Visible and UV-light removal of inorganic N-containing pollutants from waste waters.

Ilenia Rossetti *1, Antonio Tripodi 1, Elnaz Bahadori 2, Gianguido Ramis 2

¹DICCA, Università degli Studi di Genova and INSTM Unit-Genova, Genoa (Italy) * gianguidoramis@unige.it ²Dip. di Chimica, Università degli Studi di Milano, CNR-ISTM and INSTM Unit-Milano università, Milan (Italy)

INTRODUCTION

Nitrogen containing pollutants, such as ammonia, nitrites and nitrates, are substances of concern due to their increasing amount in water, mainly in agriculturally intensive areas. They are correlated to many health issues, especially for infants and children, as well as with environmental problems given they are nutrients and induce uncontrolled increase of algal growth, especially in closed basins. Conventional biological treatment is insufficient to remove these pollutants from water, so that a tertiary specific treatment is needed.

Photocatalytic processes may be effective for the oxidation of ammonia and the reduction of nitrites and nitrates [1,2]. However, in the literature these processes are poorly explored and, furthermore, the attention is mainly focused on the materials rather than on reactors and process set up. Furthermore, scale up issues are mostly unaddressed, which is one of the aspects of this work.

EXPERIMENTAL/THEORETICAL STUDY

We focused on some TiO₂-based materials, in case added with Ag, Au, Pt or Pd as co-catalysts, for the photocatalytic removal of NH_3 , NO_3^- and NO_2^- . The activity of each sample was compared by using two different slurry type photoreactors, ca. 300 mL in volume, operated either in batch or semibatch mode. In the latter case air or inert gas was continuously flown during the photooxidation or photoreduction, respectively.

RESULTS AND DISCUSSION

Ca. 32% ammonia conversion was achieved over Pd/TiO₂ sample in 5 h, with 100% selectivity to N₂. Nitrate photoreduction was less effective, leading to max 10.5% conversion after 5 h, but with insufficient selectivity to N₂ (44% NH₃ selectivity).

These results have been combined with the treatment of the same model solutions with sludge of a water treatment plant, which evidenced that the biological nitrate reduction treatment was effective and sufficiently selective, whereas ammonia oxidation activity was by far unsatisfactory.

Therefore, a two step process can be designed, with a first NO_x^- photocatalytic or biological reduction stage,

followed by the photooxidation of ammonia, abating the one originally present and the one possibly formed during the reduction step.

Process scale up has been addressed, testing some of the most interesting materials in a 10 L photoreactor c/o the ISWA facility in Stuttgart, Germany with real waste water. Maximum ammonia conversion of 4 % was achieved with commercial TiO₂ (P25 by Evonik) after 30 minutes (maximum allowed reaction time) with competitive oxidation of organics. Indeed, the COD abatement after 30 minutes of reaction was 20-30%.

Finally, testing with LED visible lamp was also carried out, achieving 40% conversion after 5 h with Ag-loaded TiO_2 sample.

CONCLUSION

In this work we have investigated innovative processes for the removal of inorganic N-containing compounds. Interesting performance has been achieved for ammonia photooxidation in semibatch conditions, using Ag/TiO₂ samples even under visible light irradiation.

Scale up has been considered to 10 L size.

REFERENCES

- M. Compagnoni, G. Ramis, F.S. Freyria, M. Armandi, B. Bonelli, I. Rossetti, Journal of Nanoscience and Nanotechnology, 17, 3632–3653 (2017).
- F.S. Freyria, M. Armandi, M. Compagnoni, G. Ramis, I. Rossetti, B. Bonelli, Journal of Nanoscience and Nanotechnology, 17, 3654–3672 (2017).

ACKNOWLEDGMENTS

The authors are grateful to Fondazione Cariplo (Italy) for financial support (2015-0186 "DeN – Innovative technologies for the abatement of N-containing pollutants in water"). I. Rossetti and E. Bahadori are grateful to Fondazione Cariplo and Regione Lombardia for financial support (2016-0858 – "Up-Unconventional Photoreactors").