Lab to pilot-scale photocatalytic treatment of antibiotics, antibiotic resistant bacteria and antibiotic resistance genes

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Abstract

Antibiotics are needed to fight serious infections. However, due to the human and veterinary abuse of the abovementioned pharmaceuticals, bacteria have developed high rates of antibiotic resistance (AR). Part of the antibiotics not metabolized by the body ends up in urban wastewater treatment plants (UWWTPs) at low concentrations, but exerting a role of stressor and favoring the development of AR. An additional concern is related to the reuse of treated urban wastewater (UWW) for agriculture purpose, making advanced tertiary treatment necessary to produce a good quality effluent.

Among the advanced treatment options of UWW, membrane processes are easily implemented by modular design. Ultrafiltration (UF) is a feasible separation process since it requires low pressure. Microbiological risk in the permeate is mitigated with UF, bacteria and other microorganisms being retained by the small pore size of the membranes (10-100 nm). However, effective antibiotic retention cannot be achieved by this physical separation, an adequate adsorption process (i.e. with activated carbon) or an oxidation process (i.e. O_3, Fenton, H_2O_2/UV, photocatalysis) being necessary. Moreover, biopolymers of effluent organic matter, especially colloidal biopolymers, play a main role as foulants in UWW tertiary treatment with UF. A compact solution combining filtration and oxidation in a single step is a possible solution, photocatalytic membrane reactors (PMRs) being an emerging technology in this field.

Slurry and immobilized catalysts are the most common configurations of PMR applications. The first configuration involves a step where a photocatalyst (usually TiO_2) in suspension is irradiated by UV

light. After oxidation by the photocatalytic process (UV/TiO_2), UWW passes through a membrane separation step where the photocatalyst is removed and recirculated to the first step, while the filtrated wastewater (permeate) is released as effluent. The immobilized photocatalyst configuration involves a membrane supporting a fixed photocatalyst layer being irradiated by UV light. Despite the photocatalytic oxidation step is shorter than in the slurry configuration, immobilized PMRs are more feasible for a scale up.

The aim of this PhD project is to develop a PMR for tertiary treatment of urban wastewater (UWW), in an optic of safe water reuse. Particular attention is payed to the efficiency for the removal of antibiotics, antibiotic resistant bacteria and antibiotic resistance genes. Light-emitting diodes (LEDs) are chosen as alternative light source (instead of traditional lamps) in the photocatalytic process involving TiO_2-P25, while ceramic ultrafiltration (UF) membranes (100 nm pore size) are selected for the filtration process.

To achieve the main aim of this study, the first part of the experimental work assesses the efficiency of UVA-LEDs-driven slurry photocatalysis in disinfection and antibiotics removal from secondary UWW in lab scale batch experiments. Azithromycin, trimethoprim, ofloxacin and sulfamethoxazole are selected as antibiotic model pollutants. Different catalyst loads (TiO_2-P25) and UV light configurations (number of LEDs) are tested in secondary UWW spiked with antibiotics. The most efficient condition to degrade antibiotics in spiked UWW is selected to assess the removal of these antibiotics in real concentration and the inactivation of total heterotrophs, *Escherichia coli*, enterococci (including their antibiotic resistant counterpart). Considering the optimized condition, one hour treatment is enough to remove the selected antibiotics under the limit of quantification (LOQ) and to reduce 2-3 log the bacterial load of the selected microbial groups. To simulate a possible storage of treated wastewater before its reuse, the photocatalytic treated water is kept in dark for three days and bacterial regrowth is assessed. A high regrowth rate was observed for total heterotrophs, reaching the bacterial load of UWW before treatment. However, the antibiotic resistant percentage is always lower than the initial value found in raw UWW. Thus, the photocatalytic process is an attractive solution for the treatment of UWW, in particular for the degradation of antibiotics, but it is also concluded that a membrane is needed aiming a more effective disinfection of UWW.

In this context, a pilot PMR is designed and installed with UVA-LEDs and a TiO_2-P25 coated membrane to treat secondary UWW, the concentrate being recirculated in the system. The production of the permeate during UF of UWW is affected by fouling, the original permeance decreasing ca. 98% after 4 h of treatment. Physical cleaning (backwash and backpulse) is not enough to restore the initial permeance of the membrane, a chemical cleaning step with H_2O_2 being necessary. The disinfection performance of the raw ceramic UF membrane is evaluated using microbiological and molecular biology analysis. Total heterotrophs and total coliforms are not found (<LOQ) in the permeate. Molecular biology analysis reveals the presence of 16S rRNA and *intI1*; however, both the genes are close to LOQ. Part of the permeate is stored for one week in dark and potential risk of bacterial regrowth is examined after 7 days. The cultivable method shows no bacterial load in the

stored permeate, whereas *intI1* decreases to a value below LOQ and 16S rRNA stabilizes at the value found immediately after filtration.

The same pilot PMR is investigated to treat secondary UWW spiked with ofloxacin, ciprofloxacin and enrofloxacin. The experiments are performed using the raw membrane without light (UF) or with light (UF+UVA), and the TiO_2 coated membrane without light (TiO_2-UF) or with light (TiO_2-UF+UVA). Considering a mass balance of the system, the following removal efficiency is found for all the three antibiotics: UF < UF+UVA < TiO_2-UF < TiO_2-UF+UVA. The removal efficiency obtained after treatment in the PMR ranged from 34% (for ofloxacin) to 62% (for enrofloxacin). Equipment and operating costs of the process are estimated. Moreover, an evaluation of scale up investment to treat 100 m^3 day^{-1} is also performed. However, further optimization of the process is needed (i.e. coating methodologies for immobilization of the photocatalyst on the membrane and photocatalytic contact time) before large scale implementation of this PMR technology.