Removal of emerging micropollutants from wastewater discharges by powdered and micro-grain activated carbon - Progress of the CarboPlus® project

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1. Introduction

Among the solutions to reduce the emerging contaminant discharges into the environment, the implementation of a tertiary treatment in actual wastewater treatment plants (WWTP) is more and more considered. Besides, emerging micropollutants, particularly pharmaceuticals and hormones (PhPHs), may be included in modifications of existing regulations.

In this context, a collaboration between the SIAAP and the OPUR research program has been initiated since 2013 to study at large scale a tertiary treatment pilot (CarboPlus® - SAUR/STEREAU) based on a fluidized bed activated carbon reactor. The objectives of this project are to i) characterize the efficiency of the process for priority and emerging pollutants removal, ii) characterize the sorption mechanism and the different parameters influencing it (organic matter competition, operating parameters, activated carbon structure and properties, etc.) and iii) determine if any improvement of the conventional quality parameters is achieved thanks to the process.

The process was initially tested with powdered activated carbon (PAC) and its performances in this configuration are already published [1]. Then, a micro-grain activated carbon (µGAC) is studied instead of PAC since January 2014. In addition to being reactivable, its intermediary size (300-500 µm) between powder (<50 µm) and grain (>1 mm) results in a simplification of the process operation, as no coagulant and flocculant are needed anymore to stabilize the bed.

To evaluate the treatment in the µGAC configuration, the fate of 131 micropollutants has been studied, including 61 PhPHs and 70 other emerging pollutants, in addition to various conventionnal wastewater parameters, such as DOC, TSS, UV-254 or nitrogen species.

This presentation aims at displaying the efficiency of this innovative process in a large WWTP application. Thus, the concentrations and the removals obtained with µGAC for a wide range of emerging micropollutants are presented. Then, the comparison of the two configurations (PAC versus µGAC) and with the scarce studies available in the literature is given [2][3][4]. Finally, the influence of the various parameters that affect the adsorption of micropollutants in the process is discussed, as well as the results of complementary lab-scale experiments performed to better understand adsorption mechanisms.

2. Materials and methods

The process studied is the CarboPlus® process (SAUR - STEREAU). This technology is based on the flowing of water through a high concentration fluidized activated carbon bed (>100 kg/m^3) with a continuous injection of a moderate fresh dose of activated carbon. The pilot studied (5 m high - surface area of 4 m^2) is fed with the discharges of the Seine Centre WWTP (Colombes, France - 240 000 m^3/day) and can treat between 700 and 1900 m^3/day, corresponding to hydraulic velocities of 6 to 20 m/h.

The project was divided in two configurations: 1) PAC in 2013 and 2) µGAC in 2014. A total of 28 (14 + 14) sampling campaigns were planned, using refrigerated automatic samplers performing 24 h flow weighted composite samples from inlet and outlet waters of the pilot.

Various general water quality parameters were analysed by the SIAAP laboratory (French accreditation) to characterize the effluents and determine if the process allows a general improvement of the water quality. Thus, dissolved organic carbon, chemical and biological oxygen demand, UV absorbance at 254 nm, total Kjeldahl nitrogen, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, total phosphor and total suspended solids (TSS) were monitored.

A total of 131 organic micropollutants were monitored including 61 pharmaceuticals (analgesics, antibiotics, anxiolytics, X-ray contrast agents) and hormones, and 70 various emerging pollutants such as pesticides (N=28), alkylphenols (N=7), phthalates (N=4), personal care products (N=7), artificial sweeteners (N=4), polycyclic aromatic hydrocarbons (N=13), chlorinated solvents (N=3), perfluorinated acids (N=2) or bisphenol A and benzotriazole. The analyses are performed by 5 laboratories: the Institute of Analytical Sciences (ISA), the Water Environment and Urban Systems laboratory (LEESU), the Central laboratory of the Police Prefecture (LCPP), the CARSO laboratory and the Water Technology Center (TZW - Germany).

3. Results and discussion

After a period of stabilization, high removals of the emerging micropollutants are reached thanks to the CarboPlus® - µGAC process, with a fresh µGAC dose of 20 g/m^3. Indeed, the 20 PhPHs quantified in influents are all removed at more than 70%. In particular, ketoprofen, paracetamol, ibuprofen, ofloxacin, ciprofloxacin, trimethoprim, roxithromycin, atenolol, propranolol, carbamazepine, oxazepam, lorazepam and estrone have removals higher than 80% in average. In addition, first results on the other emerging micropollutants show high or very high removals for diuron, terbutryn and mecoprop (60-95%), bisphenol A (60-70%), alkylphenols (60-95%), PFOS (75-95%) and X-ray contrast agents (50-70%). Finally, the general quality of the water is significantly improved thanks to the pilot. In particular, the µGAC bed seems to trap a part of the TSS (36% in average) and to remove a high quantity of organic matter (DOC - 35%; COD - 43%). Moreover, the high solid retention time (60-90 days) of the µGAC results in a biological activity within the reactor, as displayed by NO_2^- (91%) and NH_4^+ (44%) average removals.

Although these results are preliminary (not all campaigns and molecules), they tend to highlight a comparable efficiency of the CarboPlus® process in both PAC and µGAC configuration. In addition, they are in accordance with the scarce recent studies available in the literature [2][3][4], despite differences in processes and quality of waters. If this is confirmed with the remaining campaigns (µGAC dose of 10 g/m^3), this would mean that the µGAC allows similar performances with an operation simplification and a reactivability of the carbon.

The BET surface was confirmed as the most relevant activated carbon structural property to predict the efficiency of adsorption, but comparison of different activated carbons showed that bulk density was correlated to it and could be used as a tool to select the most efficient activated carbons.

4. Conclusions

The use of micro-grain activated carbon instead of PAC has several operational and economical advantages, but this type of carbon was never tested with wastewater. The first results of the study tend to indicate that the CarboPlus® process is as efficient with µGAC than with PAC despite the higher granulometry of the first one. In particular, most of the studied micropollutants have removals higher than 80% within this process, particularly the PhPHs. In addition, this operation configuration allows to improve slightly the treatment of nutrients, in particular carbon and nitrogen. However, the results are still partial at this stage of the project, another µGAC dose is currently tested on the pilot and complementary lab-scale tests are still performed to better understand the adsorption mechanisms.

5. References

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