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When UV meets clay: mechanistic insights into the degradation of zearalenone and deoxynivalenol by semiconductors supported on kaolin-group minerals

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Zearalenone (ZEN) and deoxynivalenol (DON) are globally pervasive *Fusarium* mycotoxins in cereals and animal feed, posing a persistent food safety risk. Their environmental stability is concerning: ZEN acts as a potent endocrine disruptor, whereas DON induces immunotoxic and gastrointestinal effects and has been increasingly associated with neurotoxic responses. Owing to their relative non-polarity, these toxins are poorly removed from water by conventional adsorption, motivating the exploration of UV-driven photodegradation and oxidative approaches.

Kaolinite-based materials were employed as low-cost, high-surface-area mineral supports, including kaolinite-rich material (M), synthetic calcined kaolinite nanotubes (MNC), commercial halloysite (HS), and a halloysite-containing sample (HD). The supports were loaded (~20 wt%) with TiO_2, g-C_3N_4, or TiO_2/g-C_3N_4 for ZEN degradation, and with TiO_2, Fe_2O_3, or TiO_2/Fe_2O_3 for DON removal. While ZEN was treated via photocatalysis, DON degradation required activation with peroxymonosulfate (2 mM).

Removing up to 98.8% of ZEN within 25 min of UV irradiation, the MNC-composites containing g-C_3N_4 and TiO_2/g-C_3N_4 exhibited the highest photocatalytic efficiency. The incorporation of aluminosilicate nanotubes as supports enhanced textural properties and charge separation without compromising activity. Electrochemical analyses confirmed reduced charge-transfer resistance and prolonged charge-carrier lifetimes at the mineral-semiconductor interface. ZEN degradation was governed by reactive oxygen species, with $O_2^{\bullet-}$ and •OH as the primary contributors, while electron-mediated pathways were particularly significant in the g-C_3N_4-composites. The ZEN degradation pathways proceeded through isomerization and cleavage of functional groups and the aromatic ring, generating oxygenated intermediates [1]. For DON removal, the MNC-supported TiO_2/Fe_2O_3 composites showed the highest efficiency, achieving 98.8% degradation within 45 min compared to 66.1% and 46.0% for the TiO_2- and Fe_2O_3-MNC samples, respectively. Mössbauer spectroscopy and SEM confirmed nanosized maghemite dispersed on the MNC support, providing high surface area and enhanced redox activity for efficient PMS activation. EPR spectroscopy revealed that •OH and $^1O_2$ were the predominant reactive species generated across all samples, while electrochemical analyses indicated a p-type character for the MNC-based composites containing TiO_2 and TiO_2/Fe_2O_3.

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