Synthesis Of A Layered Double Hydroxide (LDH) On A Carbon Structure For Photocatalytic Drug Degradation.

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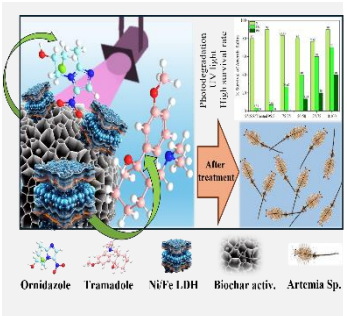

Photocatalysis emerges as an eco-friendly technology to mitigate pollution in aquatic systems by emerging pollutants such as Tramadole (TMD) and Ornidazole (ONZ). This research addresses the synthesis of Ni/Fe-LDH and functionalization with biochar to obtain BC@Ni/Fe-LDH, a new hybrid material from the solvothermal method. Characterization by PCZ, BET Surface Area and FTIR confirmed the successful synthesis and functionalization. Adsorption parameters determine the conditions of pH, dosage and adsorption-desorption equilibrium of the material. The photocatalytic activity was evaluated at various lights, experimental design and exposure time, using H_2O_2 (30% v/v) as oxidant.

Introduction

Layered double hydroxide (LDH) have the ability to bind various organic, inorganic, organometallic anions [1] and, also, to incorporate carbon-based materials from agricultural waste biomass to improves properties that contribute to photocatalytic degradation processes of emerging pollutants [2].
Therefore, this work aims to develop a new composite and evaluate its properties in the photocatalytic degradation of Tramadol and Ornidazole.

Material and Methods

The synthesis of BC, Ni/Fe-LDH and functionalization of BC@Ni/Fe-LDH was carried out according to the following illustration.

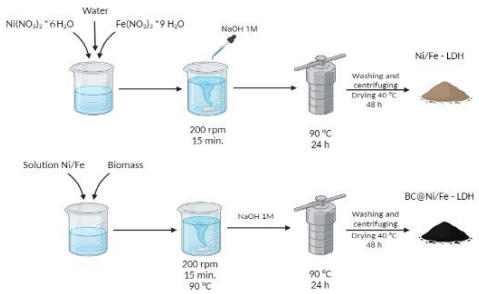

Figure 1. Functionalization of BC@Ni/Fe-LDH (hibrid).

Briefly, BC was obtained from the carbonisation of corn cob and subsequent activation with saturated KOH solution at 700ºC both in N2 atmosphere. Ni-Fe/LDH was prepared in a 3:1 ratio of Ni:Fe metals by co-precipitation of salts and subsequent curing. The composite was synthesised following the same route of synthesis of LDH precursor in the presence of BC as support material.

Point of zero charge (PZC), FTIR, XRD and BET Surface Area was used to evaluate the success of the functionalization. Adsorption parameters were performed to give the most favorable conditions for BC@Ni/Fe-LDH in presence of Tramadol (TMD) and Ornidazole (ONZ). In photocatalytic parameters, it was identified the best conditions of heterogeneous photocatalysis by multiple studies.

Samples were quantified by HPLC reverse-phase C18 and UV-Vis PDA, with acetonitrile (HPLC grade) and acidified water (acetic acid, pH<3) as movil phase in ratio 30:70, respectively, in 4 minutos at flow rate of 0,8 mL min^{-1}.

Results and Discussion

According IUPAC classification, 2.0-50 nm a pore diameter is considered mesoporous [3]. The surface area and PCZ (Table 1) of BC@Ni/Fe-LDH is between precursors. In FTIR study characteristics bands of Ni/Fe-LDH were identified in BC@Ni/Fe-LDH, such as 3410 cm^{-1} (O-H),1637 cm^{-1} (C-H or N-H), 1347 cm^{-1} (NO_3^-), 624 cm^{-1} (M-O-M) [4]. Thus, all of these thechniques confirm the successful functionalization of the hybrid material.

Table 1. BET Surface Area, Pore Diameter and PZC

Material	S_{BET} (m^2 g^{-1})	Pore diam. (nm)	PZC
Ni/Fe-LDH	51	32	5.85
BC@Ni/Fe-LDH	672	42	5.50
BC	816	7	5.09

In preliminary photodegradation tests BC, LDH and BC@LDH showed removal rates of 2, 98 and 96% respectively, which is why the hybrid was chosen to be studied considering its technical and economical advantages for future applications. In the pH effect, pKa of contaminants it's an important factor. The adsorption capacity of TMD increased at acidic pH, while ONZ showed affinity for basic pH. It was

chosen to work at neutral pH to avoid total adsorption of the polluntants.
Different dosages (Fig 2a-b) of hibrid were evaluated to know the adsorption capacity and removal of TMD and ONZ on surface. A dose of 1200 mg L^{-1} was decided to increase the TMD and ONZ remanent, and got to reach a stable equilibrium at 120 min for all concentrations (Fig 2c-d).

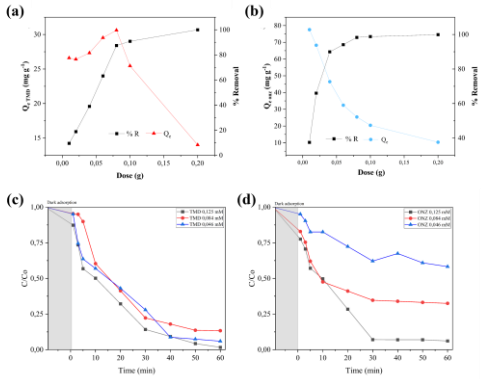

Figure 2. Effect of dose on TMD (a) and ONZ (b) adsorption. Effect of contact time on TMD (c) and ONZ (d) adsorption.

The effect of light (Fig 3a) showed that UV-C light was the most effective for removal TMD and ONZ. UV-C radiation, being highly energetic, activated the photocatalytic properties of the material, generating ROS such as OH•, OH^- and $•O_2^-$ that contributed to the efficient degradation of organic pollutants [5]. In addition, the experimental design (Fig 3b) for the photocatalytic degradation showed that ADS+H_2O_2+UV treatment was the most effective, capable of removing 95.38% TMD and 98.64% ONZ.

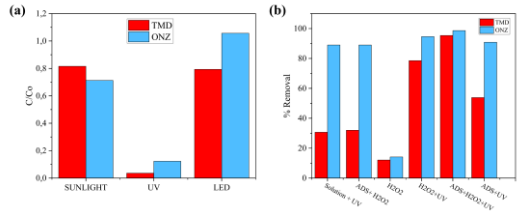

Figure 3. a) Effect of light on the photocatalytic degradation of TMD and ONZ, b) Comparison of removal treatments.

The stoichiometric dose of H_2O_2 was 6.47 mol L^{-1}. However, in Fig 4a-b, by increasing the amount of H_2O_2, an improvement in removal of contaminants was observed. Despite this, an excess of H_2O_2 may compete for the active sites on surface of the material and decrease the photocatalytic activity [6]. Therefore, dose of 9.8 mol L^{-1} H_2O_2 provided the highest degradation and got TMD and ONZ to reach equilibrium at 50 min in the system, according Fig. 4c-d.

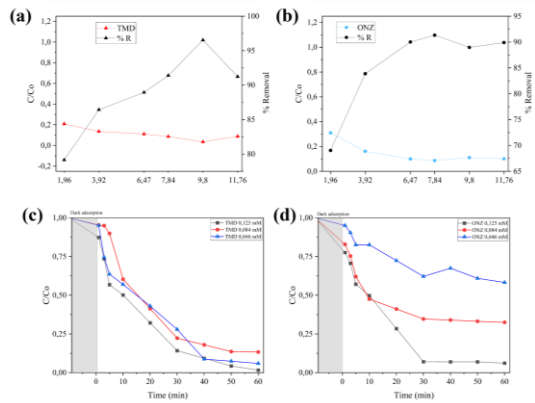

Figure 4. Influence of H_2O_2 dose on photocatalytic degradation of TMD (a) and ONZ (b). Exposure time for TMD (c) and ONZ (d).

Conclusions

This research succeeded in synthesizing and characterizing a new LDH-functionalized on a biochar structure with important structural and chemical properties, capable of degrading pharmaceutical products in aquatic systems. Adsorption tests achieved the necessary conditions for the functionalized hybrid to show a high efficiency in the photocatalytic degradation of Tramadol and Ornidazole. These results suggest that the BC@Ni/Fe-LDH is a promising material that can be used for removal of emerging pollutants in aquatic effluents.

References

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