

PhD proposal
Institut Jean Barriol - Université de Lorraine- France

Research laboratory :

Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME UMR7564 CNRS-UL) :
405 rue de Vandoeuvre, 54600 Villers-lès-Nancy

Laboratoire de Chimie et Physique : Approche Multi échelles des Milieux Complexes (LCPA2MC EA 4632)

PhD Director and co-director : Christian Ruby (Professor-LCPME) et Bruno Azambre (Assistant Professor HDR-LCPA2MC)

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Title of the PhD project : Transformation and removal mechanism of nitrate ions in contact with filtration and photocatalytic materials

The protection of the water resource is among the major issues of the twenty-first century due to the growing of population, the rapid industrialization and the intensification of agriculture. Among the various pollutants that threaten the water quality, nitrate anions are of utmost importance since the excess of NO_3^- is mainly responsible of the water eutrophication phenomena in seawater. Biological treatment used to treat nitrate in urban area, *i.e.* the activated sludge process, are difficult to use in rural area due to infrastructure and maintenance costs. Successful PO_4 passive treatments were performed recently to remove phosphate at the pilot scale by using materials such as hydroxyapatite. Other recent research work identified layered double hydroxide as potential material to reduce nitrate into gaseous species. However the result obtained are not applicable for water treatment since NO_3^- is not selectively reduced into N_2 (denitrification) but is partially transformed into ammonium (NH_4^+) and NO_x species, which are more toxic than NO_3^- [1]. In this project, we will try to modify the structural properties of the cationic sheet of the $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ layered double hydroxides, commonly called green rust (GR) (substitution of Fe^{II} by Mn^{II} or Ba^{II}) to optimize the selectivity of the reduction reaction between GR and NO_3^- . Indeed the presence of Mn^{II} should increase the redox potential of GR and the presence of Ba^{II} may favor the insertion of nitrate leading to an increase of the reaction kinetics [3].

Other ways for the trapping/reduction of nitrates will also be considered in relation with former research works achieved in LCP-A2MC laboratory [4,5]. On the one hand, the elimination of nitrates from wastewaters will be envisaged by simple adsorption process. In that respect, specific nanoporous sorbents will be synthesized and their surface will be post-functionalized with N-containing molecules and/or ammonium groups in order to enhance the affinity towards nitrates. For instance, introduction of nitrogenated species on carbonaceous materials can be achieved by ammoxidation in gaseous phase ($\text{NH}_3 + \text{O}_2$ at 250°C). For mesoporous silica or zeolites, chemical post-treatments using surfactants can be implemented in order to develop electrostatic interactions between the (positively-charged) surface and nitrates ions. In addition to processes involving simple adsorption phenomena, the photocatalytic reduction of nitrates could also be envisaged. Hence, it was shown that the presence of silver clusters on TiO_2 has a promoting effect on the photoactivity of the oxide, with about 100% conversion obtained and 98% selectivity to N_2 . In our case, we plan to study the photoactivity of silver-exchanged zeolites (already well-characterized at LCP-A2MC) and to compare it with the Ag/TiO_2 system.

For the most interesting materials, a peculiar attention will be devoted to the elucidation of reaction mechanisms, noteworthy those involving the production of NO_x intermediates. This could possibly be done through the design of a dedicated experimental setup, involving the trapping of gaseous products and their subsequent analysis by *in situ* vibrational spectroscopies. The experience acquired by LCPME and LCP-A2MC laboratories on the speciation of N-containing molecules in the gaseous, liquid and adsorbed state should be helpful for the achievement of the project.

Références

- [1] ETIQUE M., ZEGEYE A., GREGOIRE B., CARTERET C., RUBY C. Nitrate reduction by mixed iron(II-III) hydroxycarbonate green rust in the presence of phosphate anions : The key parameters influencing the ammonium selectivity, *Water Research*, 2014, 62, 29–39
- [3] ETIQUE M., JORAND F.P.A., ZEGEYE A., GRÉGOIRE B., DESPAS C., RUBY C. Abiotic process for Fe(II) oxidation and green rust mineralization driven by a heterotrophic nitrate reducing bacteria (*Klebsiella mobilis*), [4] *Environmental Science & Technology*, 2014, 48, 3742–3751
- [3] HANSEN H. C. B. AND C. BENDER KOCH, Reduction of nitrate to ammonium by sulphate green rust" activation energy and reaction mechanism, *Clay Minerals*, 1998,
- [4] ATRIBAK, I., AZAMBRE, B., BUENO LOPEZ, A., GARCIA-GARCIA, A., Effect of NO_x adsorption /desorption over ceria-zirconia catalysts on the catalytic combustion of model soot, *Applied Catalysis B: Environmental*, 2009, 92, 126-137.
- [5] WESTERMANN, A. AZAMBRE, B., Performances of novel sulfated ceria-zirconia catalysts for the selective catalytic reduction of NO_x by ethanol, *Catalysis Today*, 2011, 176, 441-448.

Job Profile

The PhD candidate will have a good knowledge in chemistry and/or physics of materials. Knowledge in analytical chemistry will be also appreciated. The candidate will have to do an oral audition either in Nancy (France) or by visio-conference in front of the members of the Institute Jean Barriol. The candidate should hold a master degree with marks higher than $\sim 12/20$. The candidate will work both in Saint-Avold and in Villers-lès-Nancy (France).