Gomis Vicens Juan

Universitat Politécnica de Valéncia (Spain) (juagovi@upvnet.upv.es)

Effects of different reactive species generated photochemically generated in the removal of pollutants from natural water

ABSTRACT

In this Doctoral Thesis the reactivity of a group of emerging pollutants (EP) present in the output waters of urban treatment plants and the implementation of a photo-Fenton process in slightly acidic pH conditions using bio-organic solubles (SBO) as auxiliary chemicals have been studied.

First, a mechanistic study was performed to investigate the role played by various reactive species in the oxidation of a mixture of emerging pollutants generated photochemically through advanced oxidation processes. These oxidizing species are the hydroxyl radical (OH•), singlet oxygen ($^1O_2$) and the excited states of photocatalysts able to act through electron transfer processes. Results show that the EP degradation from the photo-Fenton process is too complex to be explained exclusively by the direct reaction of radical OH•. More likely, OH• radical reacts with further species present in the medium, so that long-lived radicals are generated and contribute to the degradation of EP or participate in chain processes. Rose bengal, known $^1O_2$ generator, showed very low reactivity with EP under photochemical conditions. This fact together with the low values obtained for the rate constants in the reaction of $^1O_2$ with EP, indicate that degradation of EP with singlet oxygen at these concentrations is very inefficient. Electron transfer processes studied using triphenylpyrylium (TPP+) and triphenylthiopyrylium (TPTP+) showed that degradation of EP were produced through the excited singlet and triplet states of the photocatalysts, slightly higher results were obtained by using the TPTP+.

SBO, isolated from the wet fraction of municipal waste, are formed by a mixture of macromolecules with a wide range of sizes that goes from 67 to 463 kg·mol-1. Furthermore, chemical composition of SBO resembles that of natural organic matter that has been employed in solar photochemical processes for wastewater treatment.

Characterization of SBO has shown that these substances are biocompatible, stable after 24 hours of irradiation and able to improve the efficiency of photo-Fenton under slightly acidic pH.

The results obtained in the optimization of the operational variables of the photo-Fenton process in the presence of SBO suggest that the mechanism of this process has changed, so that the optimum pH value of 2,8 has shifted to values close to 4. Therefore, the hydroxyl radical is not the main specie but others species could play a role; however they have not been unequivocally identified due to the complexity process.

Moreover, SBO are able to generate reactive species; however their efficiency depends on the balance between the generation of reactive species and the inner filter effect produced by the deep color of SBO and also by the competition for the generated reactive species between SBO and the pollutants.