Ph.D. Thesis of Amal Mejri

Identification and Treatment of Emerging Contaminants in Urban Wastewater

Introduction:

This PhD thesis has been carried out at the Department of Geology, University of Sfax, National Engineering School of Sfax (ENIS) between September 2016 and June 2021. The work is a joined collaboration between the **Laboratory of Wastewater Treatment and valorization of effluents, Research and Technology Center of Water (CERTE)**, Carthage University, Tunisia, and the Solar Energy Research Centre (CIESOL) at Almeria University, Spain.

In arid Mediterranean countries, such as Tunisia, wastewater must be valued as an alternative, non-conventional source of water resources. Since the problem of water scarcity, high salinity of groundwater, and pollution of water bodies, can cause several problems to water demand. Furthermore, the main factor behind water stress, that might affect water demand, is the agriculture water needs, which is the major user of the world's freshwater. Therefore, the reuse of effluents from wastewater treatment plants (WWTPs) is becoming an increasingly widespread and necessary alternative to conventional water sources in arid and semi-arid countries. With the purpose of reuse in mind, WWTPs effluents must have a high quality, and must be free of all hazardous pollutants that cause negative effects on crops (when using water for irrigation), in water and aquatic organisms and, consequently, on human health.

In this regard, there is an increasing environmental concern about emerging contaminants or micropollutants nowadays. They escape the conventional treatment plants, and are released into the environment.

These contaminants are found at very low concentrations of the order µg L^{-1} to ng L^{-1}. For this reason, the development of tertiary treatment for micropollutants removal is becoming of particular interest.

In this context, this Ph.D. thesis aimed to apply one of the most efficient and environmentally sustainable advanced oxidation processes (AOPs), the solar photo-Fenton process, for wastewater treatment.

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Abstract:

The main contribution of this Ph.D. thesis is the application of one of the most efficient and environmentally sustainable advanced oxidation processes (AOPs), the solar photo-Fenton process, for wastewater treatment at pilot scale. This study investigated the use of solar photo-Fenton process through scalable and low-cost Raceway Pond Reactors (RPRs) to remove contaminants of emerging concern (CECs) from simulated and real urban WWTP secondary effluents at neutral pH.

In a first stage, preliminary essays have been carried out to detect and identify 31 CECs from the influent and effluent of a Tunisian WWTP, located in the north of Tunisia, named Choutrana II. The CECs detected were classified in 21 pharmaceuticals, commonly used in human and veterinary medicine, and 10 pesticides which are extensively used in the agriculture sector.

In a second stage, this study investigated the use of solar photo-Fenton process in raceway pond reactors (RPRs), to treat simulated secondary effluent from a Tunisian urban wastewater treatment plant (WWTP), with high chloride load. To this end, a mixture of three contaminants of emerging concern (CECs) was used as model pollutants at 50 μg/L each (one antibiotic, sulfamethoxazole and two pesticides, pirimicarb and imidacloprid). All the trials were conducted at neutral pH with 0.1 mM Fe^{3+}: EDDS at 1:1 molar ratio. The effect of hydrogen peroxide initial concentration (20, 30, and 90 mg L^{-1}) on microcontaminant removal was also studied.

Different liquid depths (5 and 15 cm) were selected to assess the relationship between the microcontaminant removal and the volumetric rate of photon absorption (VRPA).

Although the reaction rate was initially photolimited, after a short reaction time of 15 min, the final yield (≈ 80% of CECs removal) was limited by the photo-degradation of the Fe^{3+}:EDDS complex and excess of H_2O_2 was found at all concentrations used. Therefore, treatment times below 15 min should be used. The treatment capacity was three times higher when the liquid depth was increased from 5 to 15 cm.

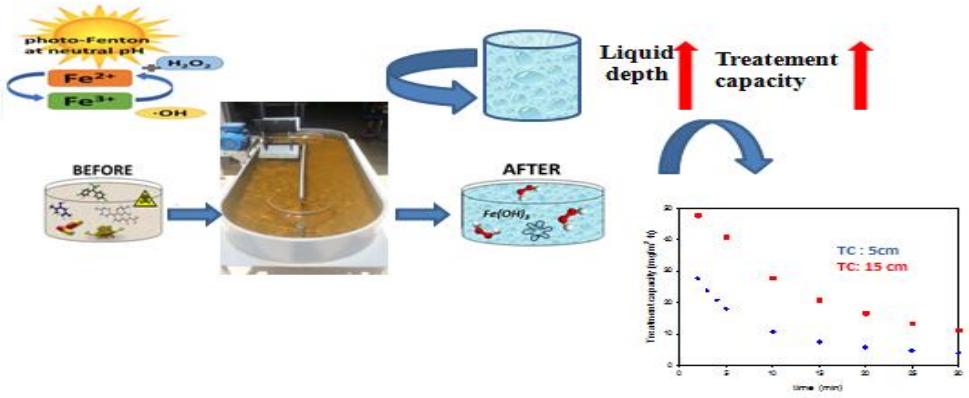
For the first time, these results show that the operation of a 15 cm-deep RPR in continuous flow mode would be suitable for large-scale implementation of the solar photo-Fenton process.

In addition, a kinetics study of the solar photo-Fenton process at neutral pH mediated by the Fe^{3+}-NTA complex (molar ratio 1: 1) applied to remove contaminants of emerging concern

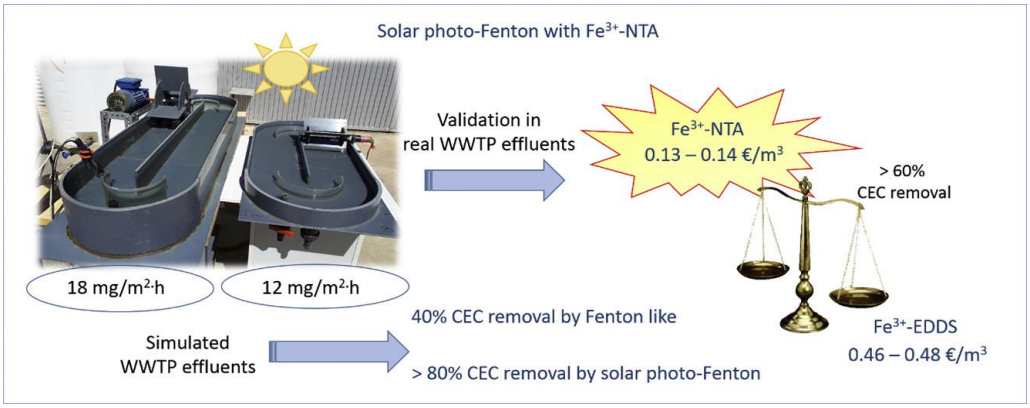
(CECs) was carried out. To this end, wastewater treatment plant (WWTP) secondary effluents were treated in a raceway pond reactor (RPR) at pilot plant scale with 0.1 mM Fe^{3+}-NTA and 0.88 mM H_2O_2 under average solar UVA irradiance of 35 W/m^2. Sulfamethoxazole and imidacloprid, at 50 μg L^{-1} of initial concentration each, were selected as model CECs.

Up to 40% of the sum of both model CECs was removed from simulated WWTP effluent by the Fe^{3+}-NTA Fenton-like process, and >80% was removed by solar photo-Fenton. The effect of liquid depth in the reactor was evaluated, showing an increase of the treatment capacity from 12 mg CEC/m^2·h to 18 mg CEC/m^2·h when liquid depth increased from 5 to 15 cm. Afterwards, these results were validated with real WWTP effluents and compared with the results obtained with the Fe3+-EDDS complex under the same operating conditions. The same CECs removal rates were obtained with Fe^{3+}-NTA and Fe^{3+}-EDDS at 5 cm of liquid depth with kinetic constants of 0.110 min^{-1} and 0.046 min^{-1} for sulfamethoxazole and imidacloprid, respectively. Conversely, at 15 cm of liquid depth, the degradation rates were lower with Fe^{3+}-NTA (kinetic constants of 0.034 min^{-1} for sulfamethoxazole and 0.017 min^{-1} for imidacloprid), whereas with Fe^{3+}-EDDS the values were 0.076 min^{-1} and 0.047 min^{-1} for sulfamethoxazole and imidacloprid, respectively. Regarding process cost estimation, the use of NTA as iron chelate for solar photo-Fenton at neutral pH at pilot plant scale resulted very cost-effective (0.13–0.14 €/m^3) in comparison with the use of EDDS (0.46–0.48 €/m^3) at the two liquid depths tested.

Raceway Pond Reactors of 5 cm (a) and 15 cm (b) liquid depth



Graphical abstract of the effect of liquid depth on microcontaminant removal by solar photo-Fenton with Fe^{3+}-EDDS in neutral pH in high salinity wastewater



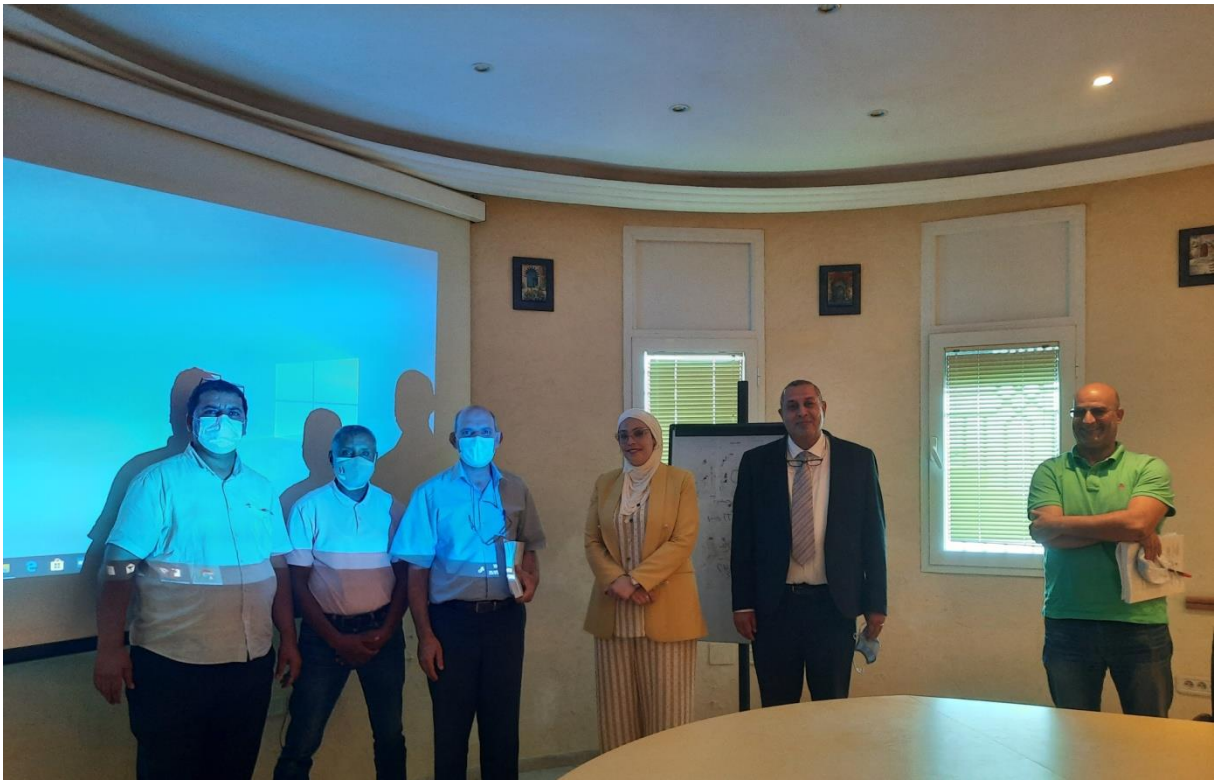
Graphical abstract of Fe^{3+}-NTA as iron source for solar photo-Fenton at neutral pH in raceway ponds reactors

Keywords: Wastewater treatment; Advanced Oxidation Process; Sulfamethoxazole; pirimicarb; imidacloprid; solar radiation; chelating agents; contaminants of emerging concern (CECs). EDDS; Real wastewater, NTA, Cost

Concluding notes

This PhD Thesis was presented at the National Engineering School of Sfax (ENIS), in 05 July 2021 in front of the members of the jury mentioned below:

Mr Mohamed KSIBI	Professor (ISBS, Sfax)	President
Mr Chedly CHOUCHENI	Professor (ISSTE, Borj Cédria)	Reviewer
Mr Moncef KHADRAOUI	Associate Professor (ISBS, Sfax)	Reviewer
Mr Amjed KALLEL	Associate Professor (ENIS, Sfax)	Examiner
Mr J.A SANCHEZ PEREZ	Professor (University of Almeria, Spain)	Supervisor (Spain)
Mr Ismail TRABELSI	Professeur (CERTE, Borj Cédria)	Supervisor (Tunisia)



This thesis is based on the following two publications, which are listed below:

- **Effect of liquid depth on microcontaminant removal by solar photo-Fenton with Fe(III):EDDS at neutral pH in high salinity wastewater** . ***Amal Mejri***, *Paula Soriano-Molina*, *Sara Miralles Cuevas*, *Ismail Trabelsi*, *José Antonio SánchezPérez. Environ Sci Pollut Res* 26, 28071–28079 (**2019**). **(IF =3.3)**

- **Fe^{3+}-NTA as iron source for solar photo-Fenton at neutral Ph in raceway pond reactors**. ***Amal Mejri,*** *Paula Soriano-Molina , Sara Miralles-Cuevas, José Antonio Sánchez Pérez.* ***Science of the Total Environment****, Volume736,(**2020**),139617-139629.* ***(IF*= 6.5)**