CLIENT-DR Scientific report

1. Objectives

- Physical-chemical characterization of the effluent samples from the wastewaters treatment plants;
- Developing of a new a methodology for removing dyes from effluent wastewater treatment plants;
- Preliminary studies for the conceptual design of a demonstration module at the laboratory level;
- Capitalization of the recovered dyes and recovery of the surfactants;
- Dissemination of the project results.

2. The summary of the 2017 proposed activities

The objectives proposed for 2017 year were realized as follows:

2.1. A number of 9 samples of influent and effluent, respectively, taken by the industrial partner (**EDAS EXIM**) from a wastewater treatment plant from the processing of food supplements were physically and chemically characterized by quantification the following specific indicators: 1) *organic loading* (COD) with values between 4200-12000 mg / L for the influent and between 40-160 mg / L in the effluent; 2) *biochemical oxygen demand* (BOD) with an average value of 30 mg / L in the effluent; 3) *total nitrogen* in the influent, between 300 - 480 mg / L and in the effluent, between 150 - 250 mg / L - well above the maximum admissible value; 4) *fat content* in influent - 200 mg / L and in effluent - 19 mg / L; 5) *the concentration of anionic detergents* of 10-20 mg / L and 25-35 mg / L for non-ionic surface agents, respectively; 6) *qualitative spectrophotometric* evaluation of effluent and influent color.

2.2. In order to develop a methodology for removing dyes from effluent wastewater treatment plants, it was first necessary to draw up a technical documentation on the problems encountered by the treatment plants of the industrial partner, documentation

based on the data obtained from the physical-chemical characterization of the influent and effluent samples in the initial stage.

The analysis of the unitary processes underlying the biological treatment of the treatment plant highlighted the change of the effluent indicators in relation to the initial design parameters of the plant, indicating their overcome in the effluent beyond the limits allowed in the emissaries.

The high content of proteins, fats and other non-biodegradable compounds, such as food dyes, has led to the need to develop of an alternative, unconventional methodology based on microemulsion extraction and photodegradation of these pollutants.

2.3. In order to prepare the conceptual design of a laboratory-level demonstrator, a series of preliminary experiments were carried out to eliminate the dyes. The experiments were first performed on synthetic waters containing three ionic colors: Purple Crystal, Rhodamine B and Metilorange. In this context, the following alternatives were analyzed: a) selecting the appropriate surfactant; b) selecting the optimal organic phase; c) estimating the optimum surfactant concentration. The evaluation of extraction efficiency in different systems indicated that the optimum extraction capacity has the system containing butyl acetate, sodium sulfocyante and surfactant (Brij 30). This extraction system was then used to study the effect of the matrix on the extraction efficiency of the dyes on 9 real samples taken from the treatment plant. Given the high non-homogeneity of the composition samples taken at regular intervals, the extraction process carried out with the previously selected system led to non-reproducible results, which required additional research to optimize the extraction system. For the validation of the treatment method, a two-step process was carried out: extraction with Brij 30 / butyl acetate / ethyl acetate / water system, followed by removal of the organic compounds by distillation and / or adsorption on granular activated carbon.

Based on the nano-heterogenic photodegradation experiments in the extraction medium, complete mineralization of organic dyes after one hour, irradiation time in the UVC field, was achieved.

2.4. Capitalization of the recovered dyestuffs in wastewater was achieved by

incorporating them in silica matrices. This was done by adapting the dual-microemulsion technique combined with sol-gel method when were obtained aggregates below 100 nm. The aggregates can be further processed as powdered nanoparticles or as thin films, depending on the purpose, for example in optically active photonic devices.

In parallel, tests were carried out to recover the surfactants by concentration using successive extractions.

The research phase ends by validating the process on different types of influent and effluent samples, giving satisfactory reproducibility.

2.5. Dissemination of the project's results was achieved through two publications in ISI journals (IF = 2.905 and 5.951), the design of the project web page and 4 communications at prestigious international conferences.

3. Presentation of the project results - parameters, performance level indicators

The results obtained in the project were published in 2 ISI articles:

a) Daniela Cadar, Nicoleta Liliana Olteanu, Elena Adina Rogozea, Adina Roxana Petcu, Aurelia Meghea, Maria Mihaly, Recovery of targeted hydrophilic compounds from simulated wastewaters using nonionic microemulsion systems, Process Safety and Environmental Protection 109 (2017) 648–658, IF = 2,905;

b) Adina Roxana Petcu, Aurelia Meghea, Elena Adina Rogozea, Nicoleta Liliana Olteanu, Cosmina Andreea Lazar, Daniela Cadar, Adrian Victor Crisciu, Maria Mihaly, No Catalyst Dye Photodegradation in a Microemulsion Template, ACS Sustainable Chem. Eng. 2017, 5, 5273−5283, IF = 5,951.

The web page of the project: http://www.nanostructuri-fluide.ro/client-dr/index.html, where the main research directions of the CLIENT-DR project can be viewed, was also designed.

4. Brief report on travel abroad about dissemination and / or training

The project results were also presented at the "14th International Conference on Nanosciences & Nanotechnologies - NN17", from 3 to 8 July 2017, a scientific event

held in Thessaloniki, Greece. During the conference two works were carried out: 1) *Photo mineralization of dyes in nanostructures heterogeneous fluids* (E.A. Rogozea, A.R. Petcu, C.A. Lazar, D. Cadar, M. Mihaly) and 2) *Removal of ionic dyes mixtures from textile industry wastewaters using microemulsions systems* (C.A. Lazar, A.R. Petcu, E.A. Rogozea, M. Mihaly).

The results were also disseminated at the “2nd International Conference on Chemical and Biochemical Engineering”, which took place from 23-27 July 2017 in Spain, in Las Palmas de Gran Canaria (University of Las Palmas de Gran Canaria. At this conference was presented the paper: *No catalyst dyes photodegradation in microemulsion template developed* by A.R. Petcu in collaboration with: E.A. Rogozea, C.A. Lazar, D. Cadar and M. Mihaly.

Many lectures in areas such as nanoelectronic, photonic, plasmonic, nanoenergy, nanomaterial, nanofabrication, nanoengineering and nanoconstruction have been attended, which have helped the participants acquire many interesting information in their field of activity. In addition, the authors participated in discussions with internationally renowned researchers.

The industrial partner participated in the Conference: “Annual Meeting and Exposition” which is the leading conference for professionals in Controlled Environments/Cleanrooms, Environmental Testing, and Nanotechnology Facilities, the ESTECH 2017, Lousiville, KY, USA, conducted between 8 and 11 May 2017. During the conference were presented the latest trends in monitoring the control of critical parameters in classified facilities, the operation of nanotechnology production facilities, the interpretation of statistically collected data, the monitoring of wastewater parameters and purified water used in production facilities, legislative limits for monitoring and control. The industrial partner also participated in the WG4 - ISO 14644-4 meeting, on the topic "Monitoring of environmental parameters (water and air).Risk Factors". The meeting was held in parallel with the plenary works of ESTECH 2017.