University of Minho
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CENTRE OF BIOLOGICAL ENGINEERING

Environmental impact of nanomaterials: assessment of toxicity in chemical and biological processes for the degradation of micropollutants

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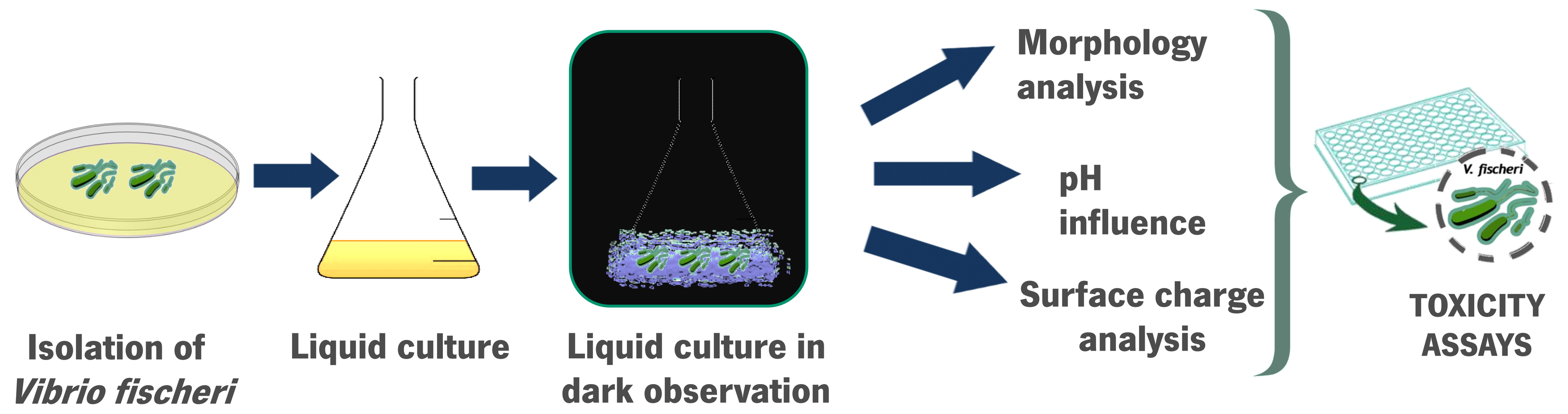
Introduction

The exceptional properties of nanomaterials have increased their use in many different areas, including electronics, construction and healthcare [1]. Nanomaterials have also been proposed on remediation of pollutants as sorbents and as catalysts of their biological and chemical removal. In this study, different nanomaterials have been applied as catalysts in chemical and biological processes for the degradation of the antibiotic ciprofloxacin (CIP). CIP is one of the most prescribed antibiotic and their persistence in effluents has increased in the last decades [2]. UV/Photocatalytic degradation of CIP was performed using TiO_2 and ZnO, due to their high photocatalytic activity [3]. CIP biodegradation was performed under anaerobic conditions. The effect of carbon materials (CM), namely Carbon nanotubes, single (CNT) or incorporated with 2% of iron (CNT@2%Fe), as electron shuttles in the process, was studied. Those materials were previously proved to accelerate up to 79-fold the rate of azo dye biodegradation in similar conditions [4]. CIP removal was monitored as well as the toxicity of the medium before and after the treatment. Toxicity assessment is highly important as it is desired that the products formed after the process are not more toxic than the initial compound. Moreover, the evaluation of the possible contribution of nanomaterials used in the process for the final toxic effect of threated solution, is crucial.

Vibrio fischeri is a marine bioluminescent bacterium, widely used in acute toxicity tests due to their high sensitivity and fast toxic response to pollutants. The bioassay is based on the changes in the bacteria natural luminescence when exposed to potentially toxic substances. The reduction of emitted light is related to the toxicity of the tested substance [5].

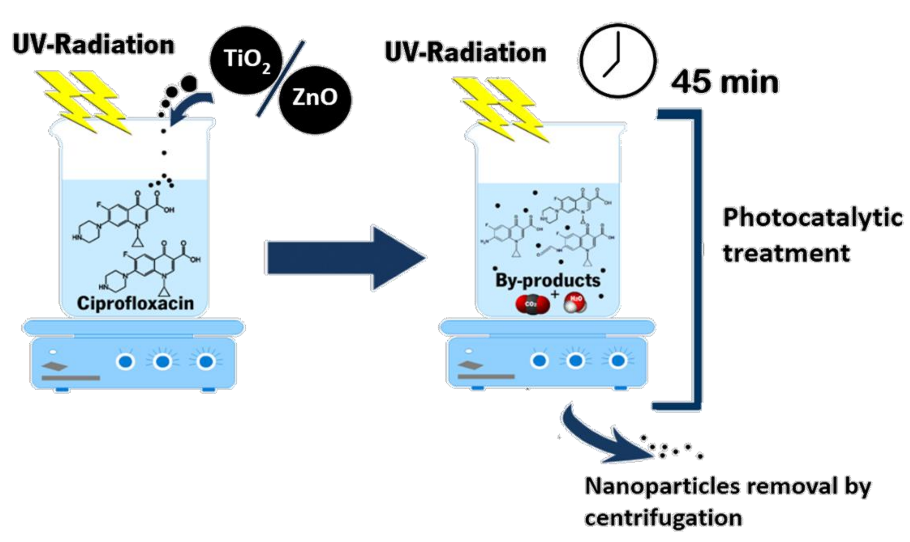
Methods

Vibrio fischeri growth

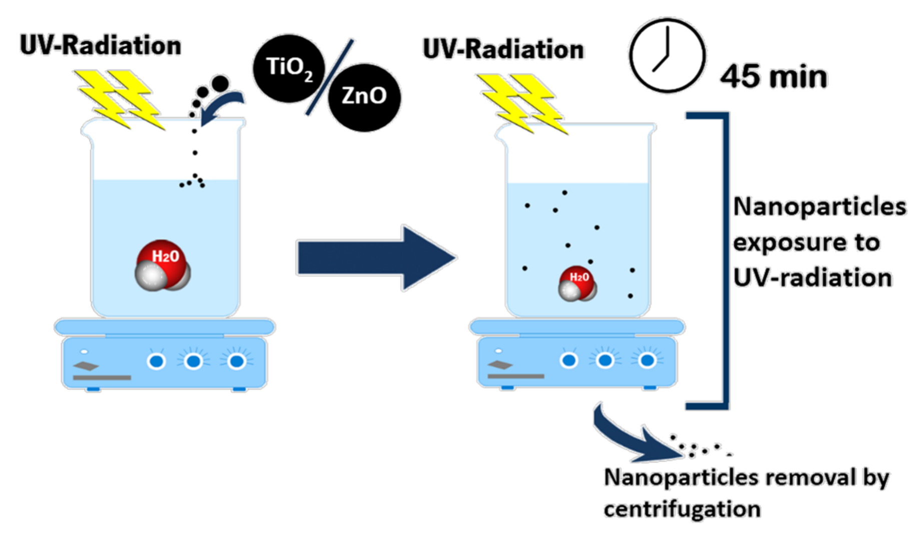


Chemical and biological processes for the removal of CIP

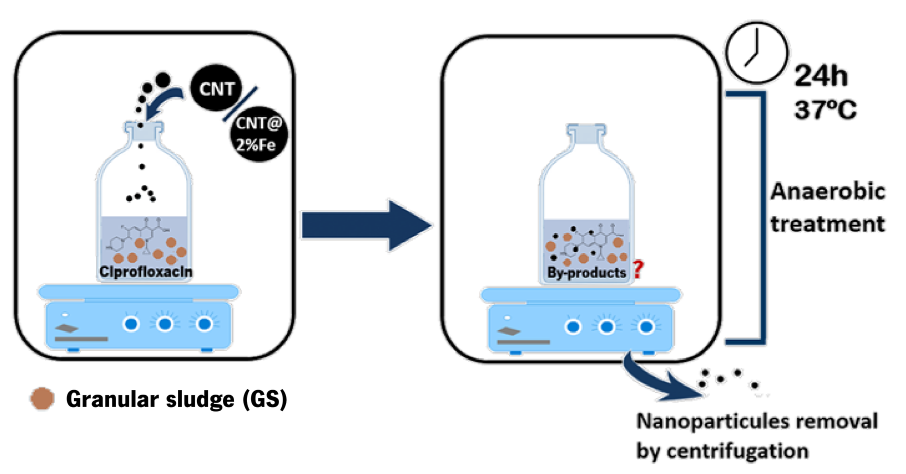
➢ **Photocatalytic treatment of CIP**



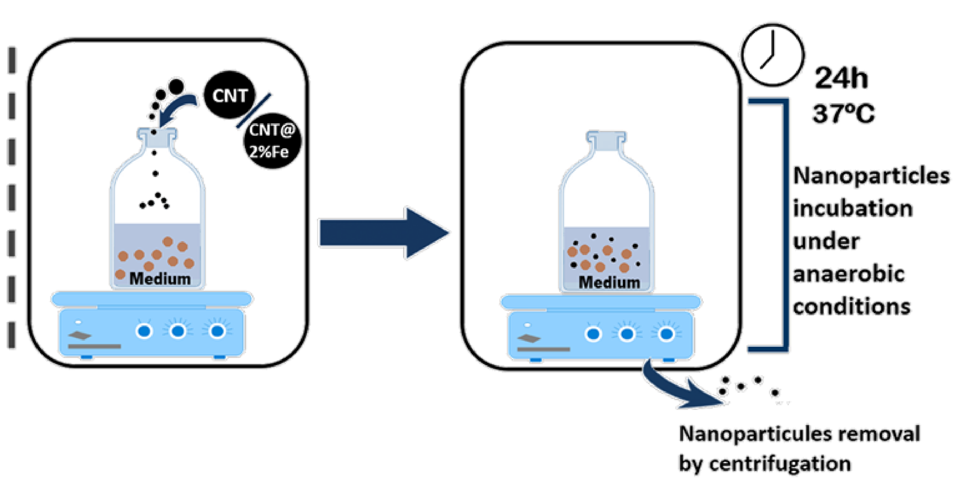
➢ **Control – nanomaterials effect**



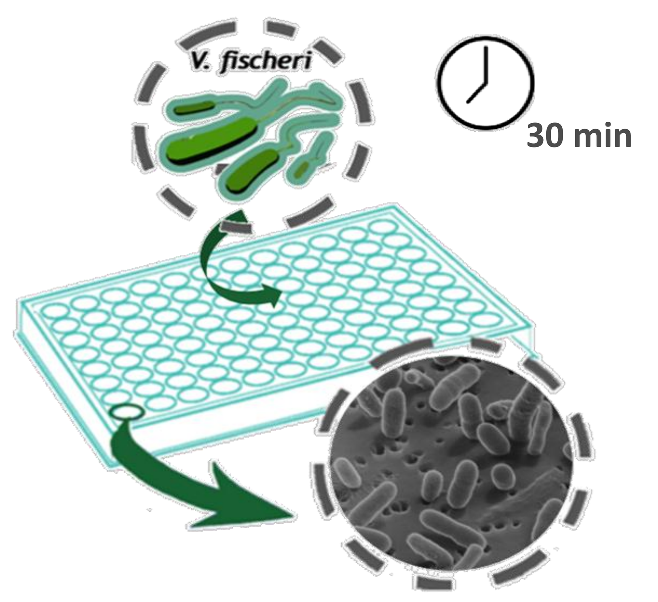
➢ **Biological treatment of CIP**



➢ **Control – nanomaterials effect**



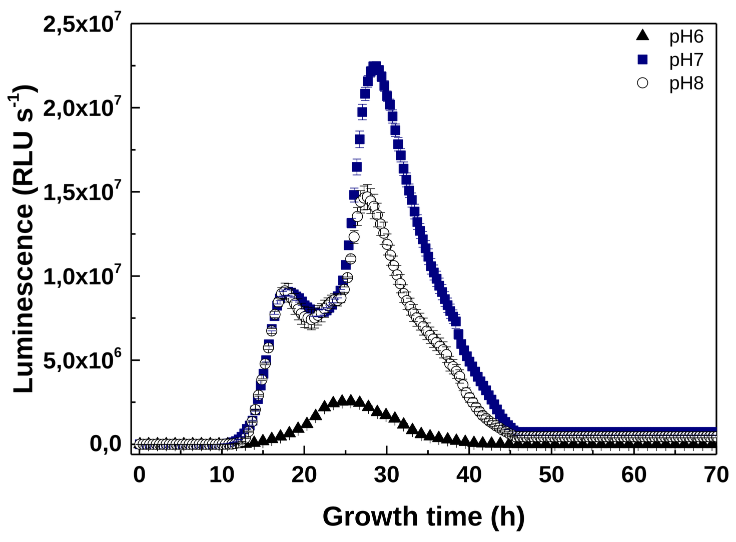
Toxicity Assay

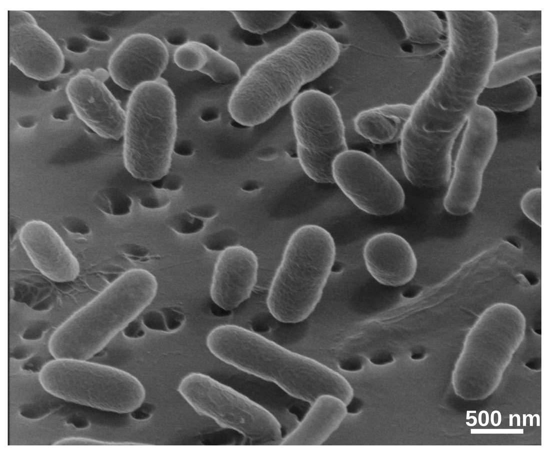


Analyzed samples

- ➢ **Solution of incubation of TiO_2**
- ➢ **Solution of incubation of ZnO**
- ➢ **Solution of incubation of CNT**
- ➢ **Solution of incubation of CNT@2%Fe**
- ➢ **CIP solution**
- ➢ **Solution after CIP treatment by photocatalysis and by biological processes**

Results





pH	Growth at specified pH[a] (ζ-potential, mV)	Exposed to specified pH[b] (ζ-potential, mV)
6	-40.8 ± 5.9	-18.0 ± 1.2
6.5	-	-37.9 ± 0.8
7	-44.5 ± 3.9	-38.9 ± 0.7
7.5	-	-37.5 ± 0.6
8	-45.8 ± 7.4	-38.4 ± 0.9

[a]Grown at the specified pH, then measured in water at pH 7
[b]Grown at pH 7, then measured in water at the specified pH

- *Vibrio fischeri* has maximum of light emission at ca. 28 h of growth
- *Vibrio fischeri* present rod-shaped cells of 2.2 ± 1 µm
- The bacteria's surface is negatively charged, when growth at pH 6, 7 and 8 or when exposed to solutions in this range of pH

Toxicity - Chemical process

Samples	Treatment time (min)	CIP removal (%)	Luminescence inhibition (%)
CIP solution	0	n.a.	62 ± 1.8
CIP treated with TiO_2	15	n.d.	34 ± 8.0
	45	100	70 ± 7.8
CIP treated with ZnO	15	n.d.	97 ± 0.2
	45	100	98 ± 0.3
TiO_2	45	n.a.	38 ± 0.3
ZnO	45	n.a.	97 ± 2.0
CIP adsorption to TiO_2	-30*	85	55 ± 8.6
CIP adsorption to ZnO	-30*	63	96 ± 0.5

n.a., Non applicable; n.d., Non detectable; -30*, 30 min without UV-radiation

- The toxicity of CIP samples decreases in the first 15 min of photocatalytic treatment with TiO_2, but increases after that time
- ZnO nanoparticles exert higher toxic effect than TiO_2 nanoparticles
- The toxicity of CIP solution treated with ZnO can not be estimated due to the high toxic effect inherent of the ZnO nanoparticles

Toxicity - Biological process

Samples	CIP removal (%)	Luminescence inhibition (%)
CNT	n.a.	28 ± 1
CNT@2%Fe	n.a.	35 ± 14
CIP solution	n.a.	56 ± 10
Bio	72 ± 2	30 ± 4
Bio+CNT	98 ± 1	19 ± 8
Bio+CNT@2%Fe	92 ± 1	26 ± 7
Abiotic CNT	100 ± 1	15 ± 9
Abiotic CNT@2%Fe	100 ± 1	26 ± 7

n.a., Non applicable

- CNT@2%Fe caused higher toxicity than CNT, however they are considered *slightly toxic*
- The toxicity of CIP solution decreases with the biological treatment
- In the abiotic processes, detoxification may be a result of CIP adsorption to CM
- The *slight toxic effect* verified after the treatment can be related with the possible formation of by-products, but also the contribution of CM

Conclusions

- CIP removal by photocatalytic processes, TiO_2 and ZnO as catalysts, was complete after 45 min of UV-radiation
- ZnO nanoparticles exerted almost 3-fold higher toxicity than TiO_2 nanoparticles
- The toxicity of the treated solution with TiO_2 was higher than the initial CIP solution,, probably due to formed products and also nanomaterials contribution
- The use of CM in the biological processes improved the removal of the CIP and also the detoxification

References

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