

# Degradation of polyphenolic contaminants using a natural polymeric dye of riboflavin-5'-phosphate cross-linked chitosan as photosensitizer

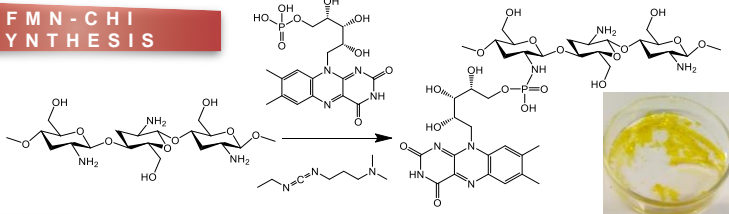
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## INTRODUCTION

The use of photosensitized processes for the degradation of pollutants can be considered as emergent green processes.[1] The sensitizer or the dye, in presence of UV o Vis radiation can act as a photosensitizer capable of generating highly oxidizing species. The dyes used in the photodegradation processes have the disadvantage of remaining in the environment after the photo-degradative process. This problem can be solved by using **polymeric dyes (PD)**, whose solubility in water varies with pH of the solution, allowing its removal. [2] In this work the development of a PD is presented, this PD is made up of natural products, flavin mononucleotide as photosensitizer (FMN), and chitosan polysaccharide (CHI) as a polymeric support, thus obtaining a polymeric dye called FMN-CHI.

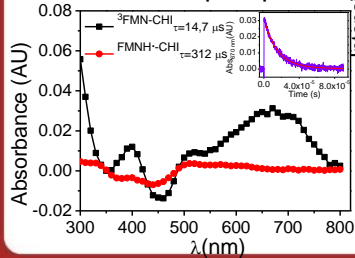
## FMN-CHI SYNTHESIS



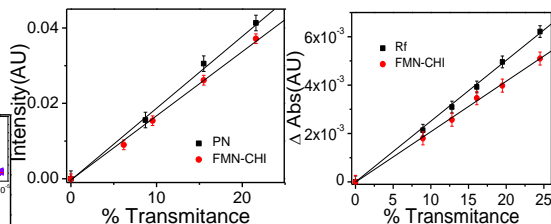
## FMN-CHI CHARACTERIZATION

FMN-CHI is more photostable than free sensitizer

### Transient absorption spectra



### Determination of $\phi_{\Delta}$ and ${}^3\phi$



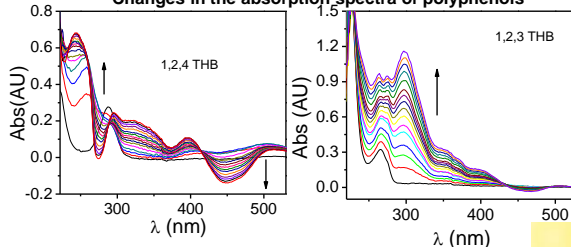
### Photophysical characterization of FMN-CHI

Sensitizer	${}^1\phi_f$	${}^1\tau$ (ns)	${}^3\phi$	${}^3\tau$ ( $\mu$ s)	$\phi_{\Delta}$
FMN-CHI	0.353	4.69	0.305	14.7	0.87
FMN	0.352	4.69	0.345	15	0.82

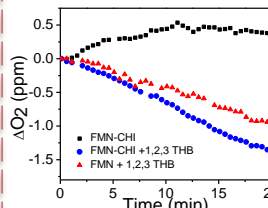
## PHOTOSENSITIZATION

In this study, we investigated the use of FMN-CHI as polymeric sensitizer in the photodegradation of polyphenolic compounds at 20 minutes of irradiation with blue Led's

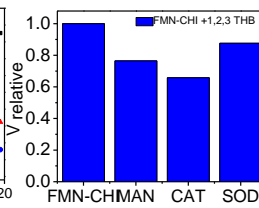
### Changes in the absorption spectra of polyphenols



### Oxygen consumption upon photoirradiation



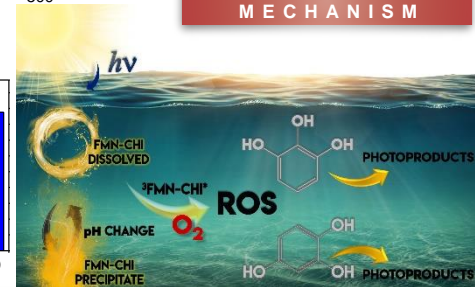
### Photogenerated ROS



### Determination of ${}^3k_{qy}$ by Laser Flash Photolysis

Sensitizer	1,2,3 THB ( $M^{-1}s^{-1}$ )	1,2,4 THB ( $M^{-1}s^{-1}$ )
FMN-CHI	$2,8 \times 10^9$	$3 \times 10^9$
FMN	$2,8 \times 10^9$	$2,5 \times 10^9$

## PROPOSAL MECHANISM



## CONCLUSIONS

- The synthesis of an FMN-CHI polymeric dye was achieved.
- An important feature is that the PD has a higher  $\phi_{\Delta}$  and is more photostable than free FMN, this may be due to the binding of the sensitizer to CHI. These results are reflected in a faster degradation of polyphenolic compounds when the PD is used in place of FMN. The pollutant degradation may be attributed to their reaction with  ${}^1O_2$  or excited triplet state of the PD.
- The polymer obtained can be removed after its use, and it can be reused several times which turns it into a novel and promising photocatalytic material.

References:  
[1] M. Luisa Marín, Lucas Santos-Juanes, Antonio Arques, Ana M. Amat, and Miguel A. Miranda *Chemical Reviews* 2012 112 (3), 1710-1750  
[2] Ferrarri, G.V., Andrada, M.E., Natera, J., Muñoz, V.A., Paulina Montaña, M., Gambetta, C., Boiero, M.L., Montenegro, M.A., Massad, W.A. and García, N.A. *Photochem Photobiol* 2014 90 (6), 1251-1256.

Acknowledgment

