

## Photoreactors and photocatalytic processes for waste and drinking water treatment

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### Highlights

- Different photoreactor configurations have been compared for water treatment.
- A new process has been designed for the removal of ammonia, nitrites and nitrates.
- Comparison with multistep biological nitrification/denitrification process is provided.
- The possibility to use part of the residual COD is explored.

### 1. Introduction

N-containing pollutants, such as inorganic ammonia, nitrites and nitrates, and some organic N-containing compounds (dyes, pesticides, drugs, etc.), are harmful contaminants for drinking water, inducing acute and/or chronic diseases, especially affecting infants and children. Furthermore, when released in waste waters, they contribute to eutrophication, or possibly contaminate ground water [1,2]. We here developed innovative photocatalytic processes for the abatement of N-containing compounds, focusing on selectivity towards innocuous N<sub>2</sub>, to be applied for the treatment of waste waters to meet law specifications. The development of efficient processes in photocatalysis is a challenging task. In particular, we focused on the design and optimization of the photoreactor, as a key for the adequate conversion of NH<sub>3</sub> or NO<sub>x</sub><sup>-</sup> and high selectivity to N<sub>2</sub>.

### 2. Methods

TiO<sub>2</sub>, SrTiO<sub>3</sub> and ZnO-TiO<sub>2</sub> have been prepared in nanosized form by using an innovative flame pyrolysis (FP) approach, able to synthesise single or mixed oxide nanoparticles, characterized by homogeneous particle size and good phase purity. Several metals such as Pt, Pd, Au and Ag were added as co-catalysts with a 0.1-0.5 wt% concentration by wet impregnation.

Specifically designed photoreactors have been set up, with external irradiation for better fitting with existing UV lamps in water treatment plants. At the moment a UVA lamp is used, with maximum emission around 365 nm and mean irradiance of 65 W/m<sup>2</sup>.

### 3. Results and discussion

Photocatalytic reduction of NO<sub>3</sub><sup>-</sup> and oxidation of NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> in water were carried out in a specifically designed Pyrex reactor, with a top quartz window. The catalysts were suspended in an aqueous solution of NH<sub>4</sub>Cl or NaNO<sub>3</sub>. The reactor was operated in semi-batch mode: the solution containing the pollutant to be photoconverted was added at the beginning of the reaction, whereas a gas stream was continuously flown through the reactor. The gas was composed of He during the conditioning-outgassing phase preliminary to every measurement. He was fed in continuous mode also during the nitrate photoreduction tests (N<sub>2</sub> is not used here to allow its quantification), whereas it was substituted by synthetic air (80 vol% He + 20 vol% O<sub>2</sub>) during the ammonia photooxidation experiments. A trap for ammonia, possibly stripped from the reactor, was placed downstream.

Comparison with commercial nanostructured TiO<sub>2</sub> revealed several differences. The samples prepared by FP exhibited higher activity with respect to the commercial photocatalyst, achieving *ca.* 35 % conversion of NH<sub>3</sub> in 5 h, without indication of decay or deactivation (0.1 mol% Pd/TiO<sub>2</sub> FP). By contrast, the commercial sample was less active and most of all its activity was rapidly ruled out. Some induction period was observed,

due to the need of sample conditioning upon irradiation. The most interesting point is that no trace of nitrites or nitrates was observed, confirming a full selectivity to the desired product, i.e. molecular N<sub>2</sub>.

The photoreduction of nitrates was also tested over the same samples. Very low conversion (<5%) was achieved with undoped catalysts, whereas also in this case Pd doping improved conversion by *ca.* one order of magnitude under the same experimental conditions. The key problem in this case remained process selectivity: 100% to the undesired NH<sub>3</sub> was attained for the undoped TiO<sub>2</sub> photocatalyst. Also in this case the addition of a photocatalyst revealed beneficial, since max 30% selectivity to ammonia was obtained for the Pd-doped sample prepared by FP.

The results allow to design a two steps process based on the same 0.1 mol% Pd/TiO<sub>2</sub> catalyst. The first step, under anaerobic conditions would convert nitrates and nitrites to N<sub>2</sub> and NH<sub>3</sub>. A second aerobic step would convert all the ammonia present to N<sub>2</sub>, given the high selectivity of the process.

This system is though as consistent with the final UV treatment of water depuration plants, which use UVA lamps for antibacterial sanitization. The addition of the photocatalyst would be useful as alternative to the tertiary nitrification-denitrification step and would add the advantage of a more robust and versatile process with respect to the slugs-based one.

A comparison was also carried out with active sludges from a water depuration plant. The opposite considerations as for activity and selectivity were derived from the results. The oxidation of ammonia was substantially inefficient, whereas the reduction of nitrates was effective (93% conversion in 5 h), but also in this case poorly selective. Mixed approaches between biological and photocatalytic treatments may be further explored in the future.

#### 4. Conclusions

These results on both reactions let us conclude that a two steps process can be designed to cope with the insufficient selectivity to N<sub>2</sub> during the nitrate photoreduction step. The ammonia produced is removed during a second, fully selective step of photooxidation. The flame pyrolysis procedure is a viable technique for the preparation of either bare or metal-doped semiconductors in nanosized form, to be used for the photocatalytic abatement of inorganic N-containing pollutants in waste or drinking waters.

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#### Keywords

Photoreactors; Water treatment; Photocatalytic processes; Photocatalytic production of H<sub>2</sub>.