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LE STUDIUM Multidisciplinary Journal

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FELLOWSHIP FINAL REPORT

Developing a new advanced treatment technique for micropollutants removal from water and wastewater

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REPORT INFO

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Period of residence in region Centre-Val de Loire: October 2017 – October 2018

Keywords :
Fe-impregnated activated carbon, pharmaceuticals, advanced oxidation processes, adsorption, photo-Fenton, ozonation.

ABSTRACT

Novel cost-efficient Fenton-like catalysts were prepared for the degradation of organic molecules in aqueous solutions. Porous activated carbons (ACs) were directly impregnated with Fe^{2+} solutions of different concentrations using the wet impregnation method. Their efficiency, as Fenton-like catalysts, was studied. Photo-Fenton tests were performed to establish the performance of the prepared Fe-impregnated ACs in relation to the degradation of organic micropollutants in aqueous solution, under different conditions. Photo-catalytic tests were carried out by means of a laboratory photo-reactor. The influence of several parameters such as solution pH value, initial concentration of the model pollutant, and hydrogen peroxide dose on the process performance was investigated. The ACs and prepared catalysts were characterized by nitrogen adsorption-desorption isotherms at 77K, FTIR, SEM, and thermogravimetric analyses. The total Fe content of the synthesized composites was estimated by the phenanthroline method using UV-Vis spectrophotometry. Photo-catalytic tests were performed in monosolute or mix solutions of MPs in order to compare the efficiency of various conventional AOPs with that of photo-Fenton-peroxone process. The results show an increase in the degradation rate in case of the heterogeneous photo-Fenton-peroxone process.

1- Introduction

The presence of emerging micropollutants in surface water, groundwater and sediments is currently of major concern, which will lead to the establishment of more stringent standards for the quality of surface water, municipal and industrial wastewater, especially in the member states of the European Union [1].

At present, emerging organic micropollutants (MPs) are poorly removed through conventional biological treatment methods [2]. With regard to the possibilities of removing trace organics from waste and drinking water, the performance of various technologies, mostly conventional (adsorption, membrane and oxidation processes), have already been investigated. Recently conducted studies showed that processes such as ozonation and adsorption on powdered activated carbon are promising treatment techniques for real wastewaters containing emerging micropollutants (MPs) [3].

For several years, the laboratory Interfaces, Confinement, Matériaux et Nanostructures (ICMN-CNRS UMR 7374, Orléans) has been active in the development of advanced oxidative processes, in particular the Ozone/Granular Activated Carbon (GAC) combined system for the elimination of phthalates and pharmaceutical compounds [4-7]. This work suggests a new approach in the field of wastewater treatment for MPs removal. A new coupling technique, which combines the power and advantages of heterogeneous Fenton (fast treatment of effluents at near-neutral/natural pH) with those of peroxone process (enhanced degradation of MPs in bulk solution and AC regeneration) will be developed. This treatment system is expected to be more advantageous as regards both its feasibility and treatment efficiency and costs [8]. One of the goals of the present research project consists in establishing the synergistic effects of coupling several advanced oxidation processes. It is of interest to carry out the implementation of the process and to determine the optimal conditions where the global process cumulates the most synergistic effects resulting in a powerful treatment system for micropollutants.

Another goal is to establish the kinetics degradation mechanisms by coupling experimental analyses and theoretical approach by modeling using chemical simulation. The degradation mechanisms of several model micropollutants were investigated. Synthetic model solutions of pharmaceutical compounds were prepared for monosolute studies (Diclofenac or Ibuprofen) and in mixture (Metoprolol, Ketoprofene, Carbamazepine, Terbutaline, Fluoxetine, and Sulfamethoxazole), respectively. The new suggested technique proved to be more efficient and cost-effective than the available techniques towards the removal of micropollutants.

2- Experimental details

Three commercial ACs (L27, X17 and S21) with various porous and chemical properties were provided by Jacobi Carbon (Vierzon, France). Raw carbon materials were thoroughly rinsed with water and dried at 75°C for one day to eliminate residual acidity or basicity due to the initial activation treatment. The aqueous solutions were prepared using distilled and purified water with a very low conductivity. ACs containing Fe were prepared by the wet impregnation method [8]. Determined amounts of ACs were contacted with precursor solutions with different iron contents.

After the washing and drying stages, the raw ACs were immersed in solutions of ferrous sulphate under constant stirring that was intense enough to preserve the shape of the initial particles. The impregnation process was conducted for 180 minutes. The obtained suspension was filtered and washed several times with water. Then, the impregnated ACs were dried at mild values of temperature, ie, 55°C. The as-prepared materials were identified as Fe-L27, Fe-X17, and Fe-S21, respectively, according to the corresponding name of the commercial activated carbons.

The three raw activated carbons have different chemical and textural characteristics. L27 presents a well-developed micro- and meso-porous system and an acid surface, X17 has a less fully developed porosity in comparison to that of L27 and an alkaline surface, and S21 is mainly microporous with a neutral surface [9]. The textural properties of the impregnated activated carbons were characterized by conventional nitrogen adsorption-desorption isotherm at 77 K using a Micromeritics ASAP 2020. The samples were previously degassed at 150°C for ~24 hours under a residual vacuum of $< 10^{-4}$ Pa. The adsorption isotherms were carried out with relative pressures ranging from 8.0×10^{-6}-0.99. Thermogravimetric analyses were performed by means of a TGA 92 Setaram apparatus, scanning electron microscopy images were recorded with a Philips CM20 – 200kV, and FTIR analyses were performed using a Thermo Scientific Nicolet 6700 FT-IR. Thus, the micro-morphological, chemical, and textural features of the obtained catalysts were determined. The phenanthroline-based spectro-photometrical method was used to determine the total iron content in the prepared composites and also the iron leakage from the spill catalysts.

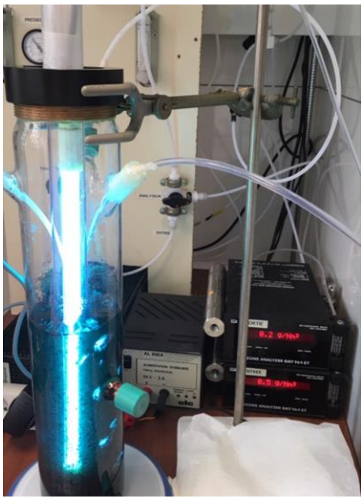

Fig. 1 Experimental set-up – batch photoreactor.

The AOPs tests were carried in batch mode. In each run, a volume of 1 L of pharmaceutical aqueous solutions (18 mg/L of mixture and 200 mg/L monosolute, respectively) was placed in the photoreactor (UV Laboratory Reactor System, Fig. 1). The mixture was stirred in dark for 2h to establish the adsorption–desorption equilibrium between the pollutant model and the catalyst surface. Then UV irradiation was performed for 2h using a Pen-Ray-Power Supply lamp (UVP Products, TQ 718, and 700 W) at room temperature. A volume of 4 mL of reaction mixture were systematically sampled, separated by centrifugation and then 1 mL was diluted and analyzed by means of a Shimadzu HPLC Nexera XR system. Synthetic model solutions of pharmaceutical compounds were prepared for monosolute studies (Diclofenac or Ibuprofen) and in mixture (Metoprolol, Ketoprofene, Carbamazepine, Terbutaline, Fluoxetine, and Sulfamethoxazole), respectively.

3- Results and discussion

Original contributions have been produced in relation with: (i) functionalization of novel carbonaceous composites; (ii) the study of the kinetics of MPs removal by the combined processes considered (Fig. 2);

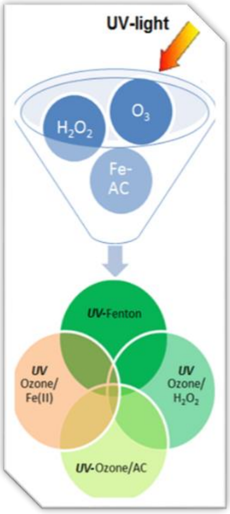

Fig. 2 Principle of Photo-Fenton-peroxone process

(iii) the study of influence of iron impregnation of GAC over the operating costs of the catalyzed ozonation pilot plant; (iv) statistical modeling and optimization of O_3/GAC pilot plant; (v) the conception and design of a new pilot-scale continuous-flow plant for wastewater treatment based; (vi) the study of the influence of parameters over the performance of a system based on heterogeneous Fenton and peroxone; (vii) the theoretical modeling and experimental identification of by-products degradation mechanisms; (viii) the statistical modeling and technical-economical optimization of the pilot plant by means of Response Surface Methodology (RSM).

AC composites containing Fe were prepared by wet impregnation method varying the iron precursor concentration corresponding to theoretical iron content (1%, 4.5%, 10%, and 20%, respectively). The total iron content in composite was determined by means of the UV method based on Phenanthroline, at two different Fe to Fe-GAC ratios in the impregnation solution for the three ACs used. 3% Fe content in the Fe-L27 composite was achieved with a Fe/Fe-L27 weight ratio of 20%. The lowest Fe content was obtained for Fe-S21 composites, whereas the Fe-X17 composites presented the highest Fe content. This value depends on the porosity of the activated carbon;

to enable the entrance of Fe into the system, the material needs to be mesoporous [8].

SEM images [8] emphasize the iron oxide aggregates formed on the surface of L27 after wet impregnation. The iron oxide aggregates seem to be located at the entrance of the porosity, which can block the pores. The presence of these aggregates results in a heterogeneous surface.

N_2 adsorption-desorption isotherms were carried out at 77 K. The micropore size distribution was obtained by the DFT method for raw GAC matrix supports (L27, S21, X17) and for thermally treated Fe-GAC. According to the obtained data, the impregnated Fe-L27 seems to be less microporous and its isotherm presents a more pronounced hysteresis than that of raw L27. In comparison with the properties of the raw L27, in the Fe-L27 there is a 12% decrease in the microporous volume. In Fe-X17, there is a very low increase in the external surface and mean pore sizes. In contrast to the other two ACs, impregnation by Fe in S21 seems to increase microporosity.

FT-IR analyses of raw L27 and Fe-L27 show that after impregnation and before heat treatment, $FeSO_4$ groups can be linked on surface functional groups and this can modify the chemical surface of the raw ACs. After the heat treatment, these grafted groups are removed and they can modify the textural properties. Due to raw S21 presents no functional group, IR spectrum of Fe-S21 heat treated at 550°C is similar.

Light irradiation tests were carried out to determine the performance of the prepared Iron-impregnated composites towards the removal of pharmaceutical compounds from aqueous solution. Fig. 3 shows the effect of AC matrix on the removal efficiency in relation to Ibuprofen molecule.

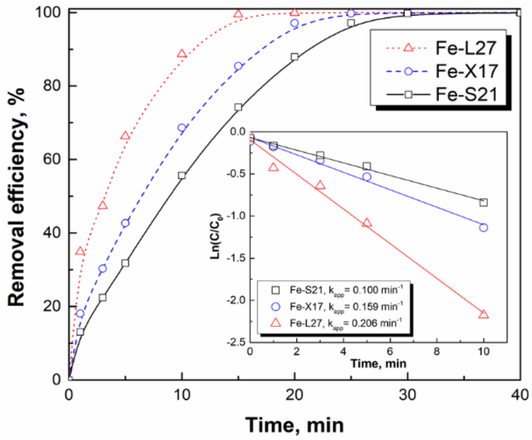

Fig. 3 Ibuprofen degradation tests with GAC support of different pH_{PZC}. Inset plot: pseudo-first order kinetics

It was found that the chemical properties of AC surface are critical in the selection of the proper matrices of Fenton-like catalysts. Among the investigated ACs, the acid surfaced AC provides the optimal micromedium to conduct the heterogeneous Fenton. The integration of the Fenton process by using Fe-impregnated ACs results in remarkable enhancement of the mineralization process. (Fig. 4). Heterogeneous Fenton based on Fe-impregnated ACs provides good removal efficiencies even at neutral pH of the treated aqueous solution.

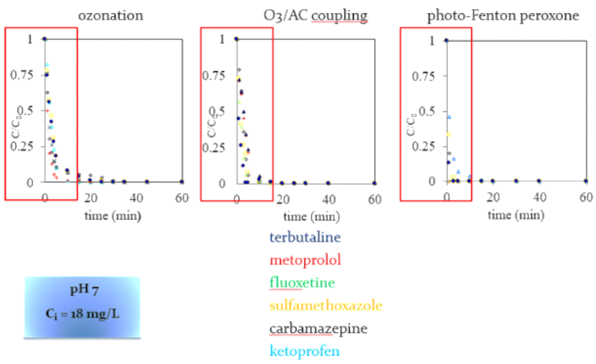

Fig. 4 Comparative efficiencies of AOPs

At the end of the fellowship, Le Studium researcher, Secula, and the host scientists, Cagnon and Vautrin-UI, organized the conference "Water micropollutants: from detection to removal". The main aim of this conference was to promote multi-disciplinary collaboration and transfer of knowledge among scientists, industry and official authorities concerning the problematic of emerging water micropollutants. The conference attendees had the opportunity to disseminate, acknowledge and discuss of cutting edge research on the thematic of emerging water micropollutants, including the development of new sensors for in-situ monitoring, innovative devices for on-site detection or laboratory analysis, and their proper removal from water and wastewater by means of cost-effective techniques. Participants included academic researchers, scientists and specialists from water processing and associated industries. The conference topic, of particular importance, emphasized the main problematics related to water micropollutants from the point of view of both industrial and academic approaches. Several outstanding experts in the field shared their views and results during the three-day event, favoring future collaboration among the participants (e.g. Dr. Şahika Sena Bayazit invited by B. Cagnon for 1 month stage at ICMN).

4- Conclusion

AC materials containing iron (II) were elaborated and used as Fenton-like catalysts to degrade pharmaceutical compounds.

Materials containing up to 3 wt.% of Fe were achieved. The thermo-gravimetric analysis emphasized the existence of two degradation stages of the prepared composites. The isotherms of N_2 showed an increase in the total surface after Fe impregnation.

The impregnation of Fe (II) on L27, which has an acidic surface, allows the photo-Fenton process to be conducted at higher constant rates.

The photo-degradation rate increased at lower values of pH. Hydrogen peroxide significantly enhanced the removal process.

In the reusability tests of the most effective prepared catalyst, Fe-L27 shows good photo-catalytic performance even after five cycles of use.

Several advantages of the suggested treatment technique can be mentioned: (i) it includes the powerful features of heterogeneous Fenton process by using Fe-impregnated acid-functionalized AC; (ii) compared to the slow and costly process of GAC adsorption, by ensuring an in-situ regeneration of GAC composites, the suggested treatment system results in much lower volumes of spent-GAC and the treatment costs are critically diminished; (iii) in-situ generation of O_3 and H_2O_2 enhances the production of hydroxyl radicals and the oxidation processes.

5- Acknowledgements

We gratefully acknowledge the financial support provided by the PIVOTS project and the Région Centre-Val de Loire (ARD 2020 program and CPER 2015 -2020), the French Ministry of Higher Education and Research (CPER 2015 -2020), and a public service subsidy from CNRS and Orléans University. Thanks are also due to The Smart Loire Valley Program's Fellowship.

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