	5.5
Conductivity (µS cm^{-1})	482	21.9
COD (mg dm^{-3})	0.69	< 15
NH_4-N (mg dm^{-3})	< 0.4	< 0.4
NO_3^- (mg dm^{-3})	< 0.7	1.5
Cl^- (mg dm^{-3})	8.75	-
TOC (mg dm^{-3})	8	-

Results and discussion

First, the transformation and mineralisation of 0.1 mM imidacloprid dissolved in MQ water was investigated. Imidacloprid was completely transformed after 30 minutes, but still a high amount of organic matter remained in the suspension. The TOC and COD values were significantly reduced in the first 30 minutes (to 46 and 70 % respectively), but after the complete transformation of imidacloprid, their reduction rate significantly reduced. After 120 minutes of treatment 25 % TOC and 40 % COD content was still measured. This suggest, that after the transformation of imidcacloprid and its main aromatic intermediates, certain products form, that do not react with HO•, or their reaction are very slow, thus they cannot be removed effectively using heterogeneous photocatalysis. The H_2O_2 concentration is increasing at a high rate during the first 20 minutes of the experiment, but it decreases after the transformation of imidacloprid. This also confirms that, the transformation of some interemediates are very

slow or negligible, as H_2O_2 forms primarily during the degradation of organic compounds, due to the $HO_2^{\bullet}$ elimination from organic peroxyl radicals.

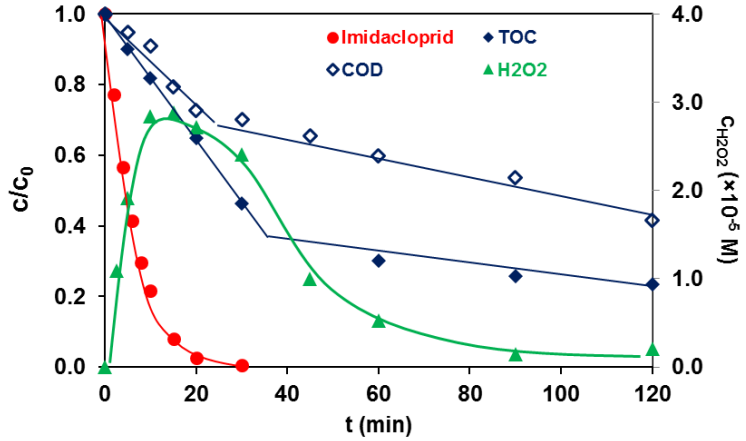

Figure 1. The relative concentration of imidacloprid, TOC, and COD content, and the concentration of H_2O_2 as a function of time

The AOX content was also measured, to investigate the dehalogenation of imidacloprid and its intermediates. The AOX content reduced at a similar rate as imidacloprid, thus no chlorinated intermediates can be observed after 40 minutes of photocatalytic treatment. The NO_3^- content was also measured to investigate the mineralization of the nitrogen-containing organic compounds. After 120 minutes treatment only 25 % of the total nitrogen content was transformed into NO_3^-, indicating that nitrogen containing organic products are highly resistant to photocatalytic treatment.

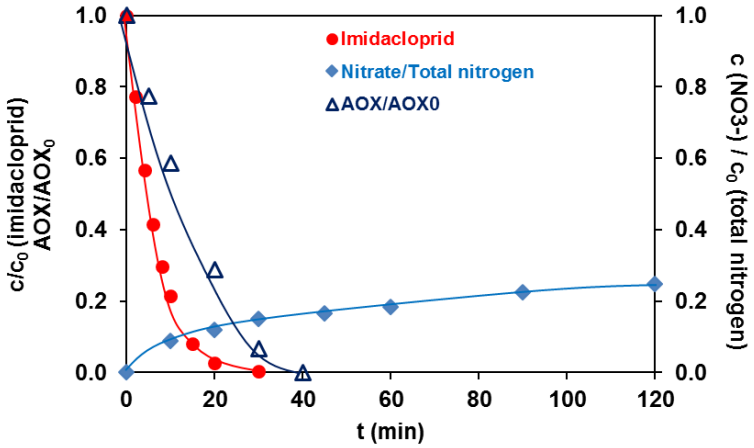

Figure 2. The relative concentration of imidacloprid, the reduction of AOX content and the conversion of total organic nitrogen to NO_3^- as a function of time

For investigation the practical applicability of the method for the removal of imidacloprid, two milde matrices (purified wastewater and tap water) were employed, with two different initial concentrations (0.10 mM and 0.025 mM).

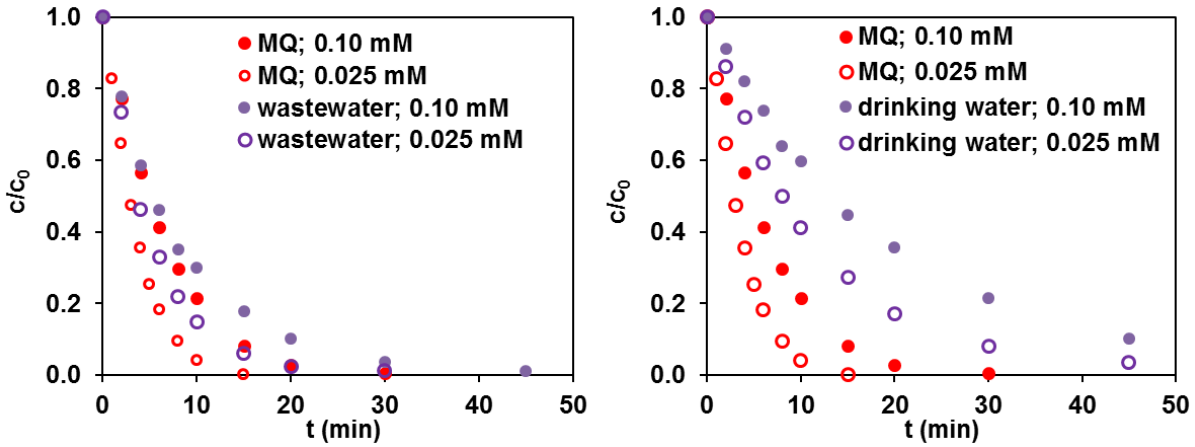

Figure 3. The relative concentration of imidacloprid versus time of irradiation in different matrices

In the case of the purified wastewater, only a slight reduction of reaction rate was observed, most likely due to the organic content of the matrix, as it could compete with imidacloprid for HO•. In the case of drinking water a much more significant negative effect was found, which is most probably caused by the high ionic content. In drinking water the initial reaction rates were reduced by 56 and 60 % for 0.1 and 0.025 mM imidacloprid respectively. The high ionic strength can initiate the aggregation of TiO_2 particles, reducing the effective surface available for light, thus reducing the formation rate of HO• and transformation rate of organic substrate.

Table 2. Initial reaction rates and relative reaction rates of imidacloprid transformation in matrices, compared to measurement taken in MQ water

	c_0 ($\times 10^{-4}$ M)	r_0 ($\times 10^{8}$ M s^{-1})	r_0/r_0^{ref}
Milli-Q (ref.)	1.00	16.7	-
	0.25	7.3	-
Purified wastewater	1.00	17.3	1.04
	0.25	5.6	0.76
Drinking water	1.00	7.3	0.44
	0.25	2.9	0.40

Conclusion

- The heterogeneous photocatalysis of imidacloprid, a neonicotinoid pesticide that causes serious environmental problems, has been investigated
- 0.1 mM imidacloprid completely transforms during 30 minutes photocatalytic treatment
- Dechlorination is effective, but only 54 % of imidacloprid can be mineralized
- Nitrogen-containing products having low reactivity towards HO• forms.
- Purified wastewater having low organic content had no significant effect on the transformation rate of imidacloprid, but tap water having high ionic content strongly inhibited the transformation due to the aggregation of TiO_2 particles

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