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Solar Light-Assisted Oxidative Degradation of Ciprofloxacin in Aqueous Solution by Iron(III) Chelated Cross-linked Chitosan Immobilized on a Glass Plate

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Abstract: The massive worldwide use of antibiotics leads to water pollution and increasing microbial resistance. Hence, the removal of antibiotic residues is a key issue in water remediation. Here, we report the solar light-assisted oxidative degradation of ciprofloxacin (CPF), using H_2O_2 in aqueous solution, catalyzed by iron(III) chelated cross-linked chitosan (Fe^{III}-CS-GLA) immobilized on a glass plate. The Fe^{III}-CS-GLA catalyst was characterized by FTIR and ^{57}Fe-Mössbauer spectroscopies as well as X-ray diffraction, revealing key structural motifs and a high-spin ferric character of the metal. Catalytic degradation of CPF was investigated as a function of solar light irradiation time, solution pH, concentration of H_2O_2 and CPF, as well as cross-linker dosage and iron(III) content in Fe^{III}-CS-GLA. The system was found to serve as an efficient catalyst with maximum CPF degradation at pH 3. The specific ·OH scavenger mannitol significantly reduces the degradation rate, indicating that hydroxyl radicals play a key role. The mechanism of catalytic CPF degradation was evaluated in terms of pseudo-first-order and Langmuir-Hinshelwood kinetic models; adsorption of CPF onto the Fe^{III}-CS-GLA surface was evidenced by field emission scanning electron microscopy coupled with energy dispersive X-ray spectroscopy. Fe^{III}-CS-GLA can be reused multiple times with only minor loss of catalytic efficiency. Antimicrobial activity tests performed against both Gram-negative (*Escherichia coli* DH5α, *Salmonella typhi* AF4500) and Gram-positive bacteria (*Bacillus subtilis* RBW) before and after treatment confirmed complete degradation of CPF. These results establish the immobilized Fe^{III}-CS-GLA as a rugged catalyst system for efficient photo-Fenton type degradation of antibiotics in aqueous solutions.

Keywords: Ciprofloxacin; oxidative degradation; water treatment; kinetic studies; antimicrobial activity

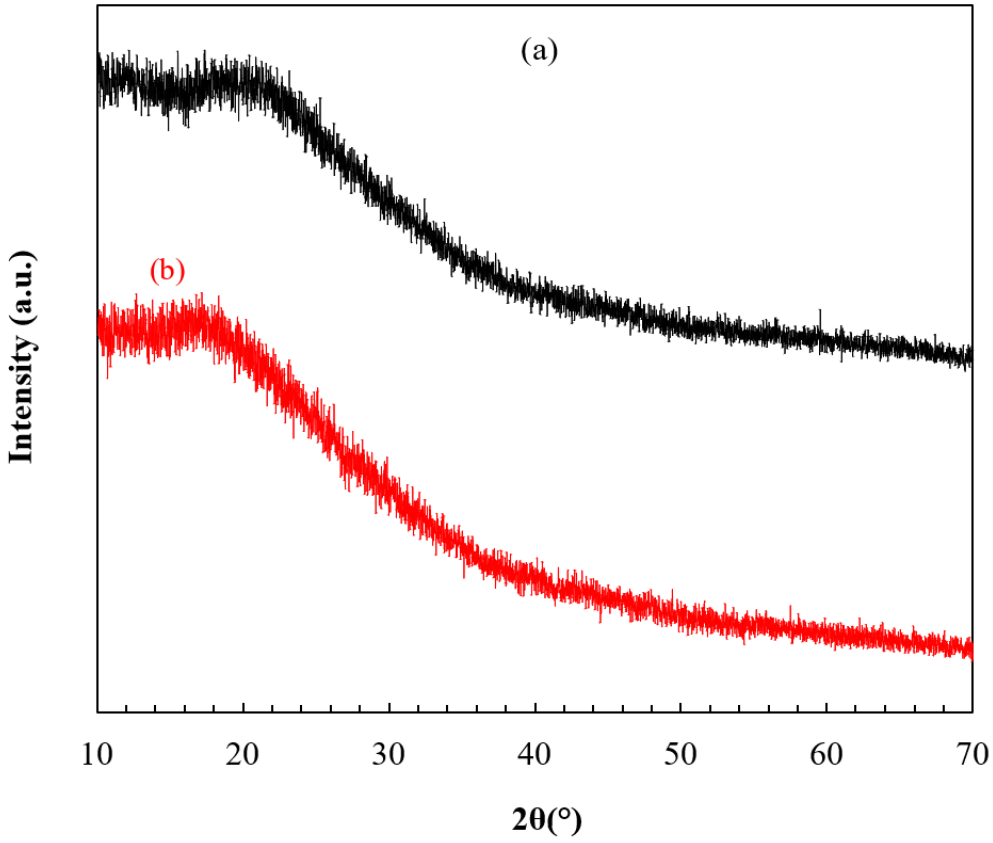
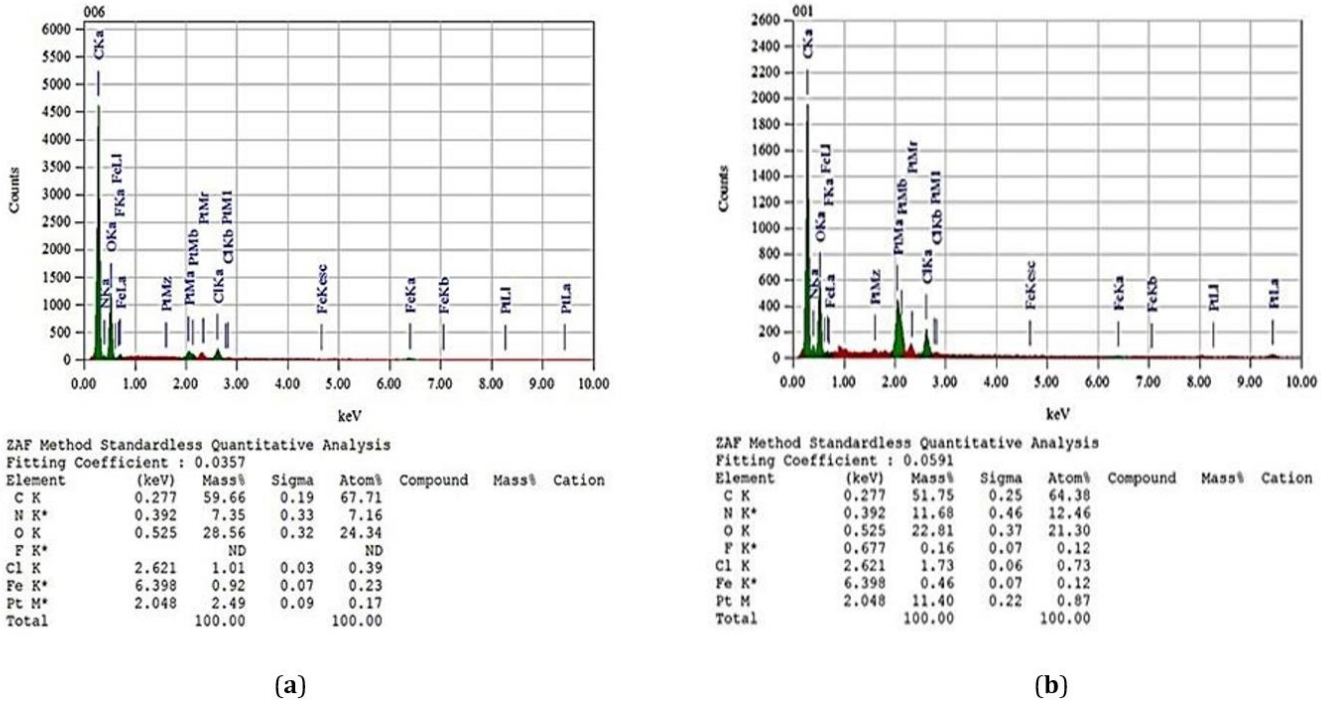


Figure S1. X-ray diffraction patterns of CS (a) and Fe^{III}-CS-GLA (b).



(**a**) (**b**)

Figure S2. EDX analysis of Fe^{III}-CS-GLA before (a) and after (b) its use in the catalytic degradation of CPF.

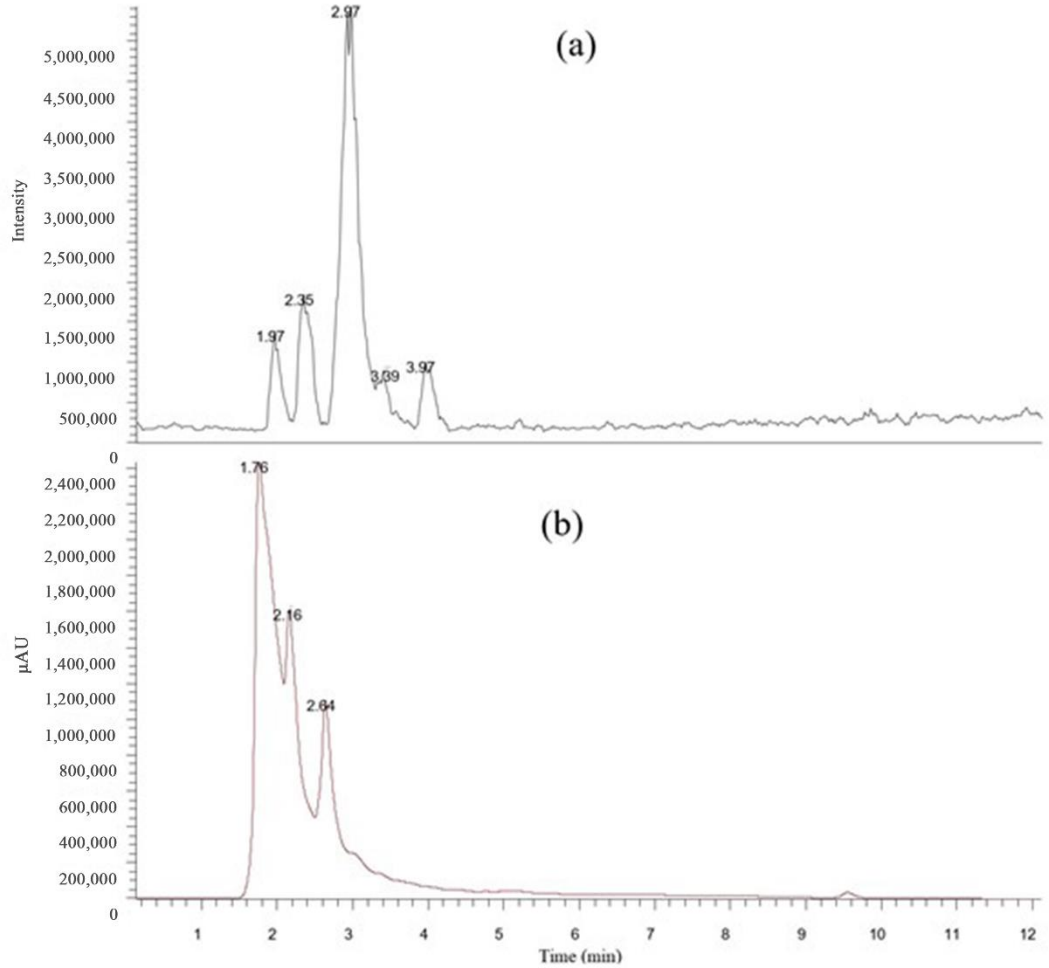


Figure S3. HPLC-UV-ESI(-)-MS chromatograms of the products obtained from solar light-assisted oxidative degradation of CPF catalyzed by Fe^{III}-CS-GLA in aqueous solution. (a) ESI(-)-MS base peak chromatogram and (b) UV chromatogram (total scan). Experimental conditions: $[CPF]_0$: 50 μM, $[Fe^{III}]_0$ in Fe^{III}-CS-GLA: 1.25 mM, $[GLA]_0$ in Fe^{III}-CS-GLA: 90 mM, $[H_2O_2]_0$: 6 mM, volume of CPF solution: 250 mL, pH: 3, light intensity: 70000-90000 Lux, solar light irradiation time: 180 min.μ