

First highly efficient degradation and dechlorination of herbicides by photocatalytic hydrogenation: Advanced reduction processes (ARP) approach

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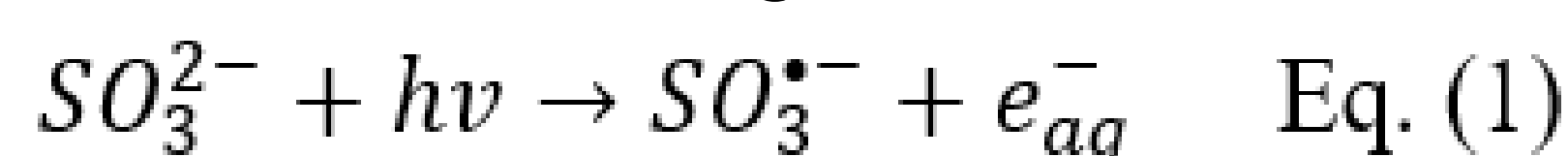
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INTRODUCTION & AIM

The widespread use of phenylurea herbicides (PUHs) such as chlorotoluron (CHL) has caused important environmental and human health concerns due to their persistence, bioaccumulation and resistance to conventional wastewater treatments. Until now, the degradation and transformation of PUHs have been the subject of numerous research. Adsorption, microbial degradation, chemical oxidation, biodegradation, and radical-based advanced oxidation processes (AOPs) have all been shown to be effective in the removal of PUHs [1]. These methods do have some serious disadvantages, though, including poor kinetics, the production of hazardous byproducts, and high costs of treatment. On the other hand, ARPs could be an effective alternate to degrade impurities and yield non-harmful byproducts unlike AOPs and other approaches [1,2].

METHOD

A model solution of CHL with initial concentration of 20 mg/L was used for the processes. CHL degradation in an aqueous environment from sole to complex processes were studied by UV based sulfite (S), palladium on activated carbon (Pd-C), and hydrogen gas (H₂) (UV/S/Pd-C/H₂) using an ARP approach (Fig. 1). Eqs. 1 and 2 shows mechanism of radicals generation in presence of UV light [1,3].



CHL degradation studies were analyzed by HPLC-UV-DAD, ion chromatography and intermediates by GC-MS.



Fig. 1. Schematic diagram of UV reactor, connected with H₂ generator connected with rotameter to regulate flow and water cooling system.

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RESULTS & DISCUSSION

The degradation of CHL by different approaches within 60 min is shown in Fig. 2a. The orders of dechlorination efficiencies were ranked as UV/Pd-C/H₂ (80.5%) > UV/Pd-C (70.1%) > UV/S/H₂ (50.5%) > UV/S (50.3%) > UV/S/Pd-C/H₂ (50.2%) > UV/H₂ (35.5%) > UV lone (20.4%).

Studies of degradation mechanism revealed that the CHL follows degradation via two basic paths. The first pathway involves partial reduction of aromatic system, forming 1-chloro-2-methylcyclohexa-1,3-diene, less probable subpath of the process, assumes the initial hydrogenolysis of the C-N bond between the aryl fragment and the urea part and then the addition of hydrogen to the aromatic system of chlorotoluene as shown in Fig. 2b.

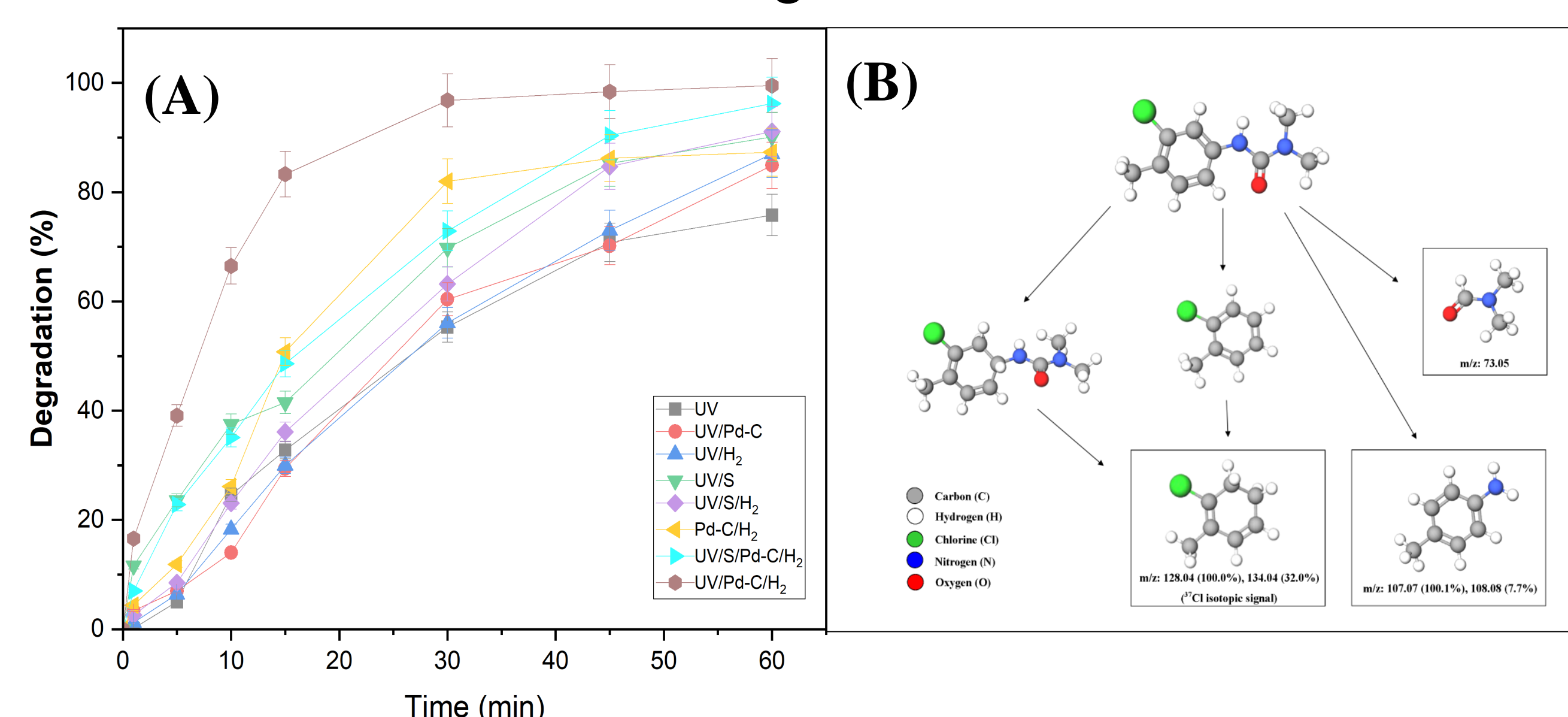


Fig. 2. (a) Degradation of CHL by various methods at conditions of Pd-C:CHL = 2:2, $r_{red.} = 10$, H₂ = 2L/h, CHL = 20 mg/L and pH = 7. (b) proposed degradation mechanism.

CONCLUSION

This study showed that the UV/PdC/H₂ process reduced CHL reduction within 1 hour of treatment along with dechlorination around 80%. Scavenging examination confirmed the presence of reducing agents (hydrated electron and hydrogen radicals). Also, process showed excellent resistance to the presence of inorganic anions and dissolved organic matter, and performed well across a wide pH range.

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