

# Photo-oxidation of ammonia in wastewater to N<sub>2</sub> under UV, Vis and Sunlight

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## INTRODUCTION

The extensive use of activated nitrogen (i.e. ammonia and nitrates) has altered the equilibrium of the nitrogen cycle, since about 121 million tons of nitrogen per year from the atmosphere are converted into reactive forms, while it was calculated that the highest amount which does not impact on Earth's ecosystems should not exceed the 35 million tons per year. The World Health Organization (WHO) guidelines set the maximum exposure level in the drinking water at 500 ppb for ammonia, which can cause can cause irritations, burns and alter the natural pH equilibria of human body.

In the present work we exploited the ability of nanostructured photocatalysts to selectively photooxidise ammonia to N<sub>2</sub> using metal promoted titania-based materials under different radiation sources, i.e. UV lamp, LED visible lamp and natural sunlight.

## EXPERIMENTAL

P25 commercial TiO<sub>2</sub> nanoparticles from Evonik were compared with FSP titania nanoparticles prepared by flame spray pyrolysis. Both semiconductors were added with metal co-catalysts (Ag, Au, Pd, Pt, Cu) by wet impregnation and reduced at different temperatures. The catalysts were characterised by XRD, N<sub>2</sub> physisorption and DR-UV-Vis.

The photoreactor used in these tests is made of glass and has a cylindrical shape, with a central hole that allows the insertion of the UVA lamp (maximum emission 365 nm, 125 W) and, once inserted, the reactor capacity is about 0.35 L. The irradiance of the lamp was measured using a photo-radiometer and it was in average 260 W/m<sup>2</sup>. The mixing is assured by a magnetic stirrer and the temperature is controlled recirculating water in the cooling jacket. This system can be used in a sealed configuration and open to air. In the first case, the reactor is outgassed flowing 100 mL/min of a mixture of He:O<sub>2</sub> (4:1), lowered at 60 mL/min during the tests. A second setup was used with an external LED lamp (white light, 30 W) and the reactor was open to air, with the lamp fixed at 100 mm over the surface of the solution.

In every reactor configuration, the liquid phase was sampled by mean of a glass syringe and the catalyst was removed before the analysis using cellulose acetate filter and the liquid analysed by UV-Vis standard methods and by Ion Chromatography.

## RESULTS AND DISCUSSION

After optimisation of the reaction conditions, the performance of the different nanomaterials has been compared under the different light sources. For the sake of brevity, the activity under white LED irradiation, the Ag- and Au-promoted samples, leading to the lowest and highest band gap among the metal promoted samples, converted between 40 and 50% after 4 h of reaction, with faster response from the Au-promoted sample. Again a plateau conversion was reached, with increasing values after few hours. As a comparative reference, the P25 catalyst showed a similar conversion pattern as for the shape, but never reaching 20% conversion in the whole course of the test. Using tap water a reduction of activity for both the Ag- (conversion 16% vs. 48%) and Au-promoted catalysts (20% vs. 49%) was observed, though the latter remained the most active one. Finally, the effect of natural irradiation with sunlight was tested. For 0.1% Ag/FSP curve the results are very similar to the reaction under UV lamp, reaching 35-40 % conversion after 4 h. Similarly promising results were achieved with the bipromoted Cu-Pt sample, which reached a conversion of 44% vs. 39% after 4 h, though the reaction rate during the first 2 hours of treatment was lower.

## CONCLUSION

The photo-abatement of ammonium has been successfully performed using titania based nanostructured photocatalysts. It was observed that in the very first hours of treatment, the conversion of ammonium peaks at a certain value, depending on the catalysts employed and the reaction conditions, then it drops and rise again, finally reaching a plateau after 24h of reaction. The continuous supply of oxygen does not boost the reaction. Moreover, the selectivity towards overoxidized product have been minimized by working at slightly acid pH.

The addition of a metallic co-catalyst does not improve significantly the performance under UV light, if compared with FSP titania, but allow the adsorption of longer wavelength. Indeed, very good performance were achieved when simulating the natural light through a LED lamp, as a 48% max conversion of ammonium was achieved using optimized conditions and either 0.1% Ag or 0.1% Au/FSP catalysts. Finally, this setup was found to be effective even in exploiting the sunlight.