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EFFECT OF IRRADIATION WAVELENGTH ON THE HETEROGENEOUS PHOTOCATALYTIC REMOVAL OF ORGANIC POLLUTANTS USING TiO₂ AND ZnO

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Abstract

The efficiency of TiO₂ and ZnO was compared during the photocatalytic removal of neonicotinoid pesticides (imidacloprid and thiacloprid) and sulfonamide antibiotics (sulfamethazine and sulfamethoxypyridazine), causing severe environmental and health problems. The differences between LEDs emitting at 365 nm and 398 nm were compared, and removal efficiencies were tested in tap water and biologically treated wastewater matrices. The effect of the most abundant anions, Cl⁻ and HCO₃⁻ on the removal efficiency and [•]OH formation was also compared. TiO₂ was more sensitive to the matrices and the irradiation wavelength. [•]OH production was higher for TiO₂, and 398 nm photons resulted in a higher contribution of [•]OH. Efficiencies were not reduced by matrix components for ZnO, which is mainly the result of increased [•]OH-production by Cl⁻. In the case of TiO₂ and 365 nm photons, the formation of CO₃⁻ from HCO₃⁻ was assumed. For TiO₂, the significant inhibition of matrices could not be explained solely by the effect of anions.

Introduction

Pesticides and pharmaceuticals are amongst the most common organic pollutants found in wastewaters, and they have been detected in water bodies. Even in low concentration, they might have several chronic effects (e.g., carcinogenic, teratogenic, endocrine disruptor), and their accumulation in the ecosystem leads to further problems [1]. The removal of these trace amounts of pollutants is inefficient with the currently used traditional water treatment methods; therefore, the application of additive processes to be required.

Advanced Oxidation Processes (AOPs) may offer a way to remove trace amounts of pollutants using highly reactive radicals. Heterogeneous photocatalysis is a widely investigated AOP, based on the irradiation of a semiconductor. The absorption of photons with appropriate energy causes a charge separation and leads to electron-hole pair formation. These photogenerated charge carriers directly oxidize/reduce the pollutants or lead to reactive oxygen species (ROS) formation via further reactions. Generally, the most important ROS is the hydroxyl radical ([•]OH) due to its high reactivity and low selectivity [2]. The most widespread photocatalysts are TiO₂ and ZnO, both having a relatively wide bandgap (3.0-3.3 eV); therefore, UV light is needed for their efficient excitation. Due to the drawbacks of traditional UV lamps, light-emitting diodes (LEDs) have recently gained popularity in water treatment. LEDs often offer longer lifetimes, higher electric efficiencies, lower prices, and more flexible photochemical designs [3]. The intensity and wavelength of the light source is probably the most important factor determining the amount and lifetime of electron-hole pairs, thus directly affecting ROS formation [4,5], but results - even for the most well-characterized photocatalysts - are few and sometimes contradicting. UV-LEDs may offer a simple way to investigate these effects thanks to their relatively narrow emission spectra and precisely tunable intensity. Beyond energy consumption, the other primary obstacle for the practical application of photocatalysis is the complex effect of matrices. The components of the treated water can lead to significantly

hindered photocatalytic activity, either by scavenging ROS/photogenerated charges, occupying the surface sites of the catalyst surface or by increasing the aggregation of the particles. The results must be carefully evaluated, as matrix components may even increase the efficiency in some cases due to the formation of selective radicals from inorganic ions (e.g., $\text{SO}_4^{\cdot-}$, $\text{CO}_3^{\cdot-}$, Cl^{\cdot}) [6]. The effect of matrices is relatively rarely investigated in detail, especially for photocatalysts other than TiO_2 [7,8].

This work aimed to compare the efficiency of two commercial photocatalysts, TiO_2 and ZnO , for the removal of four organic pollutants, two neonicotinoid pesticides, imidacloprid (IMIDA) and thiacloprid (THIA), and two sulfonamide antibiotics, sulfamethazine (SMT) and sulfamethoxypyridazine (SMP). Two UV-LEDs, emitting at 365 nm and 398 nm were used, and the effect of two water matrices, tap water and biologically treated wastewater (BTWW) were investigated. The effect of their most abundant inorganic components, Cl^- and HCO_3^- were also compared. The $\cdot\text{OH}$ formation rates were compared using coumarin (COU), as the formation rate of its hydroxylated product, 7-hydroxy-coumarin (7-HC) correlates well with the formation rate of $\cdot\text{OH}$.

Experimental

During the photocatalytic experiments, commercially available photocatalysts, TiO_2 Aeroxide® P25 (Acros Organics) and ZnO (Sigma Aldrich) were used, the concentration of their suspensions was 1.0 g dm^{-3} . Two photoreactors were used, one was equipped with 12 high-intensity UV-LEDs emitting at 365 nm (Vishay, VLMU3510-365-130, 2 W/LED), the other with a UV-LED tape with 50 diodes emitting at 398 nm (LEDMaster, 0.09 W/LED). An AX-3005DBL-3 laboratory power supply was used to provide and control the electrical power needed to operate the light sources. In the case of 365 nm LEDs 200 cm^3 suspensions were irradiated, and 100 cm^3 in the case of 398 nm LEDs. The suspensions were constantly being bubbled with synthetic air during the measurements. Before the measurements, the suspensions were stirred in the dark for 20 minutes. Before analysis, samples were centrifuged at 15000 RPM and filtered using a $0.22 \mu\text{m}$ PVDF syringe filter.

For the investigation of $\cdot\text{OH}$ -formation, $5.0 \times 10^{-4} \text{ M}$ COU was used; its concentration was determined via UV-Vis spectrophotometry (Agilent 8453) at 277 nm. The formation of 7-HO-COU was measured using fluorescence spectroscopy (Hitachi F-4500). The concentration of the neonicotinoids and sulfonamides was determined via HPLC system (Agilent 1100). A Lichrosphere 100 RP-18 $5 \mu\text{m}$ column was used to separate the neonicotinoids and their products (mobile phase: 40 : 60 MeOH : H_2O mixture; $1.0 \text{ cm}^3 \text{ min}^{-1}$ flow rate; $30 \text{ }^\circ\text{C}$). Detection of IMIDA and THIA was performed at 270 nm and 242 nm, respectively. For separation of SMT and SMP and their products, 30 : 70 MeOH : formic acid (0.1 v/v%) mixture as the mobile phase was used. UV-detection was performed at 265 and 261 nm. Initial reaction rates (r_0) were determined from the linear part of the kinetic curves (up to 20 % transformation of the model compound).

Results and discussion

The $\cdot\text{OH}$ formation rate was compared using TiO_2 and ZnO under 365 nm and 398 nm irradiation. The transformation rate of COU and the formation rate of 7-HC were determined. In the case of 365 nm irradiation and TiO_2 lower transformation rate ($3.37 \times 10^{-7} \text{ M s}^{-1}$) of COU was measured compared to ZnO ($4.68 \times 10^{-7} \text{ M s}^{-1}$), but the formation rate of 7-HC was 40% higher in the case of TiO_2 , indicating a more significant contribution of $\cdot\text{OH}$. The differences were less pronounced using 398 nm LEDs, but TiO_2 still produced higher amounts of $\cdot\text{OH}$. The yield of 7-HC was higher than 365 nm irradiation, indicating a higher contribution of $\cdot\text{OH}$ when lower energy photons are used.

ZnO was more effective in eliminating each target pollutants than TiO₂ (8-50% difference). SMP, TiO₂ photocatalyst, and 398 nm irradiation caused an extremely high transformation rate ($7.37 \times 10^{-7} \text{ M s}^{-1}$) compared to the other experiments with 398 nm LEDs ($2.48\text{-}6.43 \times 10^{-8} \text{ M s}^{-1}$). It might be caused by the fact, that in the case of 398 nm photons, only the rutile (band gap: 3.0 eV) phase of TiO₂ is excited, resulting in a different transformation mechanism. It was confirmed that, in 398 nm radiated TiO₂ suspension, the main product of SMP formed via SO₂ extrusion, which was not detected during the other experiments.

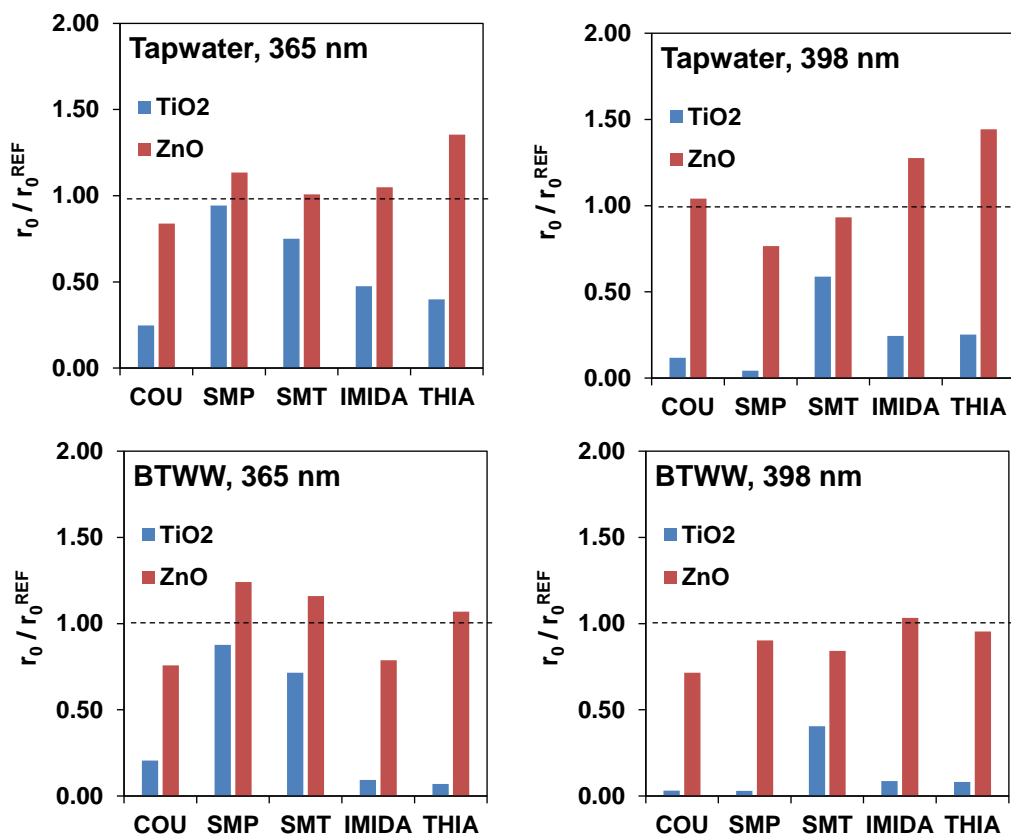


Figure 1. The effect of tap water and biologically treated domestic wastewater (BTWW) on the relative transformation rates (r_0/r_0^{REF}) of the model compounds using 365 nm and 398 nm LEDs

Experiments were performed in tapwater and BTWW matrices to investigate their effect on efficiency. In the case of TiO₂, both matrices caused an adverse effect; only minor inhibition was measured in the case of sulfonamides. ZnO was less sensitive to the matrices; even a slight increase in the transformation rates was observed in some cases. The formation rate of 7-HC also increased, especially when using 365 nm LEDs, which indicate an increased $\cdot\text{OH}$ formation (by 210-240%), as opposed to TiO₂, where it was significantly inhibited (by 80%), explaining the decreased efficiency. When using 398 nm LEDs, similar effects were determined in both matrices, and the efficiency was further reduced when using TiO₂. The matrices completely inhibited the fast transformation of SMP via SO₂-extrusion, resulting in similar reaction rates measured for the other model compounds.

To further investigate the complex effect of matrices, the effect of the most abundant anions – Cl⁻ and HCO₃⁻ – having radical scavenging ability was investigated. Their concentration was set to that measured in BTWW (120 mg dm⁻³ Cl⁻ and 525 mg dm⁻³ HCO₃⁻). Both ions have been reported to react with $\cdot\text{OH}$ and photogenerated holes, and are responsible for the reduced

transformation rates. At the same time, their reaction with electron-hole pair results in more selective, less reactive radicals (Cl^\bullet , $\text{CO}_3^{\bullet-}$). Despite its high $\cdot\text{OH}$ -scavenging capacity, in the case of TiO_2 Cl^- did not have a significant impact on the transformation rates, which may be the result of the reformation of $\cdot\text{OH}$ from Cl^- at neutral pH. In the case of ZnO , an enhanced transformation rate was detected for some model compounds, which could result from either hindered electron-hole recombination by adsorbed Cl^- , or the formation of reactive chlorine species (RCS), which react more selectively with organic pollutants. Based on these results, we can conclude that, the positive effect of Cl^- on ZnO is caused by the reduced recombination of charge carriers and enhanced $\cdot\text{OH}$ formation.

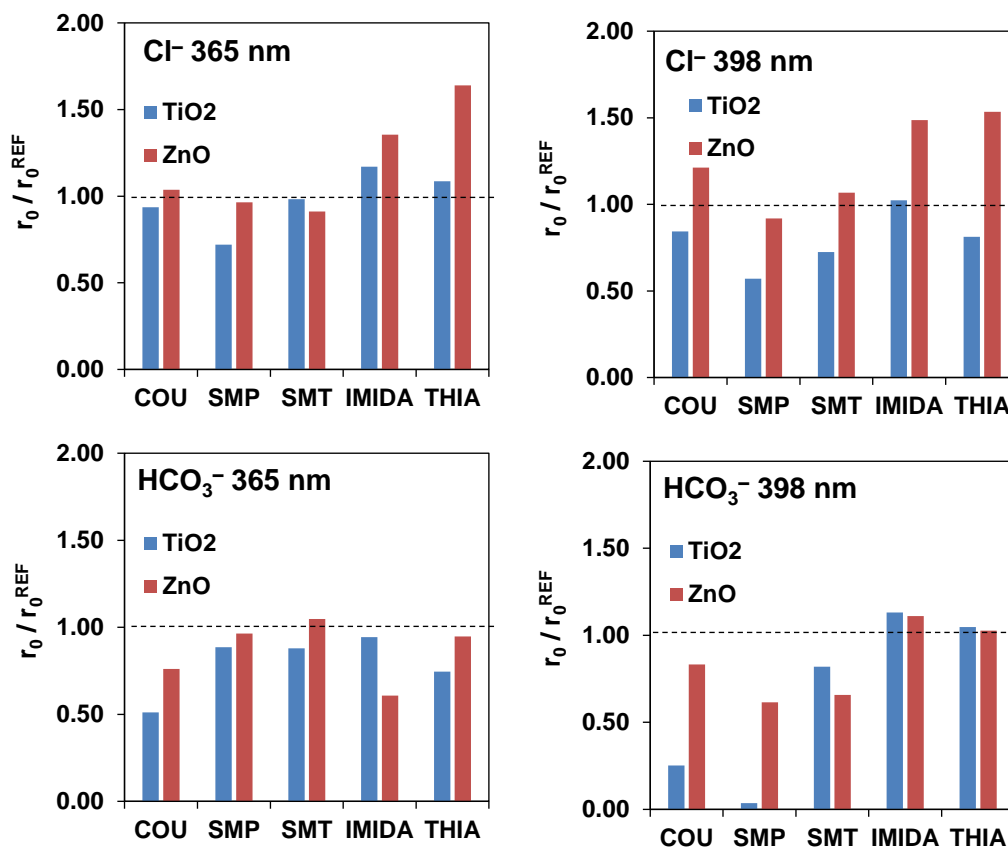


Figure 2. The effect of Cl^- and HCO_3^- on the relative transformation rates (r_0 / r_0^{REF}) of the model compounds using 365 nm and 398 nm LEDs

HCO_3^- did not affect or slightly lowered the transformation rates of the target compounds. Using 365 nm LEDs, the formation of 7-HC increased during the transformation of COU, which is the result of enhanced hydroxylation by $\text{CO}_3^{\bullet-}$. A similar effect was not detected in the case of ZnO , where $\text{CO}_3^{\bullet-}$ does not form, either when using 398 nm irradiation with TiO_2 . As opposed to Cl^- , HCO_3^- completely inhibited the fast transformation of SMP, similarly to tapwater and BTWW. The effect of these anions seems to depend on the excitation wavelength, with a less pronounced positive effect and similar or higher inhibition in the case of 398 nm photons. But even their combined effect could not explain the loss of efficiency when using TiO_2 in water matrices. The significant difference may come from the mixed-phase of TiO_2 as only exciting the rutile phase by 398 nm photons might lead to different reaction mechanisms.

Conclusions

In the case of TiO₂, the role of [•]OH is more significant than ZnO, and a higher contribution of [•]OH was measured when lower energy photons were used. TiO₂ is more sensitive to the effect of matrices compared to ZnO. For TiO₂, the effect of the irradiation wavelength is more significant due to its mixed phase with different bandgap energies. In the case of TiO₂ and 365 nm irradiation, less reactive CO₃^{•-} forms via hole scavenging, reducing efficiency, and making the COU method unsuitable for [•]OH-detection in the presence of carbonates. Cl⁻ has a positive effect when using ZnO, resulting in slightly increased efficiency in matrices due to increased [•]OH-formation.

Acknowledgments

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