# Synergistic Adsorption-Photocatalysis Process in the Removal of Nicosulfuron by a Novel Hybrid Biomass@LDH/MOF Nanocomposite

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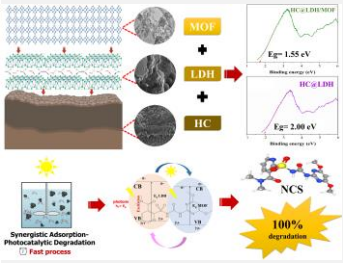


In this research, a novel Biomass@LDH/MOF nanohybrid was synthesized by co-precipitation and solvothermal treatment. Physicochemical characterization (SEM, TEM, BET, XRD, and XPS) confirmed the hybridization of this nanostructure with advanced photocatalytic properties. Corn residue hydrochar was used to support the LDH and MOF, which allowed a 300-fold increase in size. In addition, in situ growth of MIL-53(Al) crystals and LDH allowed the reduction of the band-gap (1.55eV) and the impregnation of Fe and Mg, which gives it important advantages for its photocatalytic application in the visible light spectrum. The HC@MgFe-LDH/MIL-53(Al) material was used in a synergistic adsorption-photocatalysis system to degrade nicosulfuron (NCS) in water samples, highlighting its high photocatalytic performance and achieving 100% removal of NCS with simulated sunlight irradiation in 60 minutes of reaction, without previous adsorption step.

## Introduction

Current agricultural practices depend on a high use of agrochemicals, which has increased their presence in various environmental matrices. Sulfonylurea herbicides such as nicosulfuron (NCS) have been detected in water bodies at concentrations higher (2-80 ng $L^{-1}$) than those established by environmental regulations [1].

To address this problem, several physicochemical methods have been developed for their removal, among which photocatalysis stands out for its efficiency in degrading organic pollutants [2]. However, its large-scale application faces technical and economic challenges. To improve the applicability of oxidative processes, hybrid nanomaterials that employ waste biomasses as support for metal-organic frameworks (MOF) and layered double hydroxides (LDH) are currently being explored. The aim is to reduce the problems related to the nanometric size of these structures and to optimize their optical, and catalytic properties.

These nanostructures show great potential as adsorbents [3], but their use as photocatalysts has not been studied in depth. Therefore, this research focuses on developing a synergistic adsorption-photocatalysis treatment system for NCS removal in aqueous matrices using Biomass@LDH/MOF as a photocatalyst.

## Material and Methods

### Synthesis of Biomass@LDH/MOF nanohybrid

The preparation of the nanohybrid was carried out following the synthesis route shown in Figure 1.

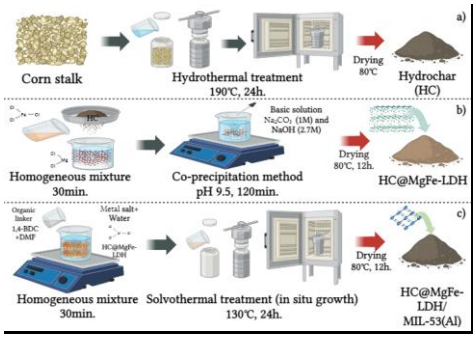


**Figure 1.** Schematization for the synthesis of HC@MgFe-LDH/MIL-53(Al) material.

### Nanohybrid characterization

$N_2$ adsorption/desorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and diffuse reflectance/UV-vis techniques were used.

### Synergistic adsorption-photocatalysis study

To study the NCS photodegradation, the synergistic effect of adsorption-photocatalysis, which consists of direct light irradiation without the previous adsorption phase, was analyzed. Photocatalytic tests were developed under irradiation at different wavelengths for 60 min (298.15K - 300rpm). Also, the behavior of the system was evaluated with a dark adsorption phase and the combination of adsorption and photocatalytic degradation as consecutive stages. An initial concentration of 50 mg $L^{-1}$ of NCS, pH 6, material dose of 2 g $L^{-1}$, and $H_2O_2$ as oxidant (7.15 mM) was established. NCS concentration before and after treatment was measured by HPLC.

## Results and Discussion

### Physical-chemical properties of the material

The synthesized HC@MgFe-LDH/MIL-53(Al) material presented better surface properties than its precursors, with high mercury porosity and a surface area of 134 $m^2$ $g^{-1}$. The use of HC as a support for MgFe-LDH/MIL-53(Al) increased the size of the material to 50 µm, which represents a 300-fold increase compared to the size of its precursors. This increase improves the contact area between the material and the fluid phase and facilitates their separation in heterogeneous photocatalytic processes. However, the reduction of the band-gap (1.55eV) is one of the most novel features of the material, since it allows it to absorb photons in visible light (Figure 2). XPS scanning of the nanohybrid confirmed the appearance of Al2p characteristic of MIL-53(Al), as well as the Mg1s and Fe2p peaks (LDH). This type of materials exhibits semiconductor-like properties with in situ growth of MOF crystals by hybridization of lattice oxygen species present on the HC surface [4].

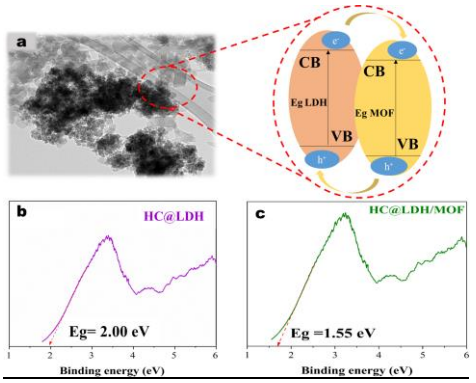


**Figure 2.** Material characteristics: (a) TEM and Diffuse reflectance spectroscopy of (b) HC@LDH and (c) HC@LDH/MOF.

### Synergistic adsorption-photocatalysis study

Figure 3a shows the photostability of NCS against visible light (LED and solar) and even against exposure to these light sources in the presence of an oxidant. However, in the presence of UV light, a photolytic degradation of 52% occurs, a value relatively similar (53%) to the removal of the contaminant by adsorption.

The process composed of independent adsorption (180min) and photocatalysis (180min) stages evidenced a removal of 92%. In comparison, the simultaneous adsorption and photocatalysis process obtained efficiencies higher than 90% under LED irradiation and sunlight in short reaction times (<60min). Although the prior adsorption step could cluster the target pollutant molecules on the material's surface and promote in situ electron transfer, it is well known that this process can lead to saturation of the active sites with catalytic properties. Therefore, without the previous adsorption step, the rapid photoexcitation of the material and the consequent generation of the electron/hole pair was achieved, causing the formation of •OH groups as a result of the photogenerated holes that oxidize the water and degrade the pollutant. Another possible route is the production of superoxide groups through the electrons transferred as a consequence of the conversion of $O_2$ adsorbed on the material [5], which consequently increased the reaction rate without the need for an additional oxidant (Figure 3b).

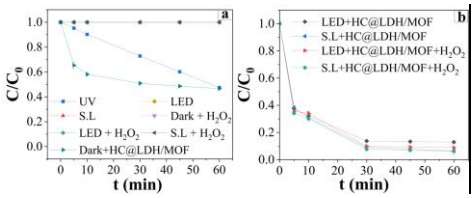


**Figure 3.** Photocatalytic degradation of NCS. a) Photostability, photoperoxidation, and dark adsorption stage. b) Adsorption-photocatalysis synergistic effect.

To analyze the degradation rate of NCS in the photocatalytic process with sunlight, kinetic models were applied, achieving a better fit of the data towards the pseudo-second-order model with a coefficient of determination $R^2$ greater than 0.96.

On the other hand, it was demonstrated that the HC@MgFe-LDH/MIL-53(Al) material can maintain its degradation efficiency for five reaction cycles with values above 97%. However, as the number of cycles increases there is a slight decrease in the photocatalytic performance attributed to the number of NCS molecules adsorbed on the surface of the material and to the intermediate products formed [6].

## Conclusions

The HC@MgFe-LDH/MIL-53(Al) material exhibits improved surface properties and reduced band gap energy compared to its precursors, giving it a higher sensitivity to visible light. Concerning NCS degradation, the synergistic adsorption-photocatalysis system gave the best results, so that the nanohybrid achieved complete removal of the pollutant in 60 min under low-cost simulated sunlight.

***References***

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