Ciprofloxacin removal catalysed by Conductive Carbon Materials

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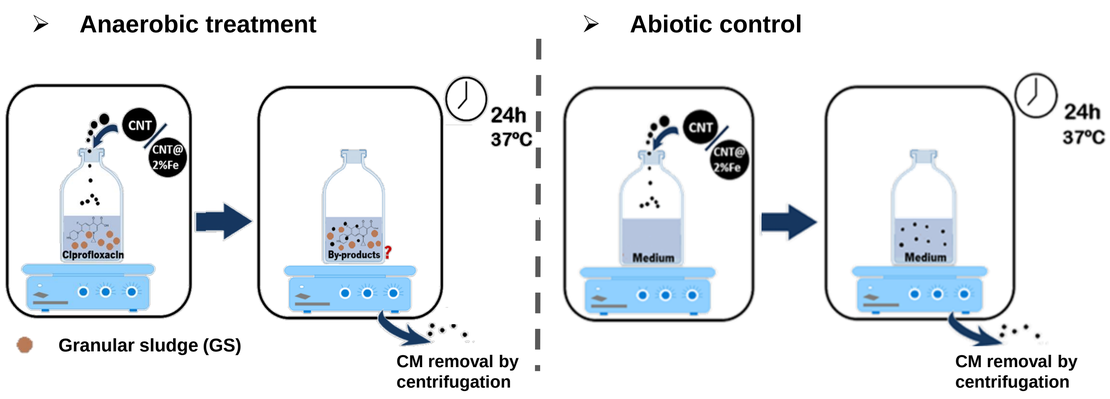
INTRODUCTION

Current wastewater treatment technologies are not effective in the removal of pharmaceuticals. In anaerobic bioreactors, the electrons produced during the oxidation of organic matter can potentially be used for the biological reduction of pharmaceuticals. However, these reactions occur generally at a slow rate, due to electron transfer limitations, and might be accelerated through redox mediators (RM). Carbon nanomaterials (CM) have been effective RM in the biological reduction of other pollutants [1,2]. For instance, CNT@2%Fe were found to increase 76-fold the biological reduction of Acid Orange 10 [3]. The magnetic properties of those composites allow their easier recover after the process by using a magnetic field. In this study, CNT and CNT@2%Fe were studied in the anaerobic removal of Ciprofloxacin (CIP). Furthermore, the potential contribution of adsorption and biodegradation processes for CIP removal was assessed.

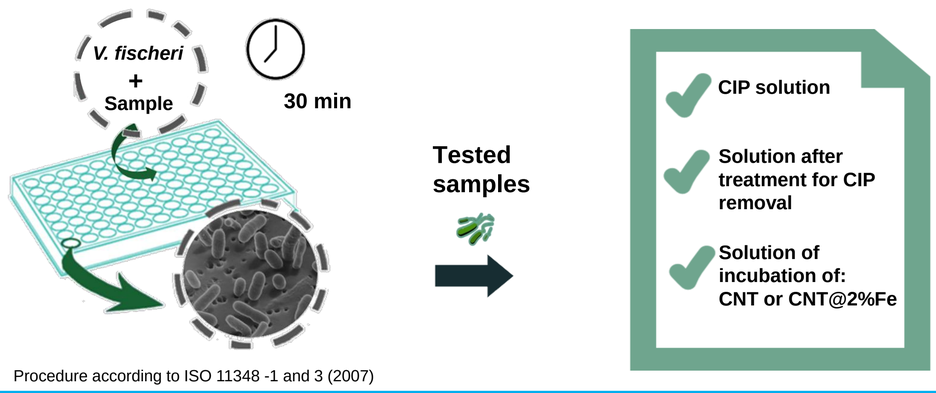
Toxicity assessment is highly important as it is desired that the products formed after the process are not more toxic than the initial compound. Moreover, the evaluation of the possible contribution of nanomaterials used in the process for the final toxic effect of threated solution, is crucial. In this sense, the detoxification of the treated solutions was evaluated towards *Vibrio fischeri* [4].

METHODS

Biological treatment for CIP removal



Toxicity assessment



Procedure according to ISO 11348 -1 and 3 (2007)

RESULTS

Table 1 –Effect of CM (CNT and CNT @2%Fe, 0.1g L^{-1}) on percentage of removal (%) of CIP (0.015 mmol L^{-1}), ethanol (30 mM) and methane production in the anaerobic assays. Also, the luminescence inhibition of *V. fischeri* in all the tested samples, after 30 min of exposure

Samples	CIP removal (%)	Ethanol removal (%)	CH_4 ($mmolL^{-1}$)	Luminescence inhibition (%)
CNT	n.a.	n.a.	n.a.	28 ± 1
CNT@2%Fe	n.a.	n.a.	n.a.	35 ± 14
CIP solution	n.a.	n.a.	n.a.	56 ± 10
Blank	59 ± 2	n.a.	1.5 ± 0.01	-
Bio	72 ± 2	95 ± 4	48.9 ± 0.4	30 ± 4
Bio+CNT	98 ± 1	95 ± 5	48.6 ± 0.2	19 ± 8
Bio+CNT@2%Fe	92 ± 1	93 ± 2	48.7 ± 0.2	26 ± 7
Abiotic CNT	100 ± 1	0	0	15 ± 9
Abiotic CNT@2%Fe	100 ± 1	0	0	26 ± 7

n.a.,Nonapplicable.

- The biological removal of CIP was enhanced 26% in the presence of CNT and 20% with CNT@2%Fe. In the abiotic assays the CIP removal was complete
- The substrate (ethanol) consumption was total after 24h in all the biological assays
- The conversion of ethanol to methane (CH_4) is in good agreement with the stoichiometry, were it was observed the total conversion of ethanol to CH_4, after treatment
- The toxicity of CIP solution decreases after the biological treatment
- The CM contributed for the final toxicity of the treated samples

DISCUSSION

Table 2 – Effect of CM on the rates (d^{-1}) of CIP reduction, ethanol consumption and methane production.

	CIP Rate (d^{-1})	Ethanol Rate (d^{-1})	CH_4 Rate (d^{-1})
Blank	24 ± 1	n.a	0
Bio	19 ± 4	0.996 ± 0.14	68.5 ± 1.9
Bio + CNT	24 ± 1	0.912 ± 0.06	62.2 ± 3.2
Bio + CNT@2%Fe	16 ± 2	0.827 ± 0.01	60.2 ± 2.0
Abiotic CNT	7 ± 1	0	0
Abiotic CNT@2%Fe	12 ± 3	0	0

- Despite the similar percentage of removal of CIP in the biological and abiotic assays, the **removal rate in the biological assays were higher than the abiotic assays**. This indicates that, in addition to adsorption on CM, the biological activity contributes for the removal of CIP
- The ethanol and CH4 rates were similar in all the conditions

Mechanisms of CIP removal

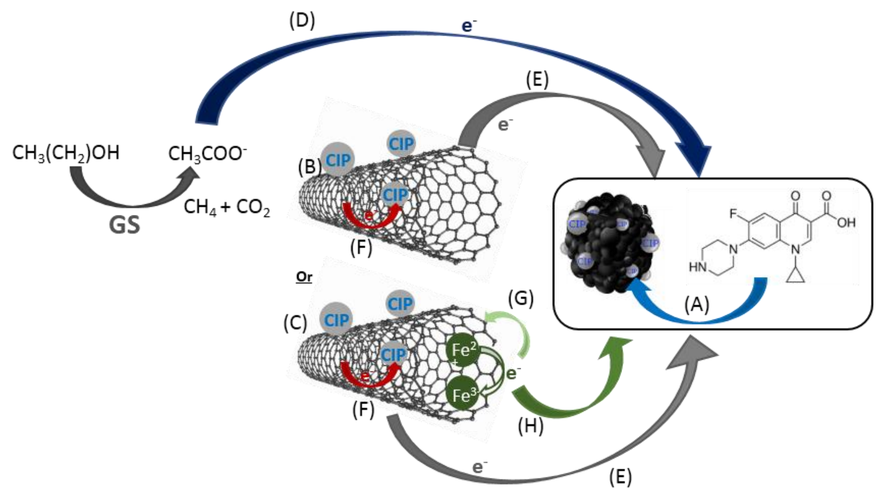


Figure 1 – Proposed mechanisms of CIP removal: adsorption on the **sludge (A)**; adsorption **on CNT (B)** or **CNT@2%Fe (C)**; **electron (e-)** flow from the biological (GS) oxidation of ethanol **to CIP (D)** or **to the CM** and then to CIP, in solution or adsorbed on biomass (E) or adsorbed on the CM (F); **e- transfer** from the abiotic oxidation **of Fe^{2+} to CNT@2%Fe (G)** and then to CIP (H) may also occur. All these mechanisms may occur independently or combined.

- CIP removal occurred by a combination of mechanisms: adsorption on sludge and/or CM and biological reduction
- The abiotic reduction is resultant from CIP adsorption on CNT and/or the electrons generated from the abiotic oxidation of Fe^{2+} of the CNT@2%Fe
- CNT@2%Fe caused higher toxicity than CNT, however they are considered *slightly toxic*
- In the abiotic processes, detoxification may be a result of CIP adsorption to CM

CONCLUSIONS

- The use of CM in the biological processes improved the removal of the CIP and promote the detoxification of samples
- The CIP removal can be resultant from the biological oxidation of the substrate and consequent electrons flow to the pharmaceutical compound
- The chemical oxidation of the Fe^{2+} to Fe^{3+} in the CNT@2%Fe can promote the reduction of CIP adsorbed in CM or in solution
- During the treatment, the substrate is completely consumed and converted to methane
- The slight toxic effect verified after the treatment can be related with the possible formation of by-products, but also the contribution of CM

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