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Sustainability statement

The increasing global demand for food has heightened the emphasis on food safety, recognizing it as a crucial component of sustainable development and public health. This review highlights advancements in modern technologies aimed at ensuring food quality and safety, particularly focusing on green detoxification methods from a chemistry perspective for the effective removal of mycotoxins. Additionally, the review explores emerging trends such as smartphone-based systems and artificial intelligence, which have the potential to transform food safety protocols. By providing a detailed analysis of the origins and toxicity profiles of various toxins and their degradation into harmless or less harmful substances, this comprehensive review establishes a foundation for future innovations in food toxin management. The progress in detoxification technologies is vital for achieving Sustainable Development Goal 2 (Zero Hunger) by ensuring the safety of food distributed worldwide. Furthermore, by minimizing exposure to toxic mycotoxins, these technologies contribute significantly to Sustainable Development Goal 3 (Good Health and Well-Being). With millions affected by contaminated food annually, the integration of advanced technology into routine food monitoring is essential for preventing outbreaks, reducing healthcare costs, and enhancing consumer trust. As the global community strives to meet the Sustainable Development Goals by 2030, investing in next-generation food detoxification methods is crucial for ensuring food safety.

Mycotoxins, such as aflatoxins, fumonisins, and zearalenone, pose significant risks for foodborne illnesses, underscoring the necessity of effective management within food systems to safeguard human health. The identification and control of these toxins are supported by various methodologies and rigorous quality assurance protocols, with organizations like the WHO and FAO implementing stringent food safety regulations. Tackling food safety issues also involves the identification and environmentally friendly detoxification of these harmful substances, which is essential for public health and consumer confidence. Traditional detoxification methods such as chemical, thermal, and biological often encounter challenges, including incomplete toxin removal, nutritional degradation, residue formation, and scalability issues in complex food products. This highlights the urgent need for innovative strategies for effective and sustainable mycotoxin removal. This study offers a comprehensive review of recent advancements, existing obstacles, and future directions, aiding researchers in assessing detoxification effectiveness and identifying degradation products through sophisticated analytical techniques. Furthermore, it examines the role of artificial intelligence and machine learning in enhancing material design, optimizing processes, and assessing contamination risks. Together, these interdisciplinary strategies create a robust framework for managing mycotoxins in food systems, with ongoing advancements in detection and degradation methods poised to improve food safety and public health, ultimately facilitating proactive measures to mitigate foodborne illnesses and protect consumers.

Contemporary green methodologies focus not only on eliminating toxins but also on precisely targeting their reactive sites. This goal necessitates a convergence of toxicology, catalysis, materials chemistry, and analytical science. Such an interdisciplinary strategy is crucial for adapting detoxification processes to real-world food situations, moving beyond idealized laboratory settings. This document explores the chemical principles that support each technology and showcases the integration of various methods to effectively mitigate mycotoxin risks and to address the evolving challenges in food safety. By embracing these innovations, researchers, industry participants, and regulatory bodies can work together to ensure a safer, sustainable and more secure global food supply chain.

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Mycotoxins in Food: Green Detoxification Technologies, Mechanisms, Matrix Challenges and Analytical Advances

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Abstract

More than 25% of the world's grain production is contaminated with mycotoxins. Conventional chemical, thermal, and biological detoxification techniques suffer from limitations such as incomplete toxins removal, nutritional deterioration, residue formation and restricted scalability in intricate food matrices. As a result, innovative solutions are probed for efficient and long-term mycotoxin removal. This review examines green detoxification technologies from a chemistry-centered perspective, starting with the intrinsic reactivity of major mycotoxins and their biological behavior. Classification, bioactivation through CYP450 pathways, oxidative stress, and direct molecular damage are discussed not as isolated toxicology topics, but as guiding principles that help explain why certain detoxification strategies succeed while others fail. Under mild, environmentally benign conditions, photocatalytic platforms based on heterojunction semiconductors, metal organic frameworks, carbon nitride, and magnetically recoverable nanocomposites enable light-driven production of reactive oxygen species that specifically degrade major toxic metabolites including aflatoxin variants, fumonisin compounds, as well as zearalenone. The selectivity, stability, and detoxifying effectiveness in actual food matrices are enhanced via adsorption-biocatalysis hybrid systems by combining high-affinity sorbents with immobilized enzymes or nanozymes. This review emphasizes the use of advanced analytical tools and biosensor technologies, particularly focusing on eco-friendly detoxification methods that minimize the formation of secondary toxins while facilitating the identification of degradation products. Moreover, unlike previous reviews that primarily focus on individual detoxification technologies, this review offers a novel interdisciplinary framework that integrates mycotoxin intrinsic chemistry, green detoxification technologies, and AI-assisted predictive strategies for selective and sustainable mycotoxin management. It also aligns these approaches with important Sustainable Development Goals (SDGs), specifically SDG 2 (zero hunger), SDG 3 (good health and well-being), SDG 9 (industry, innovation and infrastructure), and SDG 12 (responsible consumption and production). Furthermore, it critically evaluates the emerging applications of machine learning and artificial intelligence in the realms of material design, process optimization, and mycotoxin risk assessment, highlighting their potential as innovative solutions to the challenges addressed. This report is the first to offer an interdisciplinary framework for effective and sustainable mycotoxin management for ensuring food safety, summarizing recent advancements, addressing key challenges, and outlining future directions.

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1. Introduction

Microbial contamination remains a primary concern in the food supply chain and poses challenges to food production.[1] Among fungal contaminants, filamentous fungi are found across numerous food products. They produce mycotoxins which are toxic metabolites formed as secondary products and pose a significant health hazard to humans. Genera Aspergillus, Fusarium, Alternaria, and Penicillium are the most frequent mycotoxigenic fungi.[2] Mycotoxin contamination is an ongoing problem in the agricultural sector, particularly in cereal grains, and may occur during the pre- and post-harvesting phases, processing, packaging, and storage phases.[3] The most prevalent food and feed contaminants are aflatoxins (AFs), fumonisins (FBs), ochratoxin (OTs), zearalenone (ZEN), patulin (PAT), and trichothecenes, including T-2 toxins, nivalenol, HT-2, and deoxynivalenol (DON).[2] AF are potent hepatotoxic and carcinogenic metabolites from Aspergillus species; FBs inhibit sphingolipid biosynthesis and are linked to esophageal cancer; OTs are nephrotoxic agents associated with Balkan endemic nephropathy; ZEN acts as a non-steroidal estrogen causing reproductive disorders; PAT is a polyketide toxin found mainly in apples and apple products; and trichothecenes (including T-2, nivalenol, HT-2, and DON) inhibit protein synthesis, leading to immunotoxicity and gastrointestinal effects. Fusarium mycotoxins are notorious for contaminating grains in the field in the pre-harvest phase of crop production, including DON, FBs, and ZEN. Conversely, AFs produced by Aspergillus and OTs by Penicillium might occur later than expected due to suboptimal postharvest conditions, such as poor storage and transportation.[4] The Food and Agriculture Organization (FAO) of the United Nations estimates that mycotoxins contaminate more than 25% of annual global cereal production.[5] Not only do mycotoxins lead to food waste and substantial economic losses, but they are also highly hazardous to animal and human health.

Aflatoxins are among the more dangerous mycotoxins because of their pronounced toxicity, and they are officially recognized as Group 1 carcinogens for humans.[6] Exposure to mycotoxins has been linked not only to cancer risk, but also to allergic reactions and injury to important organs in the body.[7] Their level of exposure influences the severity of their effects, including genetic alterations and developmental abnormalities. For example, consuming fungus-

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affected food may lead to long-term health consequences, such as liver cancer, endocrine disruption, immune suppression, stunted growth, abdominal pain, and genotoxic effects.[8] Therefore, regulatory authorities worldwide have introduced legally acceptable limits for mycotoxin contamination in foods. As a consequence, an increase in demand has fostered in recent years for decontamination methods to produce cleaner and toxin-free grains.

Decontamination strategies must be implemented to effectively lower the levels of toxigenic fungi and mycotoxins without compromising food quality and food safety. Pre-harvest strategies continue to be the most effective primary defense against contamination, as they significantly lower the overall burden by decreasing fungal infections and toxin generation in agricultural settings. Implementing methods such as resistant crop varieties and atoxigenic biocontrol agents, such as competitive exclusion of Aspergillus flavus, has demonstrated significant decreases in aflatoxin levels under field conditions.[9] Furthermore, it is widely recognized that integrated agronomic management is crucial for reducing mycotoxins originating from Aspergillus and Fusarium.[10]

Tackling the ongoing contamination that persists despite best agricultural practices, especially in climate-stressed scenarios where total avoidance is impossible, corresponds with a chemistry-centered intervention strategy. As a result, when pre-harvest practices are inadequate, post-harvest detoxification methods such as photocatalysis, adsorption, and advanced oxidation techniques act as an essential safety measure for risk reduction, guaranteeing the safety of food and feed.[11] Although there is a concern that excessive dependence on these post-harvest techniques may diminish incentives for efficient field management, possibly resulting in a "moral hazard" where the drive for agricultural mitigation declines, it is crucial to highlight that detoxification processes cannot always completely restore heavily contaminated products to safe or marketable standards. As a result, economic limits and regulatory benchmarks, like those set by the EU and Codex, inherently exert pressure on pre-harvest management practices within effective food safety systems.[12] Furthermore, numerous advanced detoxification techniques work effectively at lower contamination levels, emphasizing the critical importance of preventative measures upstream. As a result, we position this framework within a holistic "farm-to-fork" integrated management approach for mycotoxins, where chemical measures offer extra protection against inevitable residual risks, while pre-harvest tactics aim to minimize the overall contamination load.

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To date, the food industry has been experimenting with different chemical, biological, and physical detoxification methods of mycotoxins.[13] Mycotoxins in food matrices have been widely treated with chemical agents, including ammonization, ozone, hydrogen peroxide, and sodium bisulfate, among others, to eliminate them. Nevertheless, these processes can reduce nutritional value, introduce residual toxins, or eliminate it, which is problematic for safety and consumer acceptance.[14] Using microorganisms or their enzymes to adsorb or break down toxins is generally considered a safer, biological strategy, though it can suffer from variability in large-scale production and reproducibility.[15] Physical treatments, including thermal treatments, can be effective in reducing microbial levels and toxins but may change nutritional and sensory characteristics or sometimes even lead to uneven heating within the grain mass.[4] Moreover, certain mycotoxins persist in food production, indicating that traditional heat treatments are ineffective at reducing mycotoxin concentrations.[16] As a result, an increasing amount of literature is dedicated to non-thermal methods for reducing mycotoxin levels in food and enhancing its sensory properties. As climate change rapidly affects fungal ecology, broadening the range of toxigenic species and escalating the occurrence and intensity of mycotoxin contamination, the limitations of conventional detoxification approaches have become increasingly significant. Given the changing circumstances, there is an urgent need for robust, scalable, and eco-friendly detoxification methods that can ensure food safety in real-world and climate-affected scenarios. These concerns are intricately linked to the United Nations' Sustainable Development Goals, particularly SDGs 2 (zero hunger) and 3 (good health and well-being), emphasizing the necessity for preventive and resilient approaches to secure global food security. Consequently, there is a pressing need to enhance current techniques and investigate new approaches to effectively diminish mycotoxin levels and ensure food security.

Recent developments in green detoxification technologies, such as photocatalysis, cold plasma, and adsorption-biocatalysis coupled systems, have demonstrated significant potential in the environmentally benign degradation of mycotoxins. This review offers a comprehensive analysis of these advanced detoxification methods, analytical detection techniques, and the application of artificial intelligence and machine learning in enhancing food safety management.

Photocatalytic degradation using engineered semiconductor materials has shown strong potential for removing mycotoxins under relatively mild conditions. Materials such as

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heterojunctions, metal–organic frameworks (MOFs), carbon nitride, and magnetically recoverable composites can operate using renewable light energy. They generate reactive oxygen species (ROS) like $^{\bullet}OH$ and $^{\bullet}O_2^-$, which break down aflatoxins, fumonisins, deoxynivalenol, zearalenone, and related toxins with minimal secondary pollution. In addition to photocatalysis, cold atmospheric plasma is a potent non-thermal method that generates ROS that can break the chemical bonds of various mycotoxins and inhibit growth of toxic fungi. Systematic reviews have shown that CAP is effective against aflatoxin B_1 and deoxynivalenol while essentially maintaining food composition and quality.[17]

Adsorption-biocatalysis coupled systems have rapidly progressed alongside oxidative techniques, enhancing both selectivity and operational stability in complex food matrices. These systems combine high-surface-area adsorbents such as MOFs with immobilized enzymes to capture mycotoxins and enzymatically convert them into less toxic metabolites. In edible oil systems, hybrid platforms such as PCN-222(Mn) nanozymes on fungal mycelium show promise for enzyme-mediated detoxification, photocatalysis, and synergistic adsorption.[18] Advanced analytical detection techniques support the deployment of these green detoxification technologies. While emerging tools like surface-enhanced Raman spectroscopy (SERS) and biosensors enable quick, multiplexed screening with high sensitivity, liquid chromatography-tandem mass spectrometry (LC-MS/MS) and ultra-high-performance LC (UHPLC) coupled with high-resolution mass spectrometry remain essential for identifying and quantifying multiple mycotoxins and their degradation products. Furthermore, AI- and ML-driven methods (AI=Artificial intelligence and ML=Machine learning) improves the design and optimization of detoxification materials and procedures, supports contamination risk prediction modeling, and advances the development of analytical methods and spectral interpretation, promoting precision food safety management and real-time decision support. When combined, these developments create a comprehensive, interdisciplinary framework that can more successfully and sustainably handle mycotoxin risks than conventional methods.

Detoxification research must move beyond superficial performance metrics to achieve a more profound chemical understanding, essential for developing technologies that are both effective and reliable. Contemporary green methodologies focus not only on the elimination of toxins but also on precisely targeting their reactive sites. This goal necessitates a convergence of

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toxicology, catalysis, materials chemistry, and analytical science. Such an interdisciplinary strategy is vital for tailoring detoxification techniques to practical food scenarios, rather than depending solely on idealized laboratory settings. This document represents the inaugural report that explores the chemical principles underlying each technology and showcases the integration of various interdisciplinary approaches to effectively mitigate mycotoxin risks for ensuring food safety.

2. Chemical Reactivity of Mycotoxins

Some fungus species produce mycotoxins that contaminate a variety of agricultural crops, including spices, corn, almonds, coffee beans, and soybeans.[19,20] Both humans and animals are susceptible to serious infections caused by mycotoxins. Their structural diversity (difuranocoumarins, isocoumarins, polyketides, and trichothecene sesquiterpenes) underlies substantial differences in stability, bioavailability, and toxic mode of action.[20] Because many mycotoxins are chemically bioactivated by host enzymes, they pose persistent concerns for food safety and human health across the food chain.

2.1 Classification and Key Representatives

Approximately 100,000 fungal species have been discovered, with over 500 of these producing 500 mycotoxins that are toxic. Notable mycotoxins such as aflatoxins, ochratoxins, trichothecenes, fumonisins, zearalenone, and patulin, pose significant risks to human and animal health, as illustrated in **Fig. 1**.[21]

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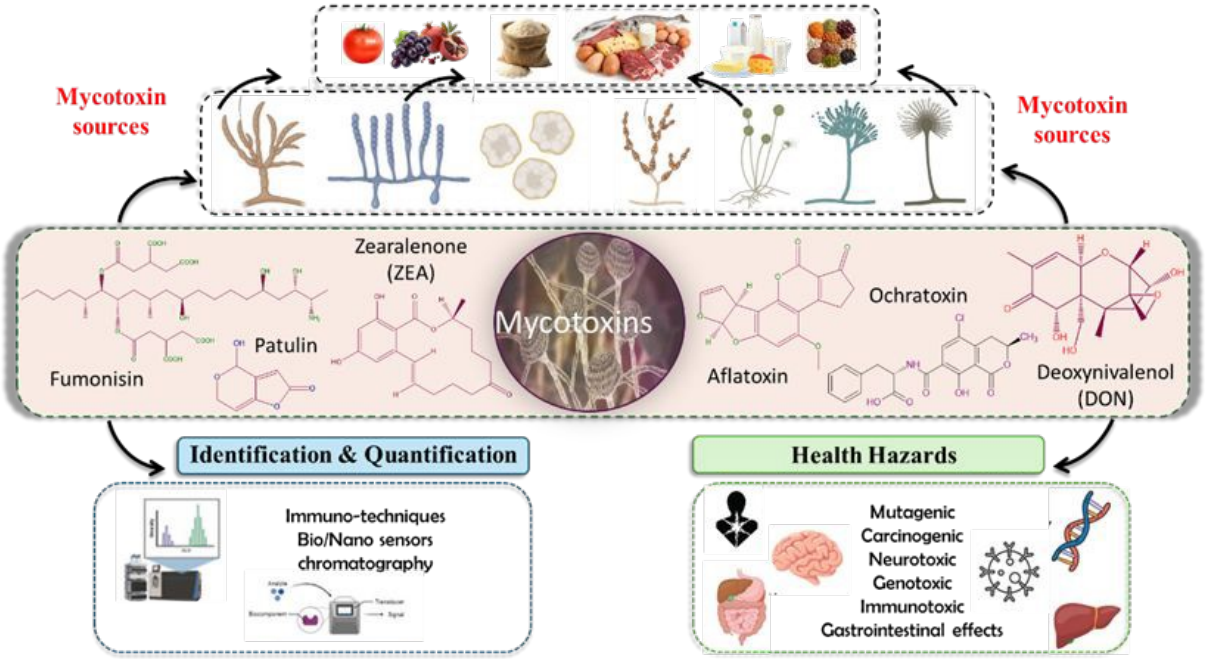

Fig 1: Schematic illustration of mycotoxins, their sources, identification and health hazards.

Aspergillus parasiticus can produce both B and G aflatoxins, while *Aspergillus flavus* produces only B aflatoxins. Aflatoxins are the most critical mycotoxins for food safety because they are extensively found in food and feed. Aflatoxin B_1, G_1, G_2, and B_2 are naturally produced as a result of biosynthesis and are commonly found in cereal grains, especially maize. Aflatoxin M_1 (AFM_1) and Aflatoxin M_2 (AFM_2) are the hydroxylated metabolites of AFB_1 and AFB_2 that can be found in the cheese, egg, wheat, as well as milk obtained from animals consuming feed contaminated with aflatoxins.18,19 AFB_1 is the most toxic and widely researched aflatoxin. It is a fungal toxin known to cause serious liver disease and hepatocellular carcinoma in animals and humans. High doses of aflatoxins also cause acute aflatoxicosis (acute liver failure), and in chronic exposure, immunosuppression and impaired growth in children.[23]

Aspergillus and *Penicillium* species produce ochratoxin A (OTA) which exists in different foods and feeds. The most frequently contaminated food products with OTA are rice, egg, milk, and beans.[24] Exposure to OTA-contaminated food has nephrotoxic effects on human health. Research has demonstrated that OTA can lead to toxicity across multiple organs; however, the kidneys remain its primary target. OTA selectively activates the kidney, including oxidative stress, mitochondrial impairment, inhibition of protein synthesis, and disturbances in cellular signaling pathways, which are epidemiologically linked with chronic kidney disease and

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Balkan Endemic Nephropathy in certain areas. OTA also contributes to immunosuppression and is categorized as carcinogenic for humans.[25]

Fusarium and certain species of stachybotrys are known to produce trichothecenes, including deoxynivalenol (DON) and T-2 toxins. Among these T-2 toxin stands out as the most common mycotoxin, classified as a fusaritoxin produced by various species of Fusaria (F. poae, F. tricinctum, and F. sporotichioides).[26] T-2 toxin has been observed in water and Chinese herbs, and it is frequently present in foods including wheat, corn, barley, and rice.[27] Once it enters the body, T-2 toxin may cause hepatotoxicity, neurotoxicity, immunotoxicity, reproductive toxicity, cardiovascular toxicity, nephrotoxicity, and carcinogenic effects.[28]

Vomiting, diarrhea, leukopenia, nausea, and bleeding are symptoms of alimentary toxic aleukia, which was predominantly associated with T-2 toxin during World War II.[29] Epidemiological studies have indicated a potential connection between T-2 toxin ad serious health conditions such as Parkinson's disease, Alzheimer's disease, beriberi-linked cardiac insufficiency, and Kashin-Beck illness.[30] Notably, DON has become the main non-nutritional factor affecting feed value because of its widespread prevalence, complications with in vitro and in vivo detoxification, detrimental impacts on human and animal health, and economic effects for both producers and consumers.[31] DON is quickly absorbed by pigs and is poorly detoxified in their gastrointestinal system, which, combined with its frequent presence in pig feed, renders these animals particularly vulnerable to its toxic effects. Concurrently, researchers in the United States identified the same compound in corn infected with Fusarium and referred to it as vomitoxin due to its association with inducing vomiting in pigs.[32]

Fumonisins (FUMs) are the Fusarium mycotoxins. These are currently divided into four major groups according to the type of moiety they contain: FA (*Fumonisin A series*), FB (*Fumonisin B series*), FC (*Fumonisin C series*), and FP (*Fumonisin P series*). The three that are most frequently found in food are FB_1, FB_2, and FB_3, which are distributed in a ratio of roughly 68: 20: 12. Unlike aflatoxins and ochratoxins, FB_1 is mainly composed of fungi that are present in the crop before harvest. Thus, the progression of such fungi is quite challenging to manage. FB_1 mostly contaminates corn and corn-based goods. Moreover, it contaminates rice at a lower level than other cereals like wheat, oats, rye, and barley.[33] The ingestion of FB_1 can lead to a cascade of diseases in animals, which include leukoencephalomalacia in horses, pulmonary

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edema and hydrothorax in pigs. There is a notable risk that infants born to mothers who consumed high levels of fumonisins during early pregnancy may experience brain or spinal cord abnormalities. FB_1 can also result in heart failure in human beings because it causes diabolical injury to the contractility of the myocardium and massive blood influx, which is referred to as Idiopathic Congestive Cardiopathy.[34]

Fusarium species (F. graminearum, F. culmorum, F. cerealis, F. equiseti, F. crookwellense, F. verticillioides, F. sporotrichioides, F. oxysporum, and F. acuminatum) are the primary producers of ZEA. Its average occurrence in cereals and other raw materials ranges between 15 and 75 percent, but in corn samples it exhibits even higher levels. The most common sources of ZEA are corn and other grains (rice, barley, wheat, sorghum, and oats), feed, food (bread, flour, cereal, and pasta), and drinks (such as beer).[35] ZEA may also be transmitted via water contaminated with Fusarium. ZEA is hepatotoxic, immunotoxic, genotoxic, carcinogenic, and toxic to the intestine, as well as having reproductive toxicity and causing endocrine disruption. Research shows that ZEA adversely affects sperm cells, Sertoli cells, and Leydig cells.[36]

Patulin is a natural mycotoxin produced by various species within genera Aspergillus and Penicillium genera. It has been found in a wide range of foods including vegetables, cereals, moulded fruits, and other products. As a low-molecular-weight unsaturated lactone, Patulin is found in numerous food sources, particularly in fruits and their processed derivatives. It is also found in tomatoes and other fruit crops, and in some consumer products, such as dehydrated foods.[37] Patulin has received global media coverage owing to its mutagenic, carcinogenic, neurotoxic, genotoxic, immunotoxic, and gastrointestinal health risks to both humans and animals. In the 1960s, patulin was recognized for its antiviral, antiprotozoal, and antibacterial activity, leading to its use as a standard cold medicine and for the treatment of nasal infections. Thereafter, it was later classified among the genuine mycotoxins because it induced toxicity in human and animal health.[38] It results in a chain of acute conditions, GIT disorders, nausea, vomiting, and long term damage to immune system, liver and kidneys.[39]

2.2 Mechanism of Toxicity

The pathology of mycotoxin can be explained through three overlapping molecular mechanisms, which are described in the subsequent sections:

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2.2.1 Bioactivation by CYP450 Enzymes

When AFB_1 induces liver injury, there is typically an elevation in hepatic stress markers such as alanine transaminase and aspartate aminotransferase, and γ-glutamyl transferase.[23] Cytochrome P450 (CYP450) enzymes play a crucial role in the bioactivation of AFB_1 converting it to exo-AFB_1-8,9-epoxide (AFBO) as shown in **Fig 2**.[40] As monooxygenases, they facilitate the insertion of oxygen into the AFB_1 structure to generate epoxidized AFBO, hydroxylated AFM_1, and AFQ_1 by combining oxygen-carrying molecules with their heme iron. AFB_1 metabolites with different carcinogenic potential, such as CYP3A4, which is important in the biotransformation of AFB1 to the hazardous product, AFB_1-8,9-epoxide, and CYP2A13, also carry out the metabolism of AFB_1 to AFB_1-8,9-epoxide and AFM_1-8,9-epoxide in the human lung. CYP450 related enzymes such as CYP2A6, CYP3A37, CYP1A5, and CYP1A1 bioactivate AFB_1, and the AFB_1-8, 9-epoxide are capable of conjugating with glutathione S-transferase (GST).[41]

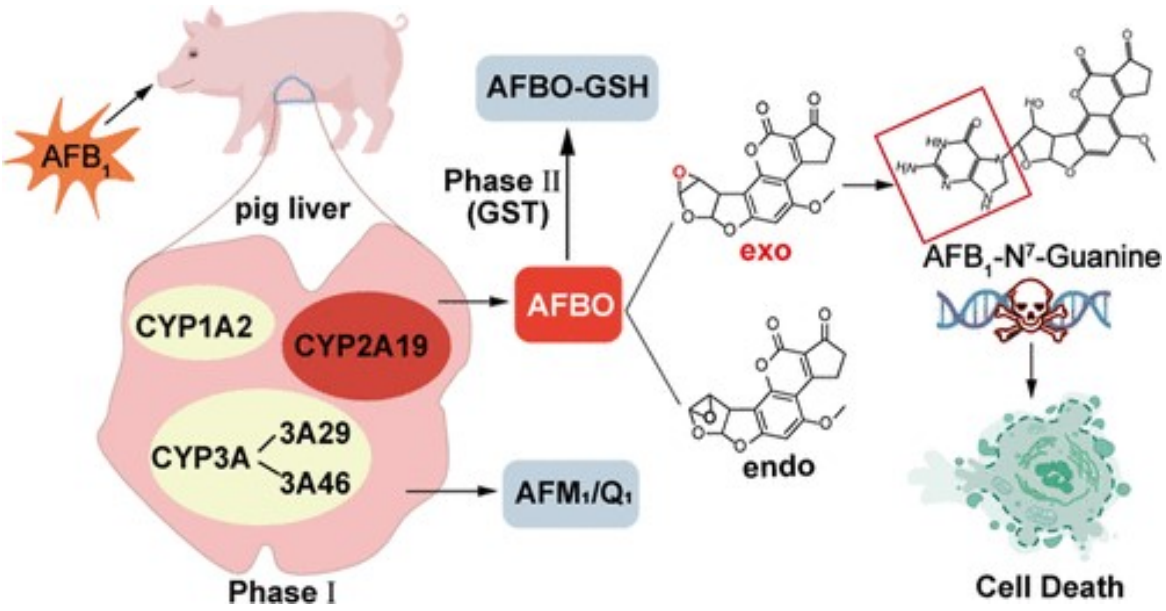

Fig 2. Key role of porcine cytochrome P450 2A19 in the bioactivation of aflatoxin B_1 in the liver. This figure has been adapted from ref.[37] with permission from the American Chemical Society, copyright 2024.

2.2.2 Oxidative Stress and Mitochondrial Dysfunction

OTA is recognized to have a complicated pathophysiology that includes the production of DNA single-strand breaks, protein synthesis stoppage, mitochondrial impairment, bioenergetic

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compromise, oxidative stress evocation, and OTA-DNA adduct production. Oxidative stress refers to an imbalance between oxidants and antioxidants, primarily caused by the overproduction of ROS and the disruption of antioxidant detoxification mechanisms.[42] ROS are primarily produced by the endoplasmic reticulum (ER), NADPH oxidases (NOXs), and the mitochondrial electron transport chain (ETC). Notably, oxidative stress and related macromolecular injury can cause mitochondrial dysfunction, leading to mutations in mitochondrial DNA (mtDNA), reduced mitochondrial membrane potential (MMP), compromised oxidative phosphorylation, extended opening of the mitochondrial permeability transition pore (mPTP), and heightened ROS generation.[43] This establishes a self-perpetuating cycle in which mitochondrial impairment worsens from oxidative stress, leading to additional ROS production and continuous cellular deterioration. OTA is toxic to mitochondria since it is known to prevent electron transfer via succinate in the electron transport chain, but only at extremely high levels.[44]

2.2.3 Direct DNA damage, disruption of macromolecular synthesis and signaling

The biogenic trade-off caused by OTA can explain the production of ROS, which lead to global oxidative injury of DNA, lipids, and protein injury caused by the formation of oxygen-free radicals and nitric oxide.[45] Physiological concentrations of ROS have essential effects in signal transduction and transcriptional activation. However, once ROS production exceeds homeostatic levels, ROS disrupts the redox equilibrium, damaging the biological macromolecules, including the phospholipid layer, proteins, and nucleic acids to affect their functioning.[42] The Nrf_2-dependent signal transduction pathway may be at least partly responsible for OTA kidney damage and carcinogenicity. Nrf_2-mediated gene downregulation lessen the oxidative stress response, and OTA effects on putative signaling molecules (growth factors, fatty acids, and/or Ca^{2+}) may change downstream PKC-regulated pathways. Furthermore, OTA may influence important metabolic processes by downregulating genes regulated by hepatocyte nuclear factor 4α (HNF4α).[46]

2.3 Recent contamination trends

Global mycotoxin contamination has shown both persistent and changed geographic patterns largely driven by climate change variability, agricultural practices, and enhanced multi-mycotoxin monitoring since 2020. The growth and production of fungi and AFs in cereals are

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influenced by temperature, moisture, soil type, and storage conditions. These fungal species grow well in the warm and humid climates of tropical and subtropical regions. Under natural conditions, rice and corn are the most frequently contaminated cereals with AFs since farming techniques have evolved. Both pre-harvest and post-harvest environments contribute to the formation of these toxins, while ochratoxin A (OTA) frequently appears in cereals, coffee, and dried fruits. Additionally, the widespread co-occurrence of multiple toxins (AFs, FBs, DON, ZEA) in a single sample poses significant health risks, as their combined toxic effects may be additive or even synergistic.[47] Out of the tested cereals, 37.6% contained at least one AF. Contamination in rice by AFB1 had been documented across multiple countries.[48] Primary factor contributing to fungal growth is insufficient drying of rice grains, particularly when their moisture content exceeds 14%. Such conditions can result in grain and husk discoloration and promote the formation of toxic secondary metabolites, including aflatoxins, which significantly compromise grain quality.[49] Additionally, spices are extremely sensitive to processing and storage conditions and are vulnerable to AF contamination. Peanuts, almonds, pigs, maize, rice and various spices are among the food and feed items most affected.[50] These tendencies reiterate that contamination is not a fixed feature but is climate-receptive and increasingly observable due to enhanced multi-analyte LC-MS detection.[51]

2.4 Global regulatory limits (EU, FDA, Codex/FAO/WHO)

The forecasts show that world cereal consumption will increase from the baseline level of 2.7 billion tons to 3 billion tons in 2030, driven by increased feed consumption (+163 million tons) and food consumption (+146 million tons). By 2030, 260 million cereal-based products are anticipated to be consumed in Europe. Mycotoxins, fungal secondary metabolites that are dangerous to food and feed, contaminate almost 60% of the world's food supply.[52] Both national and international governmental agencies have collaborated to address food and food supply chain contamination by mycotoxins. Other regulatory limits have been set by the European Union (EU), the World Health Organization (WHO), the U.S. Food and Drug Administration (FDA), and the Food and Agriculture Organization of the United Nations for major classes of mycotoxins and for individual mycotoxins.

Mycotoxins, in cereal-based products, are higher than EU and Codex levels, but further scientific evidence is required to evaluate the impact of an increase in cereal-based product

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consumption as well as the exposure levels of individual and cumulative mycotoxin contamination, correlating with the currently growing consumption trends, like flexitarian or vegetarian, or vegan diets. For the most well-known and harmful mycotoxins, maximum limits (MLs) have been set in different countries, both in general and for specific food and feed items. The EU has established a system called Rapid Alert System for Food and Feed abbreviated as RASFF to guarantee that food and feed products exceeding legal mycotoxin limits do not reach the market. However, this is not the case in other countries, particularly in Africa, lack similar regulatory frameworks, which heighten the risk of distributing foods contaminated with mycotoxins (e.g., high concentrations of aflatoxins in peanuts).[53] Regulatory measures consider both the tolerated daily intake (TDI) for chronic health risk and the acute reference dose (ARfD) for acute health risk, particularly concerning toxins like T-2 and HT-2. Initially MLs were established based on acute exposure to individual mycotoxins. However, in developing nations, chronic exposure to lower concentrations of various mycotoxins, including aflatoxins, ochratoxins, fumonisins, and zearalenone, is more prevalent than acute exposure. The exposure may be chronic (i.e., lasting for an extended period, up to a lifetime). It may result in carcinogenic, mutagenic, and genotoxic effects, as well as other critical chronic toxicities. Adverse health impacts on both humans and animals have been linked to elevated concentrations of certain combinations of mycotoxins and matrices, as established in the EU.[52] According to guidelines from the European Commission, 2 mg/kg is the maximum permissible limit set for AFB_1 and 4 mg/kg in case of aflatoxins B2, B3, and B4 for cereals or cereal-based products. For OTA, the MLs in raw cereals or their byproducts range from 3–5 mg/kg, while raw maize has a specific limit for ZEN of about 100 microgram per kg in raw cereals and 350 μg/kg in raw maize grains.[54]

The FDA employs various strategies to mitigate mycotoxin levels in the U.S. food supply, focusing on the monitoring and analysis of both domestic and imported food products. Through the years of systematic monitoring, the FDA collects data that serves multiple purposes: (a) provides estimates of the tendency and contamination level for different mycotoxins across various regions, (b) offers dietary exposure estimates to be used in making risk assessment of individual mycotoxin, (c) supplies background information to be used for developing guidelines related to these toxins, (d) tracks the co-occurrence of mycotoxins information within single commodities and (e) and evaluates the economic implications of its monitoring efforts. This

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comprehensive database also reflects the distribution of various mycotoxins in domestic grains and their products, taking into account geographic and environmental factors. The FDA can now examine food products for multiple mycotoxins in a single analysis, owing to advances in analytical technology and methods. As a result the FDA is implementing compendial procedure C-003, which enables the simultaneous determination of multiple mycotoxins while still permitting the use of traditional methods for assessing individual mycotoxins. This innovative technique can detect mycotoxins (fumonisins, deoxynivalenol (vomitoxin), ochratoxin A, aflatoxins) commonly found in human food, as well as newer mycotoxins such as zearalenone, T-2 toxin, and it deacetylated counterpart, HT-2 toxin. It is important to note that C-003 does not include patulin and aflatoxin M_1.[55]

3. Comparative applicability of green detoxification technologies

3.1 Physical methods

The conventional decontamination of mycotoxins in foods and feed is achieved through a wide range of physical methods including dehulling, heating, plasma treatment, sorting and separation, immersion and cleaning, radiation and adsorption. The effectiveness of these methods largely depends on the degree of contamination and the specific location of mycotoxins within the product. However, such procedures can sometimes yield inconsistent results and may lead to substantial product loss. Common preprocessing techniques include sorting, dehulling, and washing are typically employed for removing substandard particles from food to preserve its quality.[56] For example, cereal grains can be graded on the basis of physical characteristics, including size, shape, density, and color, which help in determining damaged grains affected by fungal infections. Sorting, washing, or separating damaged food substantially decrease contamination levels since mycotoxin contamination is not evenly distributed across grains. Specifically, Matumba et al.[57] discovered that in shelled white maize, flotation, dehulling, and hand sorting can remove at least 51, 63, and 93 percent of aflatoxins, trichothecenes, and fumonisins, respectively. Nevertheless, these methods are relatively expensive and can only be applied on a small scale. Generally, AFs and FUM can be reduced by immersing contaminated grains in water, allowing the lighter floating contaminants to be removed and discarded. Moreover, cleaning and scouring, as mentioned by Milani and Heidari,[58] significantly reduce ochratoxin contamination in grains. Despite their effectiveness these methods suffer from

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nutrient loss and high expenses due to drying and disposal of toxic extracts, making their large scale usage impractical.

Thermal treatment method has been extensively applied for managing mycotoxins contaminated feed.[56] The effectiveness of this method depends not only on temperature, time, moisture content, pH, and ionic concentration during thermal treatment, but also on the specific chemical structure and concentration of mycotoxins. High decomposition temperatures of AFB1, DON, ZEN, and FB_1 are making these toxins difficult to remove by conventional heat treatment. AFB_1 decomposes up to 78–88% in rice via traditional hydrothermal treatment (cooking) under pressure (0.10 MPa) at 160 °C for 20 minutes, and by 95% in wet peanut powder using pressure heating (0.10 MPa) at 120 °C for 4 hours. Still, thermal treatments are energy-intensive, and Maillard reactions that occur at high temperatures reduce the nutritive value of feeds. Consequently the use of heat treatment method has been restricted in the feed industry.[59]

In industrial settings, irradiation presents a promising technology for eliminating mycotoxins from feed. This technology is categorized as non-ionizing radiation (ultraviolet, infrared, and microwave) and ionizing radiation (x-rays, gamma-rays, and electron beams).[60] The finding of Khalil et al.,[61] indicates that gamma radiation effectively inhibits the growth of *A. flavus* and *A. ochraceus*. Although irradiation is potential method of decontaminating mycotoxins in feedstuffs, its safety concerns, particularly regarding mutagenesis, which could lead to the development of harmful microorganisms and the destruction of the nutritional quality of the feed. These concerns demand further investigations.

3.2 Chemical methods

Mycotoxin detoxification involves the structural modification of mycotoxins using a variety of chemical agents, including bases, acids, reducing agents, and oxidizing agents.[62] Ozone, hydrogen peroxide, calcium and sodium hypochlorite, chlorine, and other oxidants are common oxidizers. ZEN, FB_1, and AFs are degraded by ozone.[63] According to Trambete et al.[64] ozone concentration, its form, and exposure duration had a positive effect on reducing the levels of DON, AFs, and fungi. In corn, ozone can reduce AFs by 92–95%; in cottonseed or peanut meal, it can reduce AFs by 78-91%. The use of the ozone treatment process can lead to complete elimination of mycotoxins and modifications of the feed's color, protein denaturation, lipid

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oxidation, starch structure, and processing features. In addition, these treatment methods may generate toxic substances that are harmful to animal health.[64]

In mold feeds, alkaline chemicals such as ammonia, sodium hydroxide, potassium hydroxide, and sodium carbonate are used to degrade several mycotoxins. Ammonia is specifically used to lower mycotoxins such as FUM, AFs, and OTs, to levels below their detection limits.[56] Specific bases, such as sodium hydroxide and potassium hydroxide can cause harmful reactions. The potential conversion of mycotoxins to other compounds, including conjugated mycotoxins, as well as the adverse effects on ecosystem and food (alterations in dietary value, texture profile, and flavor profile) necessitate evaluation of products subjected to chemical treatment, even though these treatments may virtually eliminate the total concentration of mycotoxins.[65] The chemical processes used to reduce mycotoxins can also alter the nutritional value and palatability or produce toxic residues.

Adsorption is the most widely used method of protecting animals from mycotoxins. A range of adsorbents such as modified polymers, activated charcoal, and clay effectively immobilize mycotoxins, thereby reducing their toxic effects by preventing adsorption in the gastrointestinal tract. However, choosing efficient adsorbents might be difficult since many mycotoxins often coexist in food and their combined toxicity can increase.[66] Additionally some adsorbents that facilitate mycotoxin binding may have poor interactions with mycotoxins because of their polarity, solubility, molecular size, shape, and surface area. Along with effectiveness, concerns persist regarding feed purification, the safety of adsorbent materials, and the disposal of both the adsorption chemicals and the adsorbent-mycotoxin complexes. That's why European Union has banned the use of specific chemical adsorbents as detoxification agents in the food sector.[67]

3.3 Biological methods

Although a variety of structural and chemical cleaning techniques are designed to minimize or completely eradicate mycotoxins in feedstuffs, few strategies are practical in practice due to constraints on binding potential, biosafety, or cost-effectiveness. Hence, microbial or enzymatic biodegradation of mycotoxins is a promising approach that has attracted considerable interest. Detoxification methods are widely recognized for their biological specificity, effectiveness, and environmental friendliness. No hazardous substances deteriorate the nutritional and sensory

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attributes, such as color and flavor. It has been common practice to screen and isolate naturally occurring microorganisms with biotransformation properties against particular mycotoxins. The degradation of the toxic moiety of mycotoxins into non-toxic or less toxic degradation products, by microorganisms through the action of secondary metabolites or by secreted intracellular and extracellular enzymes, is known as mycotoxin biodegradation. Various fungi have demonstrated the ability to detoxify AFB1, with certain fungal strains, such as S. cerevisiae LOCK 0119, achieving a degradation rate of 69.0%. Additionally, research has shown that different strains of Aspergillus, including A. niger RAF106 and A. niger FS10, can degrade AFB1 by rates ranging from 88.6% to 98.7%[68]

Fumonisins can be degraded by certain fungal and bacterial microorganisms. One study indicates that the bacterial consortia SAAS79 can degrade FB1 at a rate of as much as 100%.[66] Some organisms exhibit a significant ability to degrade mycotoxins, while others may generate toxic metabolites or cannot thrive in the animal's digestive tract. Therefore, screening these microorganisms for enzymes may serve as an effective method to resolve such issues. Recently, research has focused on identifying enzymes that can break down AFB1, DON, ZEN, and FB1. Laccase and oxidase are the main fungal enzymes responsible for the degradation of AFB1. The enzyme that detoxifies AFB1, known as the aflatoxin-detoxifying enzyme, has been documented. This gene was isolated and identified in an Armillariella tabescens. The enzyme that detoxifies recombinant aflatoxin significantly reduced the mutagenicity of AFB1. AFB1 can be reduced by 90% through manganese peroxidase (1.5 U/mL) after 48 hours of the reaction.[67] Peroxidases, such as manganese peroxidase and lignin peroxidase, can greatly degrade DON.[69]

Biological enzyme processes provide considerable benefits compared to chemical and physical techniques regarding efficiency and environmental selectivity. Nonetheless, various difficulties are linked to these methods. Initially, although the byproducts resulting from enzymatic breakdown of mycotoxins are typically less harmful, they frequently retain a degree of physiological toxicity, indicating that detoxification mitigates instead of entirely removing their toxic capabilities. Furthermore, the handling and use of raw materials tainted by fungi might be negatively impacted following enzyme treatment. Moreover, the existing knowledge of enzyme varieties for mycotoxin breakdown is restricted, and there is still doubt concerning the physiological toxicity and structural traits of the degradation products.[70]

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The challenges related to nano-engineered materials mainly arise from the necessity to tackle the stability, low solubility, and elimination issues presented by mycotoxins, which are usually resistant to conventional methods. Approaches to address these problems consist of high-surface-area binding, catalytic breakdown, and recycling methods. Among these, photocatalytic detoxification is a new and promising method, providing several benefits compared to traditional techniques. This method is noted for its absence of secondary pollution, moderate reaction conditions, cost-effectiveness, high operational efficiency, and safety for the environment. Studies have concentrated on utilizing photocatalytic technology for the removal of particular mycotoxins, such as AFB1 and DON.[71] CAP has been proposed in recent decades as a promising non-thermal technology to eliminate organic pollutants and mycotoxins in food.[72] Moreover, CAP has high potential for food decontamination due to its benefits including minimal adverse effects on food quality, low chemical residue levels and long shelf life.[73]

Nanoenzymes are also attracting attention for their use in food safety due to their catalytic activity, stability, and functional versatility. Specifically, nano peroxidase-like nanozymes have found applications in biology, chemistry, and medicine due to their ability to catalyze the decomposition of H_2O_2 and produce reactive oxygen species under mild conditions.[74] Metal-organic frameworks connecting inorganic chemistry with polymer science and have well-defined porous structures based on coordination interactions between metal ions/clusters and organic molecules.[75] Hence, MOFs, owing to their distinct advantages, can serve as optimal nanozyme scaffolds for degrading mycotoxins with a pronounced increase in the degradation rate.[76]

4. Reaction Chemistry of Green Detoxification Technologies

In food chains, the most effective way to reduce mycotoxins is to prevent fungal growth in food and inhibit toxin production. To accomplish this, a number of physical, chemical, and biological processes are employed at industrial and laboratory scales, as depicted in **Fig. 3**. Nonetheless, both approaches have inherent limitations that restrict their applicability in contemporary, high-throughput food systems. These constraints must be understood to facilitate integration and the development of nano-assisted green technology.[77]

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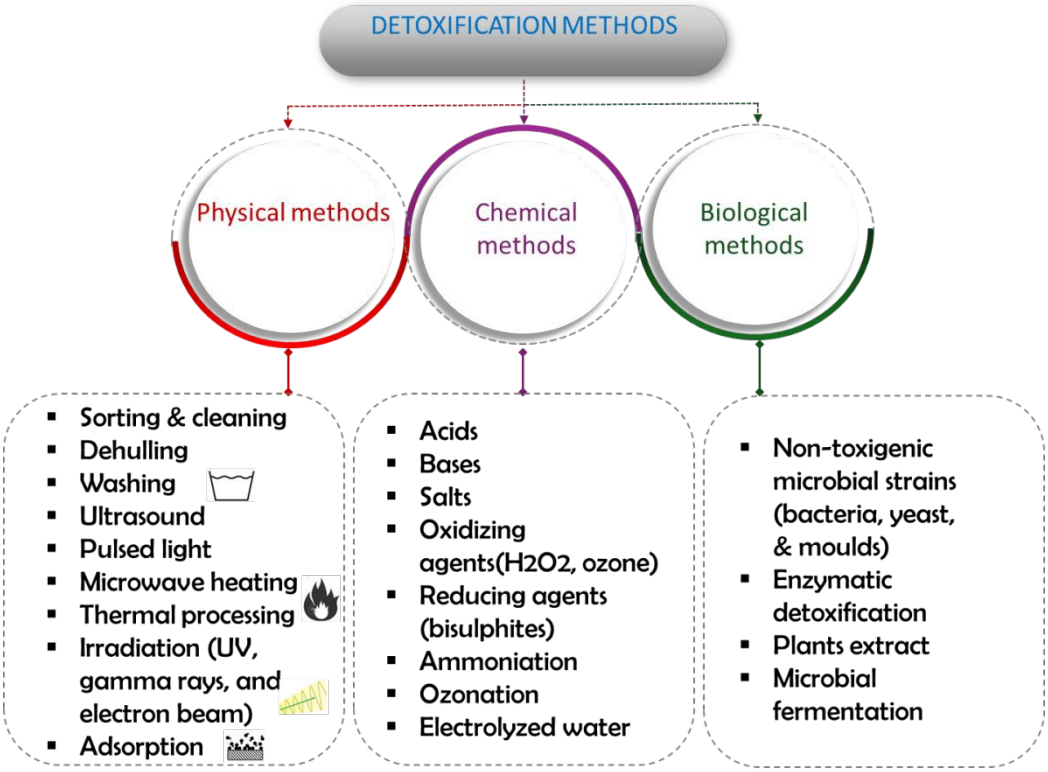

Fig 3: Detoxification methods for mycotoxins.

4.1 Photocatalytic approaches for mycotoxin degradation

Although the production of ROS is essential to photocatalytic detoxification, under actual matrix conditions, their intrinsically non-selective reactivity may also result in the unintentional oxidation of co-existing food components. **Section 5.2** delves deeper into this mechanistic limitation in relation to food matrix impacts.

4.1.1 Photocatalytic degradation mechanism

Photocatalysis has attracted considerable attention in the research community, particularly for its use in environmental cleanup. This technique for purifying mycotoxins presents multiple significant benefits compared to conventional methods. Initially, it captures renewable energy from sunlight, needing just a small amount of energy input. Furthermore, under mild reaction conditions, pollutants can be efficiently degraded through the process of superoxidation. Moreover, this method guarantees the total mineralization of organic substances while preventing secondary contamination. Finally, it employs stable, efficient, and reusable photocatalysts, improving its sustainability and practicality for environmental uses.[78] The

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creation of visible-light photocatalysts for breaking down mycotoxins has attracted considerable attention because of their capacity to utilize clean, renewable energy in low-energy environments. A good photocatalyst must be non-toxic, show remarkable stability without corrosion, and have the ability to absorb light at room temperature. Photocatalytic degradation is mainly powered by semiconducting materials that harness ultraviolet, visible, or infrared light to enhance reaction speeds. The unique characteristics and versatility of these materials have ignited investigations into binary metal oxides (II–VI, IV–VI) and their stable ternary oxide compounds (II–IV–VI), which are utilized in electronic device manufacturing, diagnostic sensing, energy transformation, and environmental photochemical remediation.[79] The general photocatalytic degradation mechanism of mycotoxins is illustrated in **Fig. 4**.

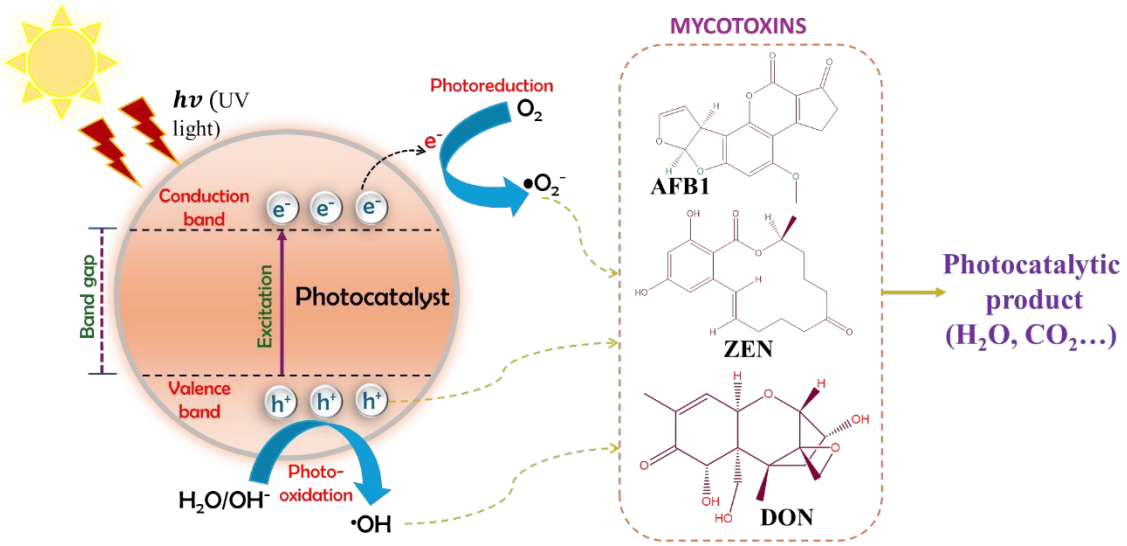

Fig 4: Photocatalytic degradation pathway for the removal of mycotoxins.

In the photocatalytic process, when photocatalysts are exposed to light with suitable energy, holes (h^+) are generated after electrons (e^-) are elevated from the valence band (VB) to the conduction band (CB). Once generated on the photocatalysts, these charges (both e^- and h^+) move to their surfaces. When these charges reach the surface, they interact with water, oxygen, or hydroxide ions, resulting in reactive species like superoxide anions and hydroxyl radicals that can decompose pollutant molecules into smaller substances such as carbon dioxide and water.[80]

The band theory of electrons describes the fundamental band arrangement of semiconductors, which includes several occupied bands. The VB signifies the uppermost fully

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filled band, whereas the CB denotes the lowest empty band. When electrons in the valence band acquire enough energy to surpass the band gap (E_9), they are able to move to the conduction band, allowing for electrical conductivity. Electrons in the conduction band may then recombine with the holes left behind, producing electron–hole pairs within the semiconductor structure. Three primary routes are available for the charge carriers: (1) they can rapidly recombine, resulting in the loss of light or heat; (2) they can become localized at defects; (3) they can migrate to the surface and engage in redox reactions occurring with adsorbed substances. The other two pathways hinder the mobility of conducting species, which negatively impacts photocatalytic activity. Conversely, the third method is crucial for successful photocatalysis. The concentration of charge carriers at the surface is significantly affected by the strength of incoming light and by the separation of charge carriers, which prevents recombination, both of which are essential for improving photocatalytic performance.[81] Superoxide radical anions ($^{\bullet}O_2^-$) are produced when electrons (e^-_{CB}) react with oxygen after the charge carriers produced by photogenic processes have been effectively transported to the semiconductor surface. These radicals can be protonated to produce hydroperoxyl radicals, which, in turn, release H_2O_2. The hydroxyl radical and superoxide are crucial for the breakdown of mycotoxins. At the same time, holes (h^+_{VB}) can directly oxidize mycotoxins, leading to their degradation or interact with water to generate hydroxyl radicals. Schematic representation of the photocatalytic reaction is shown below:[82]

$$Photocatalyst + hv \rightarrow e^-_{CB} + h^+_{VB}$$

$$e^-_{CB} + O_2 \rightarrow {}^{\bullet}O_2^-$$

$$h^+_{VB} + H_2O \rightarrow H^+ + {}^{\bullet}OH$$

$$h^+_{VB} + OH^- \rightarrow {}^{\bullet}OH$$

$${}^{\bullet}O_2^- + H^+ \rightarrow {}^{\bullet}HOO$$

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$$2HOO^{\bullet} \rightarrow H_2O_2 + O_2$$

$$e^-_{CB} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^-$$

$$h^+_{VB}/{}^{\bullet}O_2^-/{}^{\bullet}OH + Mycotoxins \rightarrow Degradation\ products$$

4.1.2 Photocatalytic degradation of AFB_1, ZEN and DON

AFB_1 generated by Aspergillus species, is acknowledged as one of the most hazardous biological toxins among different mycotoxins. The International Agency for Research on Cancer (IARC) categorizes it as a Class I human carcinogen, signifying its significant health hazards. AFB1 is roughly ten times as toxic as potassium cyanide and 68 times more deadly than arsenic. Its capacity to penetrate the human food chain greatly increases the danger it presents to public health.[83] Liangtao Yao et al.,[84] fabricated PCL-g-C_3N_4/CQDs membranes via electrospinning and modified surfaces of each of these membranes with PDA and PEI to continuously remove AFB_1. Under visible light irradiation, the modified PCL-g-C_3N_4/CQDs electrospun membranes showed a remarkable capacity to degrade AFB_1 by synergistic adsorption and photocatalysis, attaining 96.88% degradation of AFB_1 solution at 0.5 g/mL in 30 minutes. The regeneration of these membranes occurs simultaneously with the reaction under visible light and does not require any chemical or physical treatment, making it an eco-friendly process.

Fusarium is known for producing zearalenone, a secondary metabolite recognized as one of the most prevalent mycotoxins globally. This chemical has been found in many grains and poses serious health risks to humans due to its toxic nature.[85] Graphitic carbon nitride (g-C_3N_4) has been reported to photocatalytically degrade ZEN.[86] Similarly WCN-AP7 nanomaterials exhibited high efficiency in photocatalytically degrading mycotoxins in samples where both AFB_1 and ZEN degraded in 60 min with high efficiency. Moreover, the photodegradation products of AFB_1 and ZEN were detected by HPLC-MS/MS analysis. The mechanisms underlying the primary active sites and the degradation process were elucidated using density functional theory calculations and radical-trapping experiments, where superoxide ($^{\bullet}O_2^-$), and hydroxyl radicals were identified to play significant roles.[87]

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Deoxynivalenol (DON) is a trichothecene mycotoxin is prevalent mycotoxins primarily produced by Fusarium species. This mycotoxin's toxicity to humans and animals poses a significant issue for food safety and agricultural practices.[88,89] A study by Xiaojuan Bai et al showed that graphene/ZnO hybrids have significant effectiveness in the photocatalytic breakdown of DON under UV light exposure.[89] The ZnO/graphene hybrid exhibited almost three times higher photocatalytic activity than pure ZnO, degrading DON (15 ppm) with nearly 99 percent in 30 minutes. The direct oxidation of DON by superoxide radicals as well as holes accounts for this enhanced photocatalytic activity. Additionally, Pengzhen He et al.. [90] used a series of nanoscale photocatalysts based on cerium (Ce)-doped TiO_2. When compared to conventional pure TiO_2 photocatalysts, the 0.5Ce-TiO_2 photocatalyst exhibited greater photocatalytic ability for the photodegradation of DON in water under UV illumination, with an initial degradation capacity of 96% of DON at the starting concentration of 5.0 mg/L in 4 hours. Experiments on free radical scavenging revealed that the presence of valence-band hole scavenger (EDTA-2Na) significantly reduced the photocatalyst's degradation efficiency. This finding suggests that the degradation process may involve a direct oxidation reaction between DON and superoxide radicals mediated by holes.

4.1.3 Structure-Reactivity Guided Photocatalytic Detoxification Design

Recent progress in photocatalytic detoxification has created a predictive model for catalyst design, emphasizing that the inherent molecular structure is the main element influencing mycotoxin breakdown, instead of the efficacy of non-specific reactive oxygen species. Ochratoxin A (OTA), defined by its electron-dense properties and aromatic chlorinated isocoumarin framework with conjugated π-electrons, is especially prone to targeted electrophilic oxidation. Heterojunction devices are advantageous for OTA degradation, as they effectively separate photogenerated charge carriers and promote strong oxidation pathways driven by holes (h^+) and singlet oxygen ($1O_2$). For instance, a self-assembling hydrothermal method was used to create $Sr_2MgSi_2O_7$:Eu^{2+},Dy^{3+}/$BiVO_4$/NH_2-UiO-66 (SBN), which functions as a dual Z-scheme ternary heterojunction photocatalyst. The intrinsic light source of $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} allows the SBN heterojunction photocatalyst to maintain consistent photocatalytic performance.[91] The dual Z-scheme mechanism preserves redox potentials while simultaneously facilitating the efficient transfer and separation of photogenerated charge carriers during their transit. Under

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various weather conditions, the degradation efficiency of AFB_1 and OTA is greatly increased by the stable and persistent photocatalytic performance of the SBN photocatalyst. Experimental results show that the elimination efficiency of OTA increased from 64.8% to 78.1%, whereas the removal rate of AFB1 grew from 69.6% after 60 minutes of light exposure to 83.9% after four hours without light. In photocatalytic processes, $^{\bullet}O_2^-$ and $^{\bullet}OH$ were identified as important active species. Degradation pathways for AFB_1 and OTA were proposed based on analyzing degradation intermediates and predicting degradation sites using density functional theory (DFT). However, as AFB_1 pathways are addressed later in this review, we focus exclusively on OTA degradation pathways here in this section. The Fukui index was used to quantitatively assess each atom's local reactivity in the case of OTA, as illustrated in **Fig. 5(a)** and **Table 1**. In this context, a high f(+) value denotes a stronger propensity toward nucleophilic attack, while a high f(−) value implies more vulnerability to electrophilic attack.[92]

Table 1. The Fukui Index of Ochratoxin A.[91]

Atom	f^-	f^+	f^0
1(C)	0.1020	0.0351	0.0685
2(C)	0.0518	0.1142	0.0830
3(C)	0.0791	0.0613	0.0702
4(C)	0.0815	0.0315	0.0565
5(O)	0.1207	0.0276	0.0742
6(C)	0.0565	0.0559	0.0562
7(C)	0.0506	0.0875	0.0690
8(C)	0.0124	0.0177	0.0150
9(C)	0.0065	0.0108	0.0087
10(C)	0.0046	0.0070	0.0058

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11(O)	0.0180	0.0368	0.0274
12(C)	0.0222	0.0772	0.0497
13(O)	0.0368	0.0824	0.0596
14(C)	0.0235	0.0575	0.0405
15(O)	0.0184	0.0330	0.0257
16(O)	0.0426	0.0627	0.0527
17(Cl)	0.1528	0.0477	0.1002
18(H)	0.0276	0.0485	0.0381
19(H)	0.0305	0.0154	0.0229
20(H)	0.0134	0.0164	0.0149
21(H)	0.0176	0.0254	0.0215
22(H)	0.0073	0.0121	0.0097
23(H)	0.0035	0.0056	0.0046
24(H)	0.0035	0.0057	0.0046
25(H)	0.0043	0.0063	0.0053
26(H)	0.0121	0.0182	0.0152

Therefore, the atoms C1, C3, C4, and O5 have high f(−) values, making them highly susceptible to electrophilic species like O_2^- and $^{\bullet}OH$. Atoms C2, C3, C7, C12, O13, and O16, on the other hand, have high f(+) values, suggesting that these could be nucleophilic attack sites. Furthermore, atoms C1, C2, C3, C4, O5, C6, C7, O13, and O16 have high f(0) values, suggesting a widespread susceptibility to reactive species assaults.

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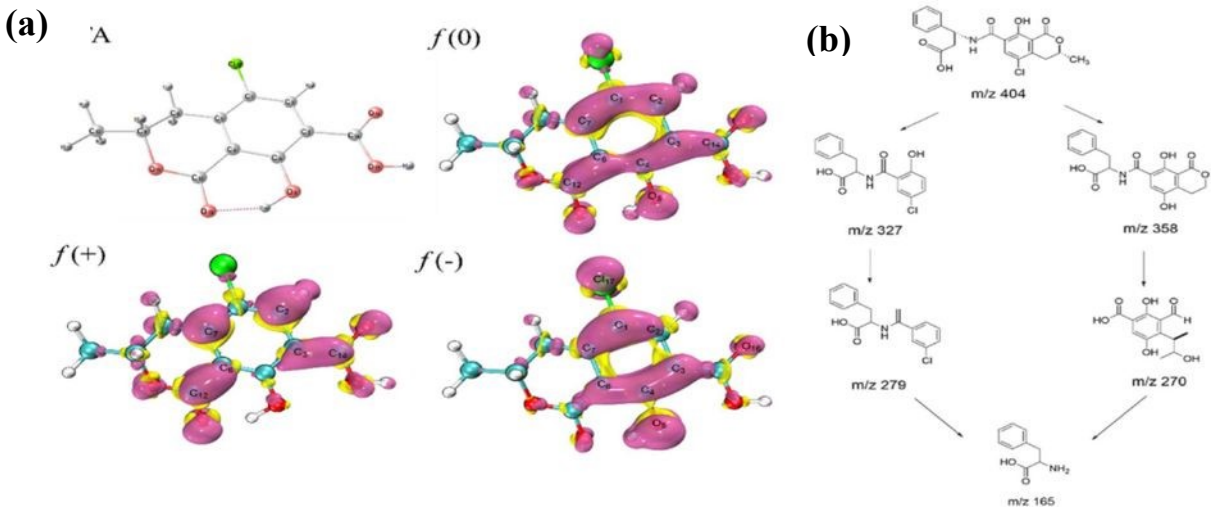

Fig 5: (a) Optimized OTA molecular structure and electrostatic potential distribution on the surface of OTA molecules; **(b)** potential pathways for photocatalytic degradation of OTA by SBN. This figure has been adapted from ref.[91] with permission from Elsevier, copyright 2026.

The attack of reactive species $^{\bullet}O_2^-$ and $^{\bullet}OH$, primarily directed at the amide bond and chlorine atom, generates the majority of these degradation products. Based on the analysis of these intermediates and the DFT-predicted degradation sites, two potential OTA degradation pathways were proposed, as illustrated in **Fig. 5(b)**.[91] Consequently, a chemistry-aligned method whereby band-structure engineering promotes the concurrent generation of oxidative (h^+, $^{\bullet}OH$) and reductive ($^{\bullet}O_2^-$) species can account for the enhanced effectiveness of the SBN heterojunction for OTA. These species specifically target the electron-rich aromatic system of OTA, allowing for electrophilic oxidation and dechlorination processes that are directly anticipated by the Fukui reactivity map.

Fumonisin B_1 (FB_1) has a very distinct chemical profile. The FB_1 molecule is made up of a long-chain aminopentol backbone with an amino group linked at C2 site and tricarballylic acid (TCA) side chains attached at C14 and C15 as shown in **Fig.6**.[93] As a result, selective π-electron oxidation routes are not preferred by FB_1. Rather, hydroxyl radical-mediated hydrolysis, deamination, and backbone fragmentation are the main processes that lead to its breakdown. As a result, oxide-based photocatalysts with strong adsorption sites for polar molecules and high $^{\bullet}OH$ fluxes, including heterojunctions containing ZnO and TiO_2, show better FB1 degradation performance. Ivana Jevti'c et al.,[95] used the solid-state approach to synthesis several ZnO-based

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nanocrystallites with ternary and binary structures (Zn_2SnO_4, Zn_2TiO_4, ZnO/SnO_2, ZnO/TiO_2). They were first tested as photocatalysts for the elimination of FB_1 under UV irradiation. The comparison of direct and indirect photolysis (sensitized by UV/H_2O_2 or $UV/S_2O_8^{2-}$) revealed that both indirect photolysis and photocatalysis with Zn_2SnO_4 were significantly more efficient than direct photolysis in degrading FB1. The investigation verified that some ions limit FB_1 degradation in the UV/H_2O_2 system, with humic acid, Ca^{2+} and NO^{3-} ions showing the least inhibition. Furthermore, Ivana Jevtić et al.,[96] used TiO_2 Wackherr as a catalyst for the photocatalytic degradation of FB_1 and FB_3 in pH medium of about 8. FB_3 (0.425 μM) was eliminated in 20 minutes, while 99% of FB_1 (1.39 μM) was degraded in the first 30 minutes of irradiation. These results demonstrate that rather than selective aromatic oxidation chemistry, FB_1 degradation is primarily regulated by its polar aminopolyol structure and vulnerability to hydroxyl radical attack.

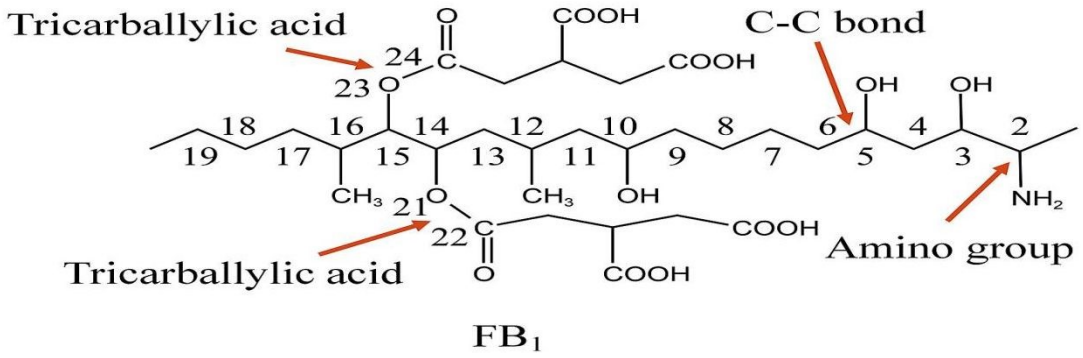

Fig 6: Chemical structure of FB_1. This figure has been adapted from ref.[94] with permission from Elsevier, copyright 2023.

4.1.4 Semiconductor heterojunctions

TiO_2 and graphitic carbon nitride (g-C_3N_4) are the most well researched photocatalysts for mycotoxin breakdown. TiO_2 photocatalysts are known for their exceptional thermal and chemical stability, effective photocatalytic degradation capability, and non-toxicity.[97] TiO_2 needs radiation from artificial UV sources or sunshine to function as a photocatalyst, although its effectiveness is usually only 5% to 8%.[98] A lot of work has been done to improve the design and

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use of effective TiO_2 photocatalysts. Its wide band gap (3.20 eV) and the rapid recombination of photoinduced electron-hole pairs, which limits its photocatalytic effectiveness, are two significant challenges that need to be addressed. Conversely, researchers are highly intrigued by the potential of g-C_3N_4-based materials as photocatalysts due to their non-toxic nature, effective visible light absorption, π-conjugated structure, improved dispersion, along with their chemical and thermal stability. With VB and CB potentials of −1.09 and +1.56 V (vs. NHE)[99–102], g-C_3N_4 displays an optical bandgap of 2.7 eV (460 nm). Furthermore, g-C_3N_4 based materials are widely used as visible-light-driven photocatalysts because of their simple synthesis from generally available, reasonably priced precursors.[103,104] Although pristine g-C_3N_4 has demonstrated potential as a photocatalyst, there are several issues that need to be resolved.[105] Low photocatalytic activity is one of its main limitations.[106] The rapid coupling of photo-generated charge carriers in g-C_3N_4 further reduces its photocatalytic efficiency.[107] Effective charge transfer is also hampered by its restricted charge carrier mobility. Additional drawbacks of pristine g-C_3N_4 include its comparatively small specific surface area and instability in photocatalytic settings, as extended exposure to light and reactive species might eventually deteriorate its performance.[108–110] To get around these restrictions, recent research has shown that creating g-C_3N_4/TiO_2 heterojunctions greatly increases the efficiency of charge separation, increases light absorption, and boosts the production of reactive oxygen species, which leads to better degradation of toxic organic contaminants, including mycotoxins, than individual components.

In summary, TiO_2 and g-C_3N_4 exhibit unique benefits and drawbacks as listed in **Table 2**. Owing to the remarkable chemical stability and powerful oxidative properties, TiO_2 has been extensively confirmed in studies on photocatalytic detoxification. Nonetheless, reliance on UV light and the fast recombination of electron-hole pairs hinders the effective use of solar energy. In contrast, g-C_3N_4 is sensitive to visible light, economically viable to produce, and free of metals, making it an attractive material for sustainable photocatalysis. Nonetheless, pure g-C_3N_4 often exhibits reduced charge-carrier mobility, constrained surface area, and photocatalytic efficiencies that are generally inferior to those of optimized TiO_2 systems. Recently, TiO_2/g-C_3N_4 heterojunctions, which integrate the excellent oxidative properties of TiO_2 with the visible-light absorption capabilities of g-C_3N_4, have attracted increased attention for their potential to enhance charge separation and improve the efficiency of mycotoxin degradation.

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Table 2. Comparison of TiO_2 and g-C_3N_4 photocatalysts.[1]

Property	**TiO_2**	**g-C_3N_4**
Band gap	~3.2 eV	~2.7 eV
Light response	Mainly UV	Visible light
Stability	Excellent	Good
Toxicity	Low	Metal-free, low toxicity
Cost	Low	Low
Main limitations	UV dependence; electron–hole recombination	Charge recombination; low carrier mobility; limited surface area
Advantages for mycotoxin degradation	Strong oxidative power; extensively studied	Better solar-light utilization
Improvement strategy	Doping, heterojunctions	Doping, heterojunctions
Hybrid approach	TiO_2/g-C_3N_4 composites improve charge separation and ROS generation	TiO_2/g-C_3N_4 composites improve charge separation and ROS generation

[1] ***Table 3.*** *Comparison data of TiO_2 and g-C_3N_4 photocatalysts are compiled and adapted from Refs.* [97-110].

The pairing of TiO_2 and g-C_3N_4 in thin films utilizes the oxidative power and durability of TiO2 with the visible-light absorption and surface adsorption properties of graphitic carbon nitride, rendering them strong contenders for the photocatalytic breakdown of mycotoxins. This synergy leads to enhanced production of reactive oxygen species and efficient charge separation at the interface, as shown in **Fig. 7**. Specifically, TiO_2/g-C_3N_4 composite efficiently degrades patulin, as the inclusion of carbon nitride lowers the band gap of TiO_2 and enhances its performance in visible light. In trials, total degradation of patulin was accomplished in a water solution exposed to visible light, whereas 85.4 percent degradation was noted in apple juice at a

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concentration of 250 mg/kg. Using ultra-high-performance liquid chromatography tandem quadrupole orbitrap mass spectrometry (UPLC-Q-Orbitrap MS), a new degradation product was identified. Superoxide ion and hydroxyl radical were found to play important roles in the photocatalytic breakdown of PAT. Moreover, photocatalytic degradation does not significantly affect the quality and nutritional value of apple juice. The findings of the zebrafish and Ames tests showed that the toxicity of the degradation product was significantly lower. These findings suggest that the TOCN photocatalyst is highly efficient at removing patulin from aqueous solutions and apple juice.[111]

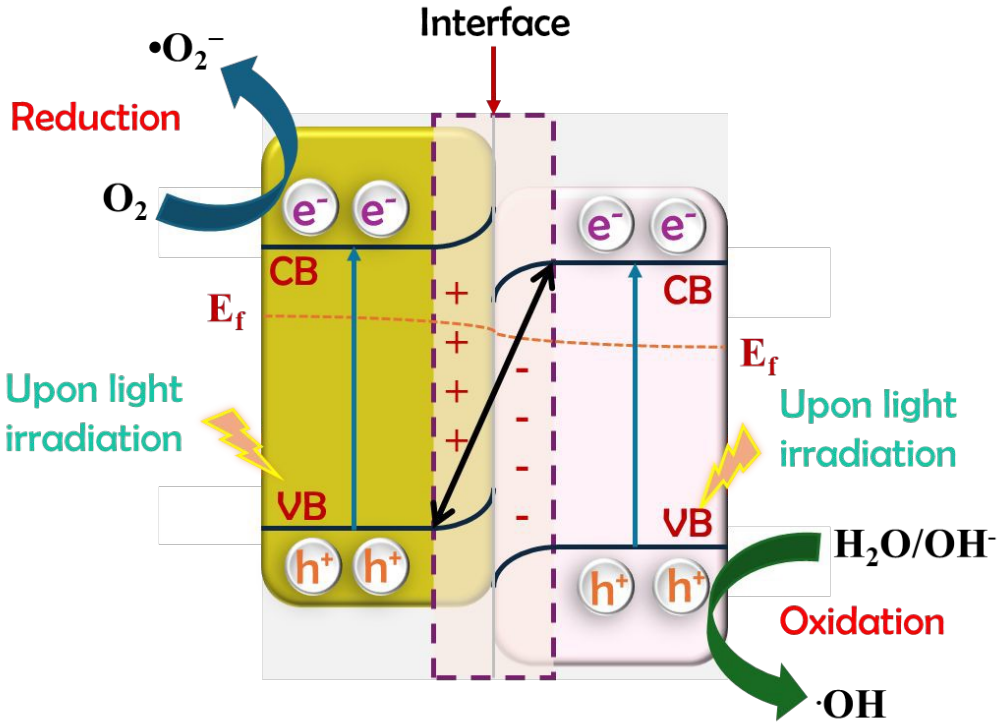

Fig 7: General mechanism for photocatalytic degradation through semiconductor heterojunctions.

Zhang et al.[112] synthesized TiO_2/UiO-67 photocatalyst via an in situ solvothermal reaction. Under visible light radiation this photocatalyst degraded AFB1 at a rate of 98.9% in 80 minutes, outperforming the performance of commercial P25, commercial TiO_2, and majority of other documented photocatalysts. Additionally, TiO_2/UiO-67 photocatalyst exhibited excellent recyclability. The separation of photogenerated charge carriers and the responsiveness to visible light were enhanced by the heterojunction formed between TiO_2 and UiO-67. The results

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demonstrated that $^{\bullet}O_2^-$, $^{\bullet}OH$, and h^+ were the main active groups in the photocatalytic activity. As a result, the T-XU uses visible light to produce photo-generated electrons and holes. These electrons and holes subsequently react with H_2O and dissolved oxygen in aqueous solution of AFB1 to produce $^{\bullet}O_2^-$, h^+, and $^{\bullet}OH$. Additionally, these active species support the oxidation AFB1 into a variety of small molecules. Samuel et al., compared the photocatalytic activity of activated carbon-assisted $GO/Cu_3(BTC)_2/Fe_3O_4$ for the breakdown of AFB1 under UV light.[113] The superior performance of this photocatalyst achieving degrading performance of 99% is attributable to the synergy of its components and larger surface area. The hydroxyl radicals and the holes were found crucial in the breakdown of AFB1. These investigations demonstrate that $GO/Cu_3(BTC)_2/Fe_3O_4$ exhibits both high adsorption capacity and synergistic photocatalytic activity, enabling the efficient break down of AFB1.

4.1.5 Plasmonic and doped nanostructures

The use of plasmonic nanostructures for enhancing photocatalytic activity has demonstrated significant promise, particularly in the areas of hot-charge-carrier injection, electric-field enhancement, and localized photothermal conversion due to their localized surface plasmon resonance (LSPR).[114] The general degradation mechanism is shown in **Fig. 8**. Moreover, doping with metals like Ag, Au, and Fe, along with non-metals such as N, C, and S, boosts visible-light activity mainly by decreasing the bandgap and improving the separation of photogenerated electron-hole pairs.[115] In a distinct study, composites of titanium dioxide loaded with silver (Ag/TiO_2) were created utilizing a simple photodeposition technique. This composite demonstrated over 90 percent inhibition of Aspergillus flavus when subjected to visible light for 15 minutes. More importantly, the concentration of aflatoxin B1, B2, and G2 was lowered by 96.02 ± 0.19, 92.50 ± 0.45, and 89.81 ± 0.52, respectively. This approach is also promising in lowering the Aspergillus flavus contamination level to avoid aflatoxin development in peanuts. This inhibitory impact was caused by $^{\bullet}O_2^-$, $^{\bullet}OH^-$, h^+, and e^-, which damaged cell structures and reduced A's Flavus spores' viability.[116] Wang et al.,[117] used hydrothermal synthesis technique to prepare a dendritic-like Fe_2O_3 at 160 °C. The dendritic-like Fe_2O_3 exhibited improved photocatalytic efficiency for the degradation of DON in water when illuminated with visible light (wavelengths over 420 nm). Over the course of two hours, this approach effectively lowered the concentration of DON, initially at 4.0 mg/mL, by 90.3%. Active radicals like $^{\bullet}O_2^-$

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and •OH- were found to interact with the active sites of DON, resulting in the creation of intermediate products. Following the photocatalytic radical treatment, HPLC-MS was employed for further analysis of the intermediates.[118]

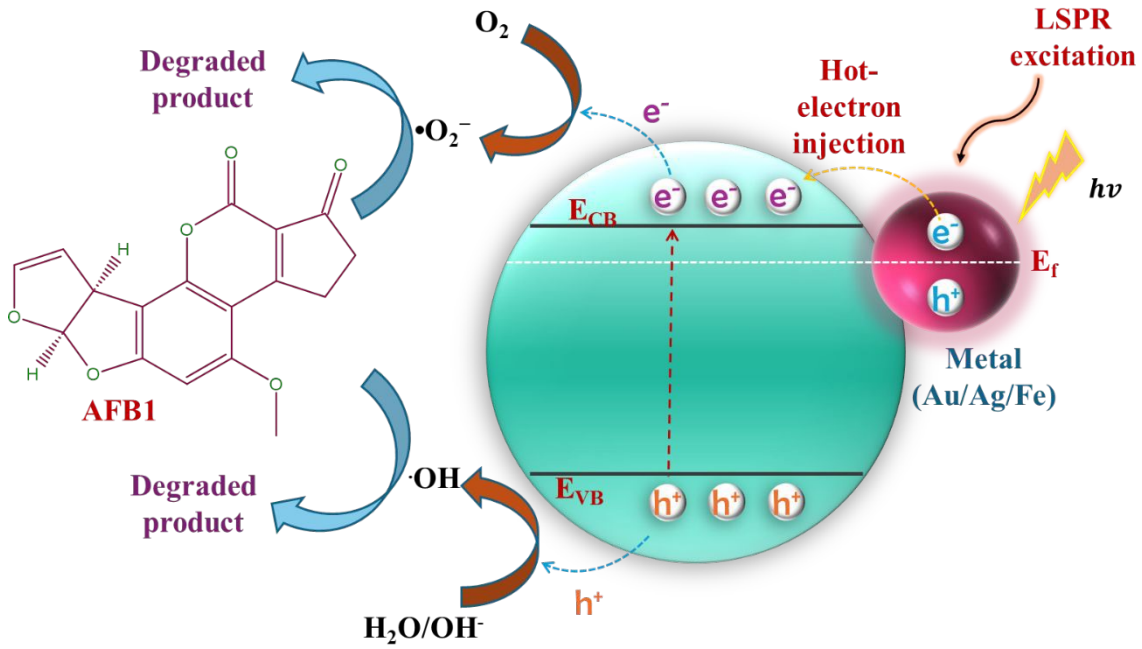

Fig. 8: Mycotoxins degradation through LSPR excitation.

In a specific study, core-shell Ag-AuNPs/g-C_3N_4 were prepared via a simple sonochemical procedure to form plasmon-enhanced photocatalysts. This approach allowed precisely control over the nanoparticles morphology and enabled intimate contact between the Au-PtNPs and the g-C_3N_4 substrate through surface anchoring and hydrogen bonding. The highly toxic and resistant mycotoxin AFB1 was used to assess the Au-PtNPs/g-C_3N_4 composite's photocatalytic performance under simulated sunlight conditions. In the presence of 0.50 mg of catalyst at pH 7.0, complete degradation of AFB1 (50 µg/L) occurred in just 1 minute under natural sunlight, demonstrating a 6.7-fold improvement over untreated g-C_3N_4. Mechanistic investigations demonstrated that the core of AuNP extended the absorption into visible light by producing a surface plasmon resonance impact. On the other hand, charge separation was made easier by the PtNP shell acting as an electron sink. Simultaneously, the g-C_3N_4 nanosheets functioned as a photoactive scaffold that responded to visible light, improving directional movement and effective charge production at the heterojunction interface. As a result of the

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combined enhancements the active species $^{\bullet}O_2^-$, $^{\bullet}OH^-$, and h^+ were produced in significant quantities, which facilitated the breakdown of AFB1.[119]

4.2 Magnetic nanohybrids

Magnetic nanohybrids have emerged as a crucial photocatalytic system for degrading mycotoxins because of their distinctive integration of intense surface activity, visible-light photochemical activity, and, most notably, facile magnetic recovery and reuse. Yang et al.,[120] investigated the potential of La-$ZnFe_2O_4$@Fe_3O_4@carbon magnetic hybrid composite for the photocatalytic breakdown of zearalenone, patulin, and AFB1. Of these, La-$ZnFe_2O_4$@Fe_3O_4@carbon showed a remarkable degradation rate of 98.37% for AFB1, exceeding the effectiveness of Fe_3O_4@carbon (69.57%) and $ZnFe_2O_4$@ Fe_3O_4@carbon (91.39%). Furthermore, this nanohybrid demonstrates outstanding stability and photocatalytic efficiency, reaching degradation rates of 98.52% for zearalenone and 97.35% for patulin. Measurements of the transient photocurrent response indicate that La doping and $ZnFe_2O_4$ co-doping significantly enhance the separation of photoinduced electron-hole pairs on Fe_3O_4@carbon. ESRA studies indicate that the main reactive radicals associated with photodegradation are $^{\bullet}OH$ and $^{\bullet}O_2^-$. Therefore, photodegradation mechanism for mycotoxins generated by damaging microbes can be proposed.

A recent study synthesized a magnetic zeolite nanocomposite (MZNC) using an extract from the medicinal plant C. cyanus, which effectively removed aflatoxin, zearalenone, ochratoxin A, and deoxynivalenol from powdered barley samples. Over 99 percent of aflatoxins, 50 percent of ochratoxin A, 22 percent of zearalenone, and 1.8 percent of deoxynivalenol were eliminated from the contaminated sample at low concentrations by the nanocomposite, with MZNC adsorption outperforming natural zeolite due to the nanocomposite's extensive surface area. The shape, chemical composition, and zeta potential of the synthesized adsorbent were analyzed. To enhance the adsorption of the target mycotoxins, the adsorption capacity was examined and refined.[121]

In realistic food matrices, nanozyme fouling is a recognized issue that has not received enough empirical attention. The primary fouling agents in food matrices are: (i) proteins competitive adsorption onto active surface sites via hydrophobic and electrostatic interactions, forming a "protein corona" that sterically blocks substrate access; (ii) polyphenols irreversible

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oxidative polymerization onto metal oxide surfaces, chelation of surface Fe^{3+} ions (critical for peroxidase-mimetic Fe_3O_4 and Fe-MOF nanozymes), and reduction of peroxidase activity by 30-70% within 3-5 operational cycles as documented in nanozyme biosensor studies in polyphenol-rich matrices[122]; (iii) polysaccharides-physical occlusion of pores and active sites through viscous gel layer formation, particularly relevant in cereal and starch-containing matrices.

Nanozymes demonstrate significant benefits regarding stability in pH and temperature as opposed to natural enzymes. For example, whereas natural laccases and peroxidases usually lose activity within minutes at 60°C, Fe_3O_4-based nanozymes retain more than 80% of their functionality under identical circumstances. Nonetheless, assessing the comparative advantages of nanozymes compared to immobilized natural enzymes in authentic food settings presents challenges, especially regarding their susceptibility to fouling. Recent research employing machine learning methods shows that supervised learning can successfully forecast activity retention in regulated synthesis conditions.[123] Nonetheless, obtaining multi-cycle operational data in actual food matrices, rather than phosphate buffer solutions, continues to be a major challenge for applications aimed at mycotoxin detoxification.

4.3 Cold plasma-based detoxification

Studies are being carried out to explore the capability of cold plasma in lowering the toxicity levels of fresh fruits. In the stages of production, gathering, and preservation, fruits may get tainted by poisons generated by molds and different microorganisms.[101] These fruits frequently serve as major sources of aflatoxins and ochratoxins, which present substantial health hazards to consumers, including the risk of cancer and liver harm.[124] Cold plasma treatment has shown promise in degrading and eliminating the mycotoxins in freshly cut fruits, reducing the risks associated with toxin exposure.[125] The importance of cold plasma technology is that it offers a non-thermal mechanism of destroying toxins in fruits by a complex reaction of reactive species. Cold plasma technology finds application in minimizing microbiological contamination and detoxification of toxins that can lead to food poisoning and exposure to mycotoxins. Additionally, cold plasma is a promising and eco-friendly technique for guaranteeing the freshness and quality of fresh-cut fruits in the food sector.[126]

The cold plasma mechanism involves two two key stages: the production of ROS/RNS and the engagement with the molecular structure of toxins. Air, oxygen, or even argon at normal

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or slightly reduced pressure can create cold plasma. RONS are generated, including O_3, atomic oxygen (O), •OH species, NO, and H_2O_2.[105] The primary components of air are nitrogen and oxygen. Consequently, the rise in the air ratio of the gas mixture containing helium, leading to an increase in the concentrations of oxygen and nitrogen, heightened the levels of reactive species since these elements are essential for producing ROS and RNS via the following processes:[127]

$$O_2 + e^- \rightarrow O + O$$

$$O + O_2 + O_2 \rightarrow O_3 \text{ and } O_2$$

$$N + O + M \rightarrow NO + M$$

$$O + NO + M \rightarrow NO_2 + M$$

$$O + H_2O \rightarrow 2OH\cdot$$

$$2OH\cdot \rightarrow H_2O_2$$

The species interact with toxin molecules present on fruit surfaces, leading to oxidative degradation through reactions involving hydrogen atoms, addition to unsaturated bonds, and bond cleavage, especially with more intricate mycotoxins like aflatoxins and patulin. Toxin compounds are altered by the heightened reactivity of RONS, transforming them into smaller, less harmful, or non-toxic substances. Moreover, through encouraging photo-oxidation and enhancing the transport of reactive species into microcrevices on the fruit's surface, UV photons and charged particles generated in the plasma work together to hasten degradation.[128] The precise mechanism of cold plasma in mycotoxin detoxification is still not fully understood. Nonetheless, it is believed that they involve chemical interactions between the toxin molecules and the reactive species formed by the plasma.[129] These reactions can lead to the breakdown or alteration of toxin molecules, making them less toxic or potentially non-toxic.[130]

Recognizing the detrimental functional groups in mycotoxin structures is crucial for evaluating detoxification mechanisms in plasma. Due to the structural similarities of mycotoxins, different compounds like DON and AFB1 (shown in **Figs. 9** and **10**) may exhibit similar or identical toxic structural characteristics, making them toxicologically alike. AFB1, specifically,

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is mainly harmful and cancer-causing because of its unique difuran ring configuration and C=C bonds.[131] The lactone ring present in mycotoxins like AFB1, ZEN, and PAT, has a C=C bond akin to that in DON, which is similarly regarded as detrimental. The alteration of AFB1's lactone ring greatly diminishes its toxicity and mutagenic capacity. Moreover, various mycotoxins contain toxic sites, such as the hemiacetal in PAT, the carboxyl group in OTB, and the epoxide ring in DON, underscoring the structural resemblances between these substances.[132]

The previously recorded reaction mechanism and product generation of DON when interacting with plasma species[112,113] suggest a complicated interaction of hazardous structural groupings. This research highlights the importance of the epoxide functional group, the development of carbonyl groups, and the key properties of the C9 to C10 double bond. The C9=C10 double bond, shown in **Fig. 9A R1**, promotes addition reactions, which can be obstructed by hydrogen atom removal from neighboring locations, as demonstrated in **Fig. 9A R2**, or through the breaking of chemical bonds, illustrated in **Fig. 9A R3**. The ring-opening reactions associated with the epoxy ring-C13 bond (**Fig. 9B R1 and R2**) and the C12-O bond (**Fig. 9B R3**) mainly occur due to the breaking at C12. In addition, the aldehyde group primarily appears at the C5, C6, and C9 sites, whereas the ketone group is mostly found at C3, C4, C7, and in the epoxy ring, as shown in **Fig. 9C and Fig. 9D**, respectively. The formation pathways for these groups feature the transformations: $-CH_3$ to $-CH_2OH$ to -CHO for aldehydes and $-CH_2$ to -CHOH to -C=O for ketones.[113]

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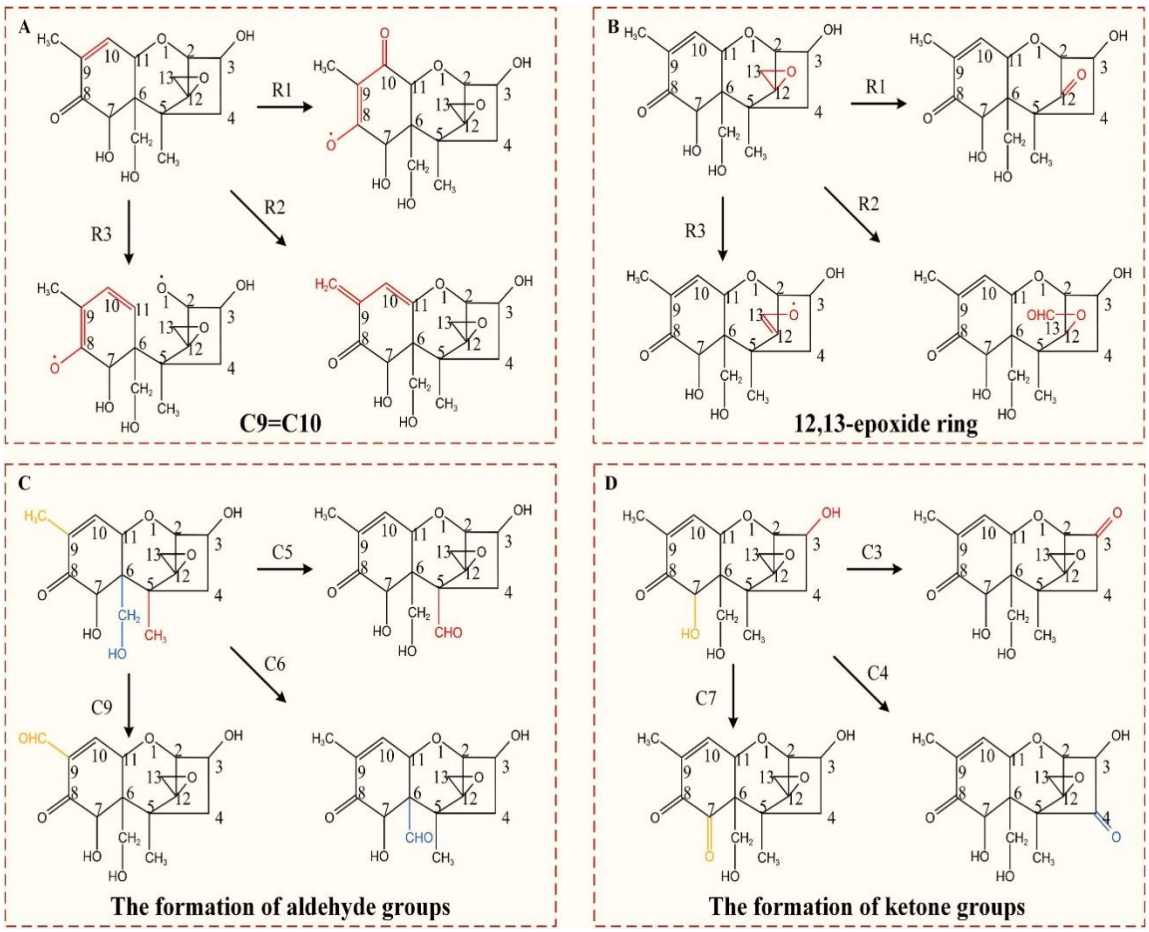

Fig. 9: Metabolic or chemical pathways leading to the decomposition of deoxynivalenol and its byproducts. This figure has been reproduced from ref.[94] with permission from Elsevier, copyright 2023.

The reaction mechanisms and products of AFB_1 degradation by O_3 have been further studied using O atoms, OH radicals, and H_2O_2,[133] with the main reactions summarized in **Fig. 10**. The first step in breaking the C8=C9 double bond is to leave behind an unstable structure in an addition pathway that undergoes three distinct reactions: direct breaking of double C8=C9 bond **(Fig. 10A R2)**, production of ketone group via hydrogen removal process (**Fig. 10A R1**), and breakage of C_6-O_7 and C_9-C_{10}.The ring-opening reaction is more likely to occur because the furan ring is more reactive at the terminal. **Fig. 10B** shows breaking of the C_6-O_7 bond and opening of the furan ring because of the H-abstraction process at the C_{10} site. H-abstraction facilitated the reduction of the carbonyl group at the C17 position of cyclopentenone, as illustrated in the H-abstraction reaction depicted in **Fig. 10C**. Reaction between lactone ring and

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H_2O_2 and O_3 molecules is only activated when the ring is opened (**Fig. 10D R1**). As observed in **Fig. 10D R2**, reduction of lactone carbonyl may occur from the O atom on lactone carbonyl abstracting a H atom of the H_2O_2 molecule. Furthermore, **Fig. 10C R3** illustrates that H_2O_2 molecules participate in H-abstraction with cyclopentenone, causing the breakage of the C15=C19 bond in H_2O_2 and leading to a modification of the benzene ring structure. As seen in **Fig. 10D R4**, H-abstraction reaction at the C18 position on the cyclopentenone can also result in reduction of double C15=C19 bond since the lactone ring and cyclopentenone share the identical C15=C19 bond.[134]

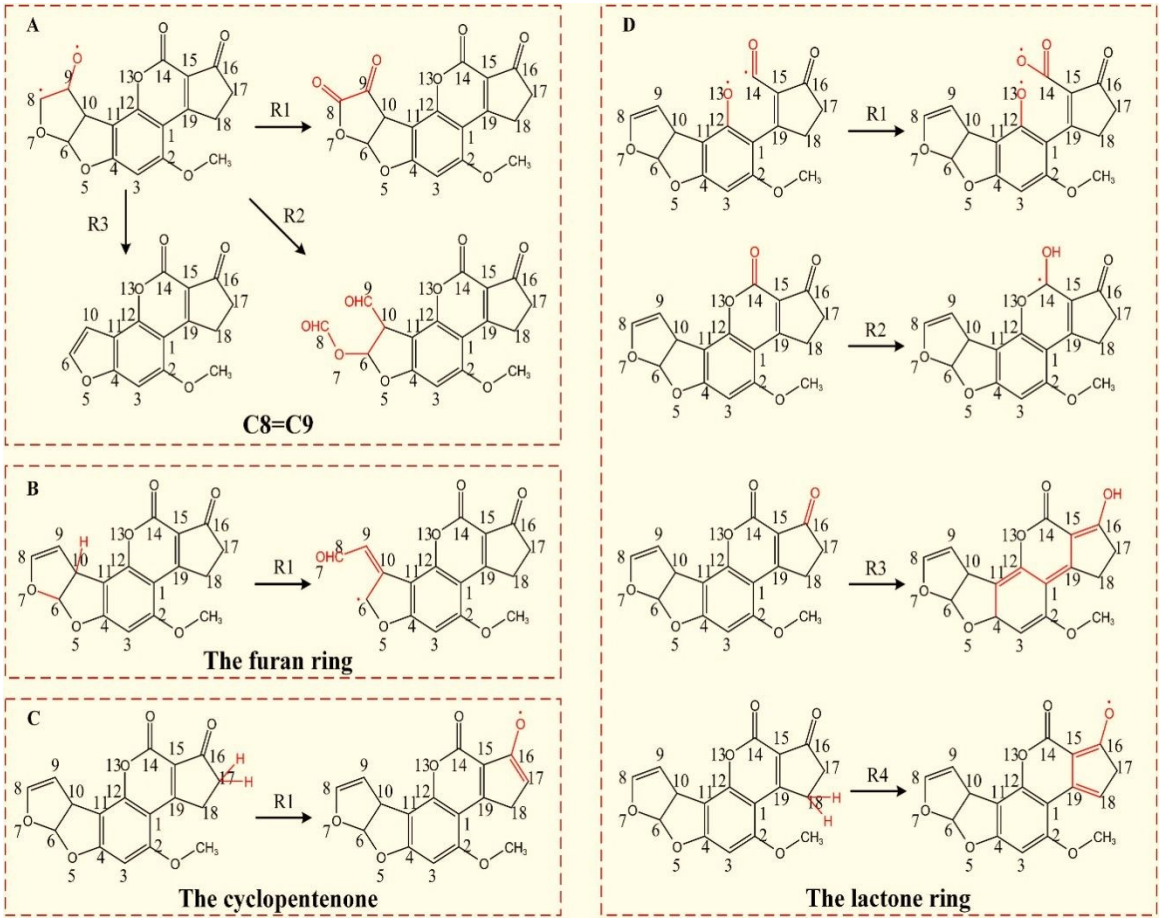

Fig. 10: Aflatoxin B_1 degradation mechanisms and byproducts. This figure has been reproduced from ref.[94] with permission from Elsevier, copyright 2023.

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4.4 Plasma configurations

Cold plasma technology is distinguished from other plasma techniques as it operates at near-atmospheric pressure and is non-thermal. Various reactor and discharge systems that generate non-thermal plasmas with high concentrations of ROS/RNS are included in cold plasma technology. These designs vary in the manner of plasma production, the reaction of reactive species with the target substrate, and the suitability of the configurations for specific food and mycotoxin-detoxification applications. Dielectric barrier discharge (DBD), Jet plasma, and plasma-activated water (PAW) systems are among the most-studied and widely used in food safety research. Each of these systems is acknowledged for its unique benefits, such as scalability, consistent application of treatment, and the capacity to regulate reactive species, which makes them especially efficient for tackling intricate food matrices.[135] Common hazardous functional groups such as C=C bonds, lactone, epoxide, hydroxyl, carbonyl, ester, and carboxyl groups are selectively cleaved or transformed via plasma discharge-driven reactions, as shown in **Fig. 11.** These reactions include processes like reduction, oxidation, ring cleavage, bond breaking, and decarboxylation inside a reactor. This method aids in detoxification and molecular simplification.

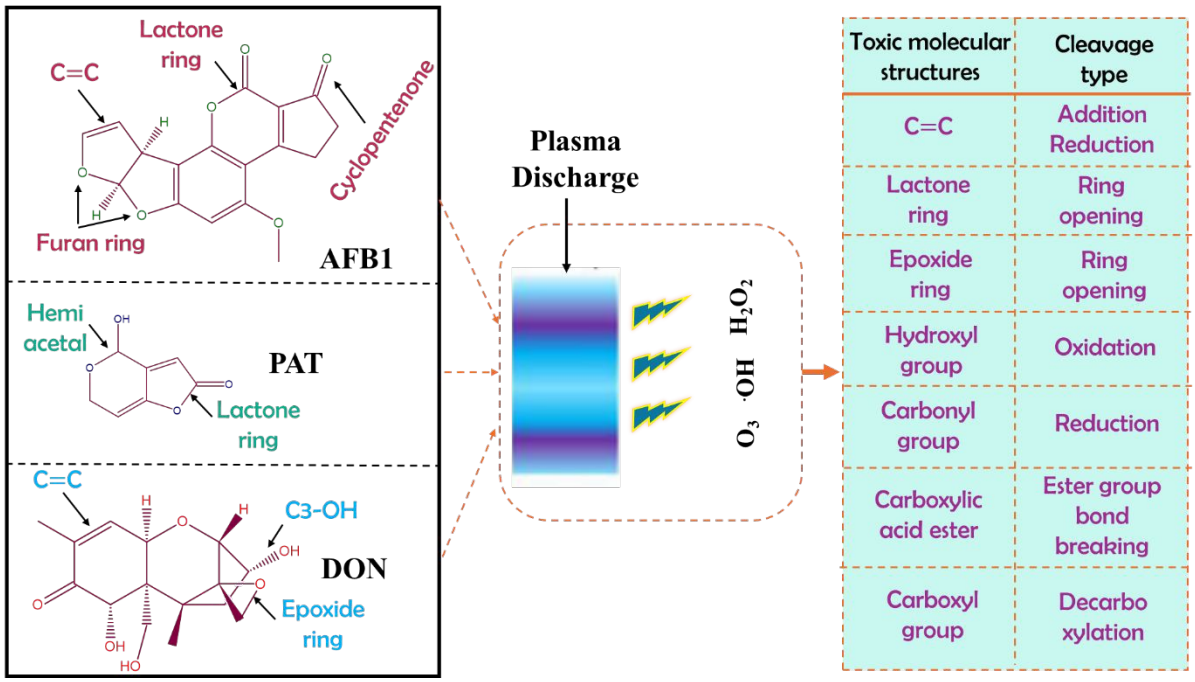

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Fig. 11: Schematic representation of the transformation routes for mycotoxins after plasma discharge.

Dielectric Barrier Discharge (DBD) is an extensively used cold-plasma method for eliminating mycotoxins from food. This technique uses two electrodes with varying electrical potentials, separated by a dielectric substance that prevents electric arcs and promotes gas ionization in the area between the electrodes **(Fig. 12)**. The setup can be categorized as either surface dielectric barrier discharge or standard dielectric barrier discharge, based on the arrangement of the electrodes and the dielectric barrier.[117] When a high voltage is applied to one electrode and the other is kept grounded, a powerful electric field is created, resulting in the ionization of the gas in the space. Furthermore, DBD plasma can be utilized for in-package treatments, where plasma is produced inside the packaging itself, thus reducing the risk of contamination during processing. This method frequently employs gases like argon, helium, or affordable nitrogen, which can additionally function as altered atmospheres inside the package.[118]

Jet plasma is typically generated via DBD inside a cylindrical chamber at atmospheric pressure, where gas is injected into the chamber (**Fig. 12**). A ground electrode shaped like a rod is located at the center of the tube, facilitating the ejection of plasma into the surrounding air, while a ring electrode with high voltage surrounds the tube. Different setups of jet plasma systems are available; for example, a supplementary ring electrode might substitute the internal rod-like ground electrode. To avoid arcing, the electrodes in this arrangement are insulated from each other and surrounded by dielectric material. Despite extensive research on jet plasma for food processing applications, its failure to adequately cover regions smaller than a square millimeter restricts its industrial utilization. A new method has been developed that employs jet plasma in bubbling columns to create plasma-activated water or to process liquid foods, which involves producing plasma in a tube that is later inserted into a liquid-filled vessel or reactor.[136]

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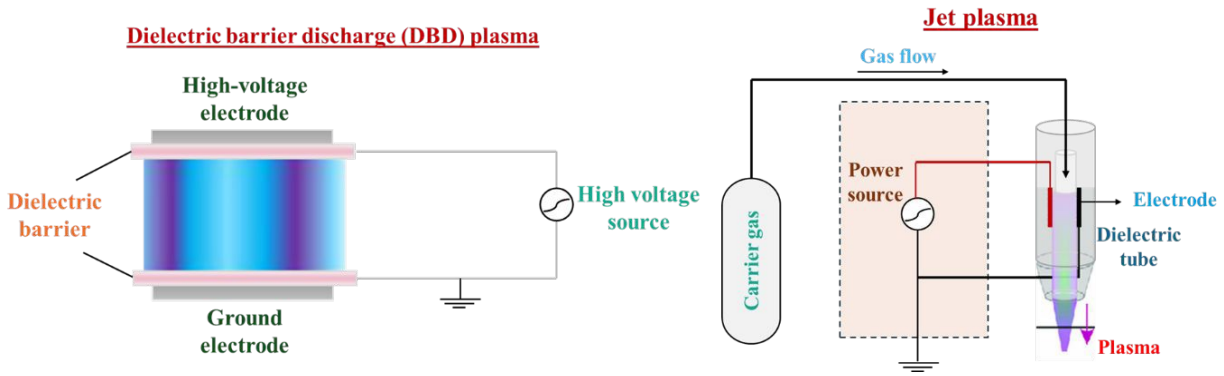

Fig. 12: DBD & Jet Plasma for food processing and mycotoxins removal

Plasma-activated water (PAW) signifies an innovative breakthrough in the food sector, efficiently addressing mycotoxin and microbial contamination due to its unique physicochemical properties. The creation of PAW utilizes a corona discharge system that operates on a direct current (DC) supply and includes a zero-voltage-switch (ZVS) circuit. This configuration consists of key elements like a transformer, an air compressor, an electrode unit, and a sample processing plate. The ZVS circuit functions using a DC input, producing an output voltage of 10 kV at a frequency of 100 Hz to generate plasma under atmospheric pressure. Plasma is created between two stainless steel electrodes, generating a discharge that looks like a streamer, while the air pump helps maintain a plasma plume to avert spark formation. Dry air acts as the transport gas, while the pump maintains a consistent airflow of 2.5 liters each minute.[73,137]

A research study evaluated the efficiency of cold atmospheric-pressure plasma in deactivating mycotoxins in corn.[138] Cold plasma effectively decontaminates mycotoxins in corn, including AFB_1 and fumonisin B_1, which are among the most commonly detected. A treatment lasting only 10 minutes led to a notable decrease in contamination, reaching about 65% removal rates for both AFB_1 and fumonisin B_1, specifically 65% and 64%, respectively. This approach shows potential not only for diminishing these toxic mycotoxins but also for tackling aflatoxin contamination in corn.[139] A 10-minute treatment with high-voltage atmospheric cold plasma resulted in an 85% decrease in aflatoxin levels. This method entails the creation of reactive entities, such as charged ions, free radicals, and gaseous molecules, that efficiently break down mycotoxins. Furthermore, the generation of these reactive species is affected by the ambient gas and relative humidity. Employing cold atmospheric-pressure plasma generated by an air surface

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barrier discharge device, AFB_1 was effectively removed from contaminated corn surfaces, with maximum decontamination achieved after 240 seconds of exposure, leading to total decontamination success.[140]

In another study, AFB_1 concentrations in maize inoculated with A. flavus demonstrated a gradual decrease of 23.4%, 41.8%, 64.4%, and 80.0% after CAP treatment for 2, 4, 8, and 12 minutes, respectively.[141] Additionally, the CAP degraded away 95.3% of the AFB1 in a suspension of A. niger cells in 30 seconds.[142] When wheat and rice inoculated with A. flavus were subjected to CDPJ-produced CAP at varying current and electrode distances, AFB_1 was reduced by 95 %, of which 45-56 % was attributed to the wheat and rice samples.[143] According to Sakudo and Yagyu,[144] time-dependent changes in AFB_1 were observed with a maximum decrease of 75.8% and 82.5% after 1 min and 30 min of CAP exposure, respectively. Wang Y. et al.[145] (2022) examined CAP produced using SMD and its effect on Fusarium graminearum. They found that DON production was significantly reduced across all samples tested, and the magnitude of the effect depended on exposure duration. Interestingly, a 6-minute CAP treatment reduced DON levels by more than half. Equally, according to Chen et al.[146], applying CAP generated at 50 KV to wheat took 8 minutes and was enough to reduce DON by more than 62–84%. Wang et al.,[147] showed that CAP produced using GPSDP was effective in removing OTA in raisins. In contrast, the authors observed 62 percent degradation at 4 minutes and 100 percent at 10 minutes of treatment without compromising the matrix's quality.[147] Another study highlighted the value of CAP made with DBD in reducing PAT in fresh-cut apple slices while simultaneously enhancing their qualitative attributes. The highest probability of a 55–99% decrease in PAT was seen with 23 kV at 2.5 and 8.5 minutes, respectively, indicating the high voltage and ideal exposure duration.[148]

4.5 Adsorption-biocatalysis coupled systems

Despite the effectiveness of single-adsorption catalysts and combined adsorption-photocatalysis systems in eliminating mycotoxins, their application in the food industry encounters numerous substantial challenges. These obstacles encompass the risk of nutritional loss, unpredictable degradation processes, and higher energy usage.[149] The combination of adsorption and biocatalysis addresses the shortcomings of conventional techniques by employing enzymes that demonstrate a significant level of selective degradation.[133] The biocatalytic alteration of

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mycotoxins facilitates their transformation via known biochemical routes, guaranteeing a secure and sustainable detoxification process that functions under mild conditions. As a result, creating hybrid systems that combine adsorption materials with enzyme selectivity offers a promising approach for controlling mycotoxins, holding considerable potential for commercial use in sustainable food safety.

Researchers have extracted, purified, and genetically engineered microbial-derived enzymes that can specifically recognize and convert toxic mycotoxins into inactive or less poisonous metabolites.[150] This molecular-precision biocatalytic decontamination approach exhibits high catalytic activity with minimal secondary pollution. Considering these benefits, using these modified enzymes directly on tainted food items offers a viable method for lowering mycotoxin concentrations while maintaining the food's nutritional quality. Presently, the mycotoxin detoxification enzymes available in the market mainly focus on AFs, ZEN, DON, OTA, and PAT. Nonetheless, their real-world use is constrained by issues like low stability and activity, frequently necessitating multiple days to attain the intended reaction.[151]

Adsorptive support-based enzyme immobilization technique has emerged as a valuable innovation in food detoxification, as it is promising for enhancing enzyme performance in food safety processes. By immobilizing enzymes on designed substrates by covalent tethering, matrix entrapment, or interfacial deposition, structural integrity and functional competence can be improved.[152] The proximity of the enzyme-substrate interface is increased by the resulting adsorption-enzymatic catalysis systems, which leverage the regulated physicochemical characteristics of the supporting materials, thereby significantly boosting the overall catalytic capacity of the enzymes and improving their selectivity in molecular recognition.136,137 The efficiency of immobilized enzymes for eliminating mycotoxins in food has been demonstrated a transformative approach of bifunctional adsorption-biocatalytic systems to industrial applications.[154] The logical architecture and controlled physicochemical characteristics of the support materials greatly enhance the overall catalytic capacity of the enzymes and consequently improve their selectivity in molecular recognition in multiphase food matrices.

Hierarchical mesoporous adsorbents, particularly COFs and MOFs, have become a desirable matrix for enzyme immobilization. Their large specific surface area and versatile surface chemistry make them effective for this purpose.[155] Researchers have devised various

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strategies, including the integration of magnetic nanoparticles and the creation of hydrogel networks, to improve recovery and reusability of enzyme catalysts in a variety of food items. For instance, Yan et al.,[156] used co-immobilization to fix cysteine and porcine pancreatic lipase in a multi-level mesoporous zirconium MOF (CMC@HMMOF-Cys/PPL). Fixated enzyme was subsequently immobilized in an aerogel via an in-situ assembly protocol that proved highly effective for eliminating PAT in apple juice. By reacting with Zr groups, the OH groups on the HMMOFs allowed co-immobilization of the carboxyl groups of biomolecules with Cys and PPL without the need for cross-linking agents. In comparison to other carriers, this method showed exceptional superloading abilities that were 16 and 4 times higher, respectively. BET confirmed that HMMOFs exhibit a high adsorption capacity of 38.41 mg/g for PAT. Due to the consistent increase in removal capacity, PPL exhibited efficient biodegradation of PAT. Furthermore, the system's selectivity, storage stability, and reusability were assessed with the use of simulated apple juice. Subsequently, CMC@HMMOF-Cys/PPL was loaded into a continuous flow reactor to effectively remove PAT from real apple juice in a continuous manner. Moreover, the biologically derived components exhibited enhanced biosafety profiles and did not significantly affect the quality of apple juice.

Using a specific approach, enzymes were fixed on polydopamine-coated membranes that contained reactive catechol and quinone groups. These functional groups facilitate the immobilization of catalysts via spontaneous conjugation with biomolecules that possess thiols or amines, removing the necessity for external coupling agents. To efficiently lower ochratoxin A levels in wine, a polydopamine-coated magnetic porous chitosan (MPCTS@PDA@pancreatin) was produced via ultrasound. This approach led to a notably quicker detoxification rate for OTA than the unbound enzyme, as well as improved acid resistance (pH 3.0–7.0) and heat stability (17–47 °C). Additionally, MPCTS@PDA@pancreatin demonstrated strong catalytic performance across eight cycles during magnetic separation.[157] Zhang et al. reported a co-immobilization system featuring a nanocarrier modified with an aldo-keto reductase that facilitates in the effective breakdown of PAT in fresh pear juice.[158] Cellulose nanocrystals (CNCs) were attached to magnetite nanoparticles (DA/PEI@Fe_3O_4/CNCs) to create the nanocarrier. This system accomplished an impressive 98% decrease in PAT levels in pear juice with the use of NADPH as a coenzyme, while maintaining the juice's quality. It showed a detoxification effectiveness surpassing 87% across five successive cycles, although there was a

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62% reduction in activity over a duration of 14 days. The improved stability and reusability of the reductase can be linked to its large surface area, robust magnetization, and the existence of oxygen and amine groups. Nonetheless, integrating coenzymes into food systems continues to be a challenging task.[158]

Amphiphilic laccase-inorganic hybrid nanoflowers (Lac NF-P) have been reported for their efficiency in eliminating mycotoxins from consumable oils.[159] This method entails the entrapment of laccase in inorganic nanoflowers by co-precipitating copper sulfate pentahydrate with a phosphate solution that contains laccase. Afterward, Concanavalin A (ConA) is employed to cross-link the amphiphilic polymer Pluronic F127 (PEO-PPO-PEO) with Lac NF, creating a hybrid system that demonstrates remarkable stability and dispersion in both aqueous and oily environments. This approach maintains the catalytic characteristics of the enzyme, allowing effective toxin adsorption while ensuring a localized aqueous microenvironment. Confocal microscopy verified the localization of Lac and ConA, whereas BET surface area and pore diameter evaluations showed negligible mass-transfer resistance. Moreover, tannic acid (TA) functioned as a redox mediator, promoting the breakdown of AFB1 via cationic radicals produced by the enzyme, which notably boosted laccase's catalytic efficiency. The findings indicated that Lac NF-P demonstrated a 134-fold and 3.2-fold enhancement in AFB1 degradation efficiency over free laccase and Lac NF, respectively. Crucially, the process maintained the quality of peanut oil, and there was no indication of catalyst leakage. Toxicological evaluations showed that the breakdown products were almost non-toxic to human liver cells. This study highlights the capability of amphiphilic immobilized enzyme catalysts in efficiently removing mycotoxins from edible oils and dairy items while maintaining the natural enzymatic function, with the introduction of a redox mediator further boosting AFB_1 degradation.

Chen et al.,[159] created an inorganic hybrid nanoflower (InHNF-ZHD518) that includes a zearalenone lactonase, facilitating the quick and targeted immobilization of ZHD518 on crude cell extracts without requiring organic solvents. The immobilized biocatalyst exhibited a notable improvement in specific activity, attaining a forty-to-six percent rise in comparison to the free enzyme. It preserved structural integrity over a wide pH spectrum and demonstrated remarkable reusability, maintaining a significant portion of its initial performance after several usage cycles. In practical detoxification experiments with beer samples, ZEN degradation using InHNF-

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ZHD518 exceeded 50%, whereas the free enzyme significantly diminished its effectiveness under comparable conditions. The InHNF method provides numerous benefits, such as eco-friendly enzyme immobilization, direct processing without the need for purification, and improved catalytic efficiency, demonstrating its significant promise for use in industrial biocatalysis and the production of food enzymes. **Table 3** summarizes mycotoxin detoxification pathways.

Table 4. Mycotoxins detoxification through specific strains/enzymes.

Target mycotoxins	Degrading strain/degrading enzymes	Sources	Degradation rate/Degradation products	Degradation mechanism	Degrading condition	Ref.
AFB_1	MCO SOD	*Pseudomonas aeruginosa* HNGD-JZ06	98.6% 96% AFQ_1, *epi*-AFQ_1	-	pH 7 & 40℃ for 24h	[160]
	Ery4 Laccase	*Saccharomyces cerevisiae* ITEM 17289	AFQ_1, *epi*-AFQ_1, AFB_{2a}, AFM_1, AFB_1-8,9-dihydrodiol or AFB_1-dialehyde	Reduction	Sodium acetate 1mM & pH 5	[161]
	BsCotA Laccase	*Bacillus subtilis*	44.8-100%/AFQ_1	Oxidation	In the presence of 0.1-5 mM MS	[162]
	CotA Laccase	*Bacillus licheniformis* ANSB821	AFQ_1, *epi*-AFQ_1	Oxidation	-	[163]
	CotA-Q441A	*Bacillus subtilis*	AFQ_1, *epi*-AFQ_1	Oxidation	High degradation rate in the pH range 5.0-9.0 & 50 ℃ in 5h	[164]
	Lac3-Laccase	*Trametes* sp. *C30*	91%/$C_{16}H_{22}O_4$, $C_{14}H_{16}N_2O_2$, $C_7H_{12}N_6O$, and $C_{24}H_{30}O_6$	Breakdown of the double bond of the furo-furan ring and	Optimal conditions	[165]

				the lactone ring		
	fmb-103 Laccase	*Bacillus vallismortis* fmb-103	60%	Codon-optimized methanol stimulation	pH 7 & 37℃	[166]
	Manganese peroxidase	*Kluyveromyces lactis strains* GG799	90%/AFB_1-8,9-dihydrodiol	-	pH 4.5 & 40℃ for 36h	[167]
	Rh-DypB dye-decolorizing peroxidase	-	96%/AFQ_1	Hydroxylation	96h at 25℃	[168]
	DypB dye-decolorizing peroxidase	-	$C_{17}H_{14}O_6$, $C_{16}H_{14}O_6$, $C_{16}H_{14}O$, and $C_{17}H_{14}O_7$	-	-	[169]
	ATTM Lactonase	*Bacillus megaterium* HNGD-A6	86.78%/AFD_1, $C_{14}H_{16}N_2O_2$	-	pH 8.5 & 80℃	[170]
	TV-AFB_1D	*Trametes versicolor*	60%	-	pH 7 & 32℃ for 48-72h	[171]
ZEN	*Bacillus subtilis*	-	65%~100%	-	-	[172]
	RmZHD	*Rhinocladiella mackenziei*	-	Deprotonated nucleophile(Ser105) attacked C1 of ZEN	-	
	FSZ	*Aspergillus niger*	75-80%/$C_{18}H_{26}O_4$	Breaking the lactone bond	pH 7 & 28℃	
	ZenH	*Aeromicrobium* sp. HA	$C_{18}H_{22}O_5$	Breaking the lactone bond	pH 7 & 55℃	[173]
	SHP Peroxidase	Soybean hulls	54-85%/13-OH-ZEN, 13-OH-	Hydroxylation of	In buffer with stepwise	[174]

			ZEN-quinone	the aromatic group	addition of 100μM H_2O_2 in 1h	
	*Po*DyP4-Dye decolorizing peroxidase	*Pleurotus ostreatus*	13-OH-ZEN, 13-OH-ZEN-quinone, 13-15-OH-ZEN, ZEN-dimer, and 15-OH-ZEN dimer	Hydroxylation of the aromatic group	pH 6 & 40℃ for 2h	[175]
	CotA-Laccase	*Bacillus licheniformis*	15-OH-ZEN, 13-OH-ZEN-quinone	Hydroxylation of the aromatic group	87% at 80℃ for 30min	[176]
	Zhd11D	*Phialophora attinorum*	-	-	pH 8 & 35℃	[177]
DON	DepA-dehydrogenase	*Devosia mutans* 17-2-E-8	3-keto-DON	Converting C3-OH into keto group	-	[178]
	DDE	*Devosia* sp. JA3	82.51%/3-keto-DON	-	pH 7 & 37℃ for 12h	[179]
	YC12-C3 YC12-C10	*Coix lacryma-jobi*	3-deoxy-6-demethanol-DON	Deoxidization & demethanal	pH 7 & 28℃	[180]
	DDH-dehydrogenase	*Pelagibacterium halotolerans* ANSP101	3-keto-DON	Oxidation of DON to 3-keto-DON	-	[181]
	SDH-dehydrogenase	*Ketogulonicigenium vulgare* Y25	3-keto-DON	-	-	[182]
	*Yo*DDH-dehydrogenase	*Youhaiella tibetensis*	90%/3-keto-DON	Dehydrogenation of DON to 3-keto-DON	pH 4.5 & 40℃	[183]
	DLK06-RS13370 Acyltransferase	*Acinetobacter pittii* S12	78.32%/3A-DON	Acetylation of DON	-	[184]
Ochratoxin	Aspergillus	-	94%	-	-	[185]

A	oryzae strain M30011					
	BnOTase1-3 peptidase	*Brevundimonas naejangsanensis* ML17	100%/OTα	-	-	[186]
	*Af*OTH Carboxypeptidase	*Alcaligenes faecalis* subsp. *Phenolicus* DSM 16503^T	High degradation rate	OTA hydrolysis	-	[187]
	*Ps*SDO Amidase	*Pseudaminobacter salicylatoxidans* DSM 6986^T	OTα	Breaking the amide bond of OTA	-	[188]
	ADH3 Amidase	*Stenotrophomonas acidaminiphila*	OTα & L-β-phenylalanine	Catalytic break down	-	[189]
	Chrl-3858681-3267 Amidase	*Stenotrophomonas* sp. 043-1a	OTα & L-phenylalanine	Hydrolysis	-	[190]
	Chrl-3858681-771 Amidase	*Stenotrophomonas* sp. 043-1a	OTα & L-phenylalanine	Hydrolysis	-	
	Nh-9 Nudix hydrolase	*Bacillus velezensis* IS-6	89%/ OTα	-	pH 7 & 37℃	[191]
OTA **OTB**	ANL-Lipase	*Aspergillus niger*	100%	-	Complete degradation in 3h	[192]
PAT	RL12 Lipase	*Ralstonia* sp. SL312	80%/$C_7H_{11}O_4^+$	-	pH 7.5 & 37℃ for 24h	[193]
	PLE esterase	*Porcine liver*	97.8%/DPA	Breaking of lactone ring	-	[194]

	HRP Peroxidase	Horseradish	53.2%/DPA	Breaking of lactone ring	-	194
	LA lipase	*Aspergillus niger*	76.3%/Hydroascladiol	-	-	194
	MgAKR (Aldo keto reductase)	*Meyerozyma guilliermondii*	88%/Ascladiol	-	pH 6 & 16℃	195
	*Mr*MnP (Manganese peroxidase)	*Moniliophthora roreri*	95%/Hydroascladiol	-	30℃ for 24h	196
FB_1	Fumonisin esterases	-	-	Cleavage of TCA ester at C6	-	197
	FumD1 Fusion enzyme	-	100%/2-keto-HFB1	-	pH 7 & 25℃ for 24h	198
	FumPHTA Amino transferase	-	40%/2-keto-HFB1	-	pH 3-4 & 50-60℃	198
	FumUPTA	-	40%/2-keto-HFB1	-	pH 3-6 & 50-70℃	
	FumTSTA	-	70%/2-keto-HFB1	-	pH 3-10 & 50℃	

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4.5.1 Mechanistic basis of the synergistic interactions in adsorption-biocatalysis systems

Hybrid adsorption–biocatalysis systems have shown remarkable detoxification efficiency. As a result, researchers are focusing on the mechanistic basis of interfacial catalytic synergy. Understanding how this synergy facilitates toxin capture, activation, and degradation in complex food matrices is becoming increasingly important. Existing studies offer substantial evidence indicating that spatial, physicochemical, and catalytic interactions produce genuine synergistic effects instead of simple additivity in hybrid adsorption-biocatalysis systems. Reaction kinetics can be accelerated by achieving spatial confinement effects and synergistic interactions by co-localization methods and synergistic cascade reactions.[199] Despite these advances, research remains limited on the use of enrichment techniques in combination with biochemical cascade processes for mycotoxin decontamination in food matrices. Fu et al.,[200] developed a hybrid catalyst PL-GOx-Fe_3O_4@COF by attaching glucose oxidase (GOx) and Fe_3O_4 nanoparticles to an amphipathic covalent organic framework. Fe^{3+} ions decreased inside the COF pores during the production process. A Schiff base reaction was then used to immobilize GO_x on the surface **(Fig. 13)**. This design improved intermediate diffusion efficiency by allowing GO_x and Fe NPs to be loaded separately but restricted within a single compartment. Additionally, to increase the mass transfer efficiency for use in culinary oils, an aldehyde-functionalized triblock copolymer was grafted.

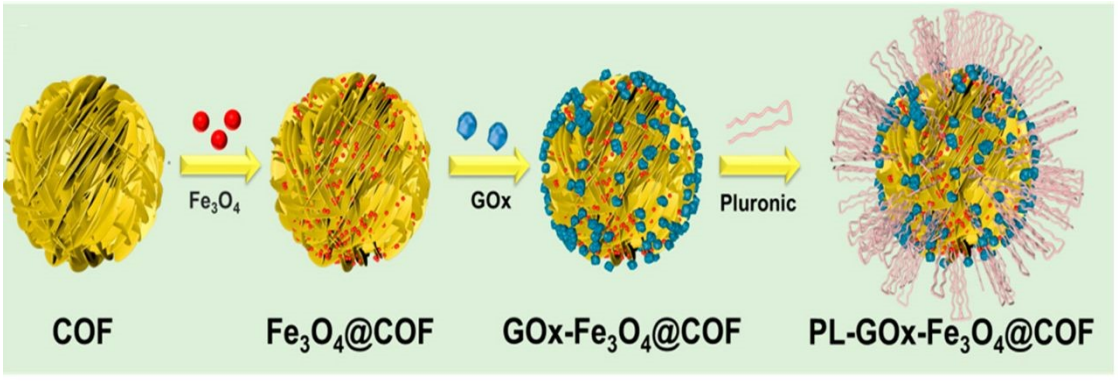

Fig. 13: Preparation process of PL-GO_x-Fe_3O_4@COF metal–biological hybrid catalyst. This figure has been adapted from ref.[200] with permission from American Chemical Society, copyright 2024.

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This hybrid catalyst effectively created a metal-biological cascade system for mycotoxin elimination by combining the Fenton reaction with enzymatic catalysis. The π-π stacking interaction between COFs and mycotoxins (particularly AFB_1) facilitates facile separation in edible oils, enabling targeted detoxification of mycotoxins. Mechanistically, the ongoing generation of hydrogen peroxide by glucose oxidase triggers the Fenton reaction, resulting in the formation of reactive oxygen species. Simultaneously, the oxidation reaction produces gluconic acid, influencing the microenvironment and stabilizing the Fe^{2+}/Fe^{3+} redox cycle. Consequently, the detoxification effectiveness of the cascade system for AFB1 was sixfold higher than that of merely combining free GOx and Fe_3O_4. Importantly, after six reuse cycles, the enzymatic activity stayed intact with no considerable morphological alterations. Crucially, the nutritional properties of peanut oil were mostly maintained, and both the degradation products and the processed oil showed low toxicity to human liver cells, highlighting the technique's promise for mycotoxin removal in vegetable oils. Furthermore, porous materials like metal-organic frameworks and biochars can maintain ideal enzyme performance by adjusting local pH and moisture levels, even in difficult bulk environments. In conclusion, selective sorbents can improve turnover efficiency beyond simple concentration effects by locating toxins close to catalytic sites, showcasing a genuine synergistic interaction instead of just additive performance.[18]

5. Matrix effects in real food systems

The influence of the physical, chemical, and biological environment of food on the behavior, detection, bioaccessibility, bioavailability, and eventually the detoxification of toxicants and contaminants in actual food systems is referred to as the matrix effect. In the context of food toxin detoxification, it's crucial to understand that the exposure and detoxification pathways of toxic substances are influenced not only by the chemical properties of the contaminants. The effects of matrices across various domains have been observed in physicochemical interactions, physiological processing, analytical quantification and risk assessment. The food matrix is a complex arrangement of nutrients, non-nutritive compounds, and structural components, which consist of proteins, carbohydrates, lipids, fibers, minerals, water, and microstructures such as cell walls and emulsion droplets. In contrast to isolated chemical systems, natural foods provide diverse environments where interactions among matrix components and xenobiotics can notably

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influence solubility, release kinetics, transformation, transport, and absorption. These interactions are essential for assessing bio-accessibility, which is the portion of consumed contaminants that are released from the food matrix in the gastrointestinal system, and bioavailability, the fraction that eventually enters systemic circulation, affecting both toxins and naturally occurring bioactive compounds.[201,202]

One of the major obstacles to applying mycotoxin detoxification technology from lab settings to actual food systems is matrix effects. Recent reviews indicate that mycotoxin removal in complex food and feed matrices is still much more challenging than in simplified aqueous systems because of strong interactions with proteins, lipids, and polysaccharides that lower mass transfer efficiency and catalytic accessibility.[203] These effects are especially noticeable in lipid-rich and processed food matrices, where hydrophobic mycotoxins' accessibility to photocatalytic or enzymatic breakdown processes is further reduced by their partitioning into fat phases. Due to diffusion constraints and competing adsorption effects, detoxification efficiencies reported in model aquatic systems are frequently much higher than those observed in real food systems. In this regard, a recent study showed that tubular O, S co-doped g-C_3N_4 activated peroxymonosulfate under visible light completely degraded aflatoxin B_1 in edible oil systems in 120 minutes, demonstrating its applicability in realistic food matrices.[204] Heteroatom co-doping was identified as the root cause of the improved catalytic performance because it produced electron donor–acceptor sites, promoted peroxymonosulfate adsorption, and accelerated interfacial electron transfer processes, all of which encouraged the production of reactive oxygen species. In comparison to pristine g-C_3N_4, the system showed a notable 6.57-fold increase in catalytic activity, highlighting the significance of electronic structure engineering in overcoming matrix-induced constraints.[204] These results demonstrate that efficient mycotoxin detoxification in actual food systems necessitates both increased catalytic activity and logical material design that can operate under challenging matrix circumstances.

Present food-safe mitigation methods involve surface passivation using food-grade polyethylene glycol (PEG) or zwitterionic coatings, which efficiently minimize protein adsorption without adding harmful residues. Moreover, employing metal-organic frameworks (MOFs) or covalent organic frameworks (COFs) for shell encapsulation provides steric hindrance against larger macromolecular contaminants, allowing the selective penetration of

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small molecule toxins via size-specific porosity. Additionally, using magnetic separation along with mild alkaline washing at a pH of 8-9 and at room temperature between cycles can aid in restoring surface activity while maintaining the structural integrity of the nanozyme architecture, leveraging Fe_3O_4-based hybrids.[205] To substantiate claims of industrial preparedness, it is advisable that upcoming research emphasize standardized multi-cycle activity testing performed within the applicable food matrix rather than utilizing buffer solutions.

5.1 Mechanistic basics of matrix effects

There are various physicochemical and biological effects within food matrices that influence the behavior of contaminants. These pollutants can attach to food components either covalently or non-covalently. Phenolic compounds can engage with proteins and dietary fibers, thereby diminishing their release within the digestive system and changing their bio-accessibility. These interactions may entrap toxins within the food matrix, influencing the quantity accessible for absorption or metabolism. The availability of compounds, whether mechanical or enzymatic, is affected by the structure of the food matrix, like whole plant cell walls or emulsified fat droplets. For fish, the complete matrix structure has demonstrated its ability to delay the stomach's emptying of lipids and influence the postprandial bioavailability of long-chain omega-3 fatty acids relative to unstructured oil, emphasizing the important function of matrix structure in transport and release dynamics.[206,207]

Within the gastrointestinal system, the food matrix considerably influences luminal factors like pH, bile salt levels, and enzymatic activity, which subsequently affect transporters and metabolic enzymes in the mucosal layer. The existence or lack of dietary fats, carbohydrates, and proteins can impact micelle development, transporter activity, and the enzymatic breakdown of simultaneously ingested toxins. Moreover, the structure of food matrices influences the speed at which food moves through the gastrointestinal tract, thus altering the interaction of harmful compounds with digestive and microbial enzymes. The gut microbiota significantly influences interactions with food matrices and toxic substances, resulting in biotransformation or detoxification activities. Investigation into how polyphenols and fermentable fiber interact, along with their resulting bioactivity, has been influenced by microbial metabolism.

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Matrix effects are essential in determining the release of mycotoxins and other environmental contaminants from food and their subsequent detoxification. The food matrix can either promote or hinder the bio-accessibility of hydrophobic contaminants. The matrix's composition can greatly influence microbial detoxification mechanisms. Acknowledging these matrix effects has led regulatory bodies to consider actual dietary exposures and matrix interactions in their risk evaluations. Existing frameworks highlight the importance of incorporating bio-accessibility and matrix factors into contaminant risk assessments to improve public health safety and diminish uncertainties in exposure calculations. Moreover, matrix effects are essential not just for physiological results but also for the analytical identification of toxins. In mass spectrometry quantification techniques like LC-MS/MS, co-eluting matrix elements can either hinder or boost the ionization of target analytes, resulting in erroneous quantification and possibly deceptive conclusions about exposure or detoxification effectiveness. Thus, thorough method validation needs to incorporate evaluations of matrix suppression or enhancement along with extraction efficiency.

5.2 Collateral oxidation and nutrient deterioration during photocatalytic detoxification

5.2.1 Non-selective nature of ROS in complex food matrices

Reactive oxygen species, which are essentially non-selective oxidants, are produced by photocatalytic platforms, mainly hydroxyl radicals, superoxide anion radicals, and valence band holes (h^+).[208] The absolute molar concentration of oxidizable co-substrates (polyunsaturated fatty acids, tocopherols, carotenoids, proteins containing oxidizable thiols, and aromatic residues) greatly surpasses the mycotoxin concentration by many orders of magnitude in a complex matrix such as whole grain or crude oil. The large excess of oxidizable matrix constituents increases competition for ROS and may reduce the fraction of reactive species available for mycotoxin degradation.

5.2.2 Quantitative evidence on nutrient loss vs. toxin removal

Relevant standards are provided by atmospheric cold plasma (ACP), which functions via a mechanistically similar ROS-mediated route. ACP effectively degrades aflatoxins, DON, ZEN, OTA, fumonisins, and T-2 toxin in grain matrices as reported in literature[125] But of all plasma species, lipids are "the most sensitive to oxidation" because of •OH-mediated H-abstraction from

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unsaturated carbon bonds, which starts lipid peroxidation chain reactions, as demonstrate by Hojnik et al. (2017).[209] Although photocatalysis and ACP differ in ROS generation pathways, both rely heavily on highly reactive oxidative species and therefore face similar selectivity challenges.

TiO_2-based photocatalytic systems have demonstrated substantial AFB_1 degradation efficiency, often exceeding 80% in both model and food-related matrices. Nonetheless, the reactive oxygen species generated during treatment may induce the oxidation of unsaturated lipid constituents in oil-based systems, potentially leading to the formation of secondary oxidation products such as aldehydes and hydroperoxides. Nonetheless, studies evaluating mycotoxin removal and lipid degradation simultaneously, are limited. Over 90% of the patulin in the simulated apple juice is removed by photodegradation, but as byproducts, tiny organic acids, aldehydes, and furans are produced,[210] each of which has a unique toxicological and organoleptic character. Beta-carotene and fat-soluble vitamins (A, D, E, and K) are especially reactive to $^{\bullet}OH$ and singlet oxygen produced under UV-photocatalytic conditions.[211]

Despite multiple laboratory studies demonstrating high degradation efficiencies for AFB_1, DON, ZEN, OTA, and patulin (surpassing 80-95%), quantitative assessments of nutrient degradation remain limited. Few studies simultaneously evaluate mycotoxin removal in conjunction with lipid oxidation indicators (peroxide value, TBARS, MDA), protein oxidation markers (carbonyl content), vitamin retention, and sensory characteristics. Consequently, the balance between detoxification effectiveness and the preservation of nutritional quality is insufficiently defined. This knowledge gap significantly hinders the practical implementation of photocatalytic detoxification technologies in complex food matrices, such as whole grains, nuts, and edible oils.

6. Analytical validation of detoxification

The existence of various mycotoxins in tainted food can result in additive or synergistic toxic impacts. Due to the intricate nature and variety of food matrices, combined with the strict regulatory requirements established by food safety organizations, it is crucial to utilize analytical tools capable of accurately detecting and measuring different mycotoxins in food items, as shown in **Fig. 14**. A thorough evaluation of different mycotoxins is crucial for accurately assessing risks, ensuring food safety, offering legal protections, and protecting public health.[212]

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Dependable and uniform documentation of degradation performance is crucial for the analytical validation of mycotoxin detoxification research. These studies must at least encompass the measurement of parent compound degradation using LC-MS/MS, total organic carbon (TOC) removal for insights into mineralization, verification of transformation products with high-resolution mass spectrometry (HRMS), and a preliminary structural safety assessment of identified products employing in silico toxicity prediction methodologies.

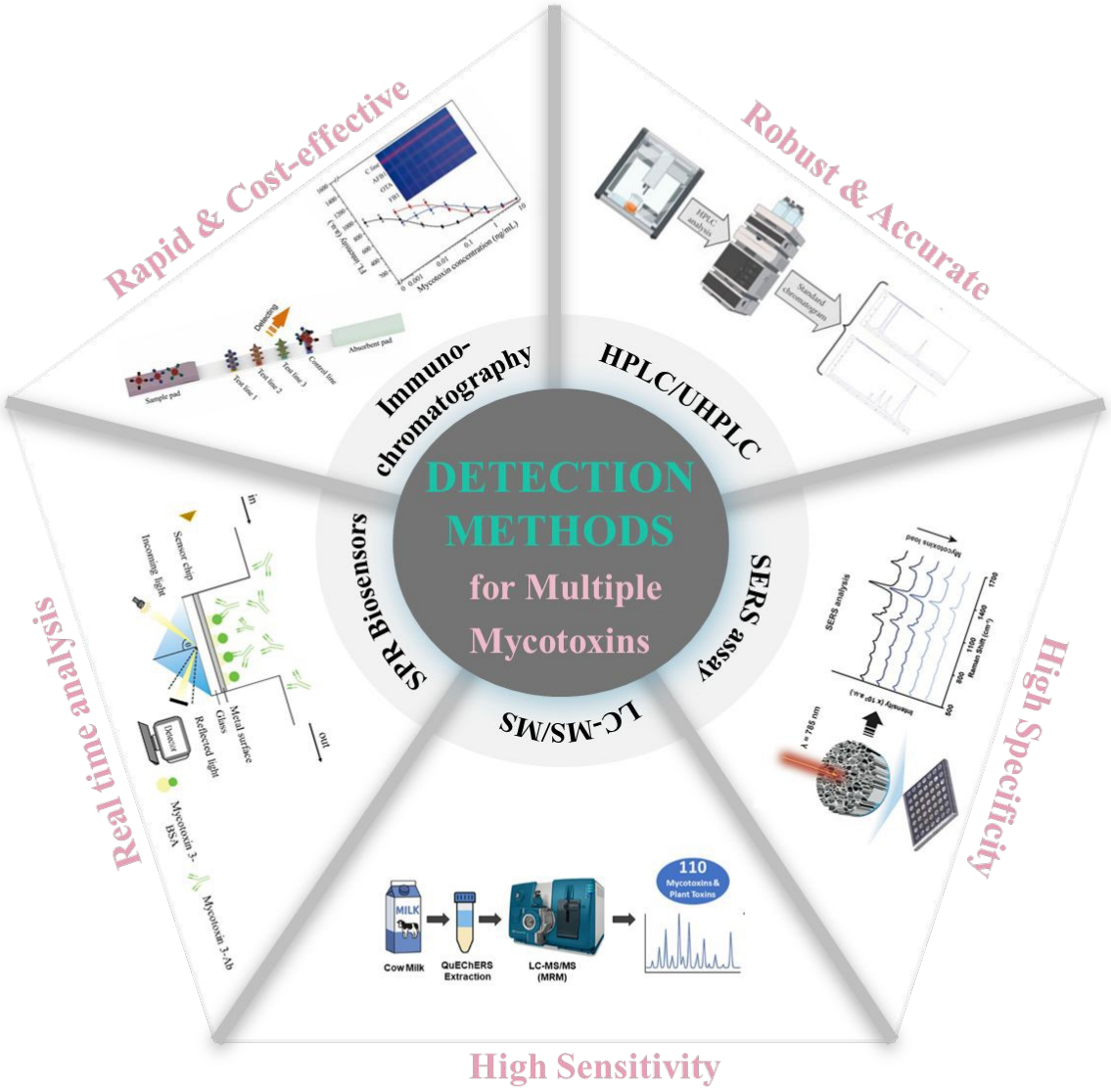

Fig 14: Detection methods for multiple mycotoxins.

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6.1 Liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS)

This method employs liquid chromatography to differentiate co-eluting mycotoxins by taking advantage of slight variations in their physicochemical characteristics, whereas tandem mass spectrometry provides excellent sensitivity and selectivity. The process starts with the ionization of the analyte, usually through electrospray ionization (ESI), followed by a two-stage mass analysis (MS1 and MS2) that produces intricate fragmentation patterns for accurate identification and quantification. This approach is especially beneficial for examining intricate matrices, including medicinal plants, grains, and processed foods, where different mycotoxins can exist together and possibly interact to increase toxicity.[213] LC-MS/MS enables the concurrent identification of multiple mycotoxins in a single analytical process, improving thorough risk evaluation and ensuring adherence to regulatory requirements. Nonetheless, the substantial expenses linked to LC-MS/MS systems, such as the initial capital, continuous upkeep, and the specialized knowledge needed for operation, can pose major obstacles. Additionally, the sensitivity of these systems can be influenced by matrix effects found in intricate food samples, underscoring the necessity for thorough sample preparation and method validation procedures.[202]

6.2 High and Ultra-High-Performance Liquid Chromatography (HPLC/UHPLC)

The advent of HPLC and its improved version UHPLC has greatly enhanced the examination of various mycotoxins. These technologies improve resolution, shorten analysis durations, and boost sensitivity. Significantly, UHPLC uses columns with particles smaller than 2 μm at elevated pressures, enhancing separation efficiency while reducing solvent usage and time. When combined with high-resolution detectors, both HPLC and UHPLC, in conjunction with high-resolution mass spectrometry (HRMS) enable accurate quantification of mycotoxins even at trace levels.[214] These systems significantly reduce the risk of false positives by enabling accurate mass measurements that distinguish closely related compounds. However, the cost of the UHPLC systems and the requirement for highly specialized technical expertise pose challenges for their widespread adoption in less-equipped laboratories.

6.3 Immunochromatographic Assays (ICA)

Lateral flow assays (LFAs), also known as immunochromatographic assays, have become quite popular for preliminary mycotoxin screening in the field due to their affordability, ease of use,

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and fast results. These assessments leverage the specificity of antigen-antibody interactions, enabling the rapid identification of target mycotoxins, such as AFB1, OTA, and ZEA, within minutes. Recent technological advancements have improved their use by creating multiplexing systems capable of identifying several mycotoxins in one test. Due to their strengths, ICAs are qualitative or semi-quantitative, which limits their ability to offer the strict quantitative metrics necessary for regulatory compliance. Typically, they are not as sensitive as more sophisticated chromatographic or mass spectrometric techniques, and problems like antibody cross-reactivity and matrix interferences can compromise the assay's specificity and accuracy. Consequently, while ICAs are ideal for swift, on-site evaluations and preliminary choices, further analysis with more sophisticated methods is often necessary to back a comprehensive risk assessment and measurement.[215]

6.4 Surface Plasmon Resonance (SPR) Biosensors

SPR is a label-free optical method of sensing biomolecular interactions in real time by monitoring slight variations in refractive index at the interface between a metal-coated sensor surface. SPR biosensors have proven helpful in detecting mycotoxins in complex matrices and for simultaneously detecting multiple targets, including corn and wheat. This method provides major benefits, such as removing extra labeling reagents, which simplifies sample preparation and minimizes variability in assays. The primary function of SPR biosensors includes the attachment of particular bioreceptors, like antibodies or aptamers, to a sensor chip. Upon introducing a sample with mycotoxins, the binding interactions on the sensor surface lead to a change in the resonance angle, enabling immediate and accurate assessment of the analyte. This ability for immediate detection is especially advantageous for high-throughput screening and on-site assessments, where rapid results are essential.[216] Nevertheless, obstacles still exist in utilizing SPR technology for mycotoxin studies. Complicated food matrices may cause nonspecific binding, leading to false positives or reduced assay sensitivity. Moreover, cross-reactivity in antibodies raises further issues, requiring precise optimization of sensor surface chemistry and thorough validation to guarantee specificity and accuracy. Upcoming innovations in sensor design, such as improved surface functionalization and integration with microfluidic systems, are anticipated to overcome these challenges and enhance the effectiveness of SPR for thorough multi-analyte detection.

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6.5 Surface-Enhanced Raman spectroscopy (SERS)

SERS synergistically merges the molecular fingerprinting ability of traditional Raman spectroscopy with the signal enhancement provided by metallic nanostructures, typically consisting of gold or silver nanoparticles. This advancement allows for the identification of mycotoxins at extremely low concentrations; thus, SERS presents itself as a valuable tool for food safety assessments. It is useful for the concurrent analysis of mycotoxins like AFB1, ZEA, and OTA in corn, showcasing its strong suitability for multiplexed analysis.[217] The primary advantages of SERS involve rapid analysis durations, often achievable within seconds or minutes, and preservation of sample integrity, made feasible through low-power lasers. The advantages are also useful, especially in scenarios where high throughput and constrained sample processing are major issues. The reproducibility of nanoparticle synthesis and the uniformity of the substrate, however, make SERS performance dependent. Variations in the size, shape, and distribution of nanoparticles can result in uneven signal enhancements, complicating the quantification process. Moreover, food matrices may pose difficulties in adhering to the enhancing surface, resulting in matrix interferences and lower sensitivity.[218,219] To address these challenges, it is crucial to improve substrate fabrication, involving the creation of more uniform engineered nanostructures and enhanced sample-preparation methods. These enhancements will bolster the strengths, dependability, and analytical abilities of SERS for detecting multiple mycotoxins across a variety of foodstuffs.

6.5.1 Comparative assessment and method selection considerations

For the detection of mycotoxins at trace levels, liquid chromatography-mass spectrometry (LC-MS/MS) is the gold standard since it is more sensitive, specific, and dependable than HPLC.[213] Mycotoxins with various chemical structures are being effectively quantified simultaneously using this method in a single run.[220] However, its usage in quick or field-based applications is limited by its high cost, significant sample preparation, and need for trained operators. The first official methodology for the detection of T2 and HT2 mycotoxins in cereals and cereal products, as well as N in edible vegetable oils, was released by the European Committee for Standardization (CEN). Numerous investigations have reported using the LC/MS-MS approach

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to determine multimycotoxins, including 35 mycotoxins in pharmaceutical matrices, 12 fusarium mycotoxins in beer,[221] and 17 distinct mycotoxins in barley and malt.[222]

Biosensors in the food sector provide considerable benefits in lowering mycotoxin levels by enabling quick, straightforward, and cost-effective sample assessment. These instruments guarantee consistency, reliability, and precision, while also facilitating on-site sample testing, thus improving food safety and quality management.[223, 224] Recent developments in the application of biosensors for food mycotoxin detection have been reported by Oliveira et al.[225] Mycotoxin detection mostly uses optical (surface plasmon resonance, or SPR and fluorescence), piezoelectric (quartz crystal microbalance, or QCM), and electrochemical (impedimetric, potentiometric, and amperometric) transducers.[226] Peptides, enzymes, antibodies, cells, and nucleic acids are common recognition elements; however, aptamers, molecularly imprinted polymers, and recombinant antibodies can also be employed. To increase the biosensor's sensitivity, metal nanoparticles, carbon nanotubes, and nanofibers are promising options. These materials are biocompatible and possess unique physicochemical properties.[227] However, matrix effects, inadequate long-term stability, and fluctuations in biorecognition element activity in real dietary situations can influence biosensor performance.

Optical biosensors are recognized for their sensitivity, specificity, and affordability, providing the benefit of direct detection. Among the commonly used techniques in this area are surface plasmon resonance (SPR) and fluorescence resonance energy transfer (FRET). SPR is recognized for its quick and sensitive outcomes. This method allows detection without labels and facilitates both qualitative and quantitative analysis of multiple contaminants simultaneously in real-time.[228] SPR-based biosensors have been evaluated for AFM_1 in milk[229], OTA in coffee [230], and DON, ZEN, and T-2 toxin in wheat. A relative standard deviation (RSD) of 2.81% was found for zearalenone.[231]

Surface enhanced-Raman spectroscopy (SERS) has attracted significant attention in recent years as a robust analytical technique for identifying mycotoxins, due to its remarkable specificity, narrow bandwidth, resistance to photobleaching, non-invasive nature, and capacity to enable multiple detections with a single laser wavelength for excitation.[217, 232] In recent years, SERS has been investigated as a mycotoxin detection method.[233,234] However, many of these studies utilized complicated SERS-active substrate fabrication, requiring specialized expertise

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and sophisticated equipment, limiting accessibility for wider audiences and uses. Moreover, those that focused on more readily available SERS substrates either relied on secondary labeling with a Raman reporter molecule[235] or targeted the identification of specific mycotoxin types.[236] Aflatoxin B1, zearalenone, and ochratoxin A are some of the mycotoxins frequently detected in corn, as shown in **Fig. 15**. Gabbitas et al., devised a fast, label-free SERS method that allows for the concurrent detection of these three mycotoxins. The distinct Raman spectra of each mycotoxin act as unique chemical signatures, enabling their easy differentiation. The detection limits for AFB1, ZEN, and OTA were set at 10 ppb (32 nM), 20 ppb (64 nM), and 100 ppb (248 nM) in corn, respectively. Additionally, concentrations of AFB1, ZEN, and OTA reaching 1.5 ppm (4.8 μM) were precisely oredicted via multivariate statistical analysis of the SERS spectra from established concentrations, resulting in correlation coefficients of 0.74, 0.89, and 0.72. All analyses were finished in less than 30 minutes, suggesting that label-free SERS paired with multivariate analysis offers a promising method for the quick and concurrent identification of mycotoxins in maize, with possible uses for different types of mycotoxins and other crops.[217]

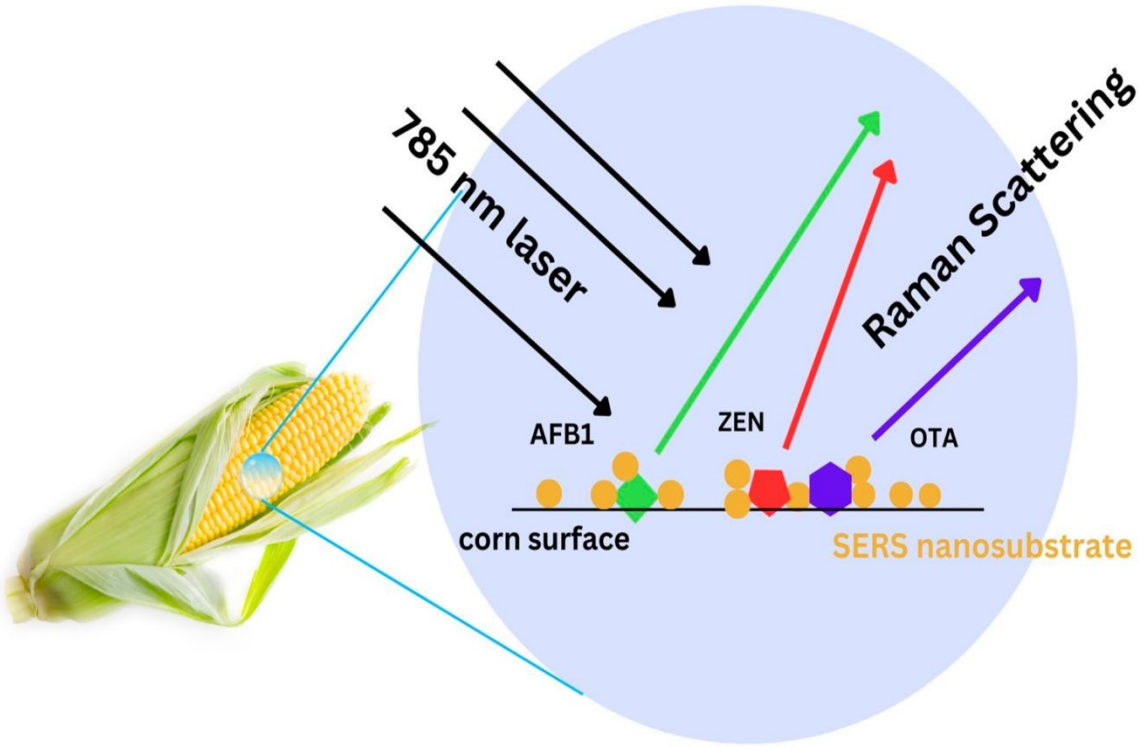

Fig 15: Diagrammatic representation of the established method for identifying mycotoxin analytes (such as AFB1, ZEN, and OTA) on maize; the agricultural crop (corn) was treated with

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SERS nanosubstrate and briefly combined with mycotoxins that were present on its surface. A Raman microscope with a 785 nm laser was used to collect Raman spectrum data. This figure has been adapted from ref.[217] with permission from mdpi, copyright 2023.

Practically, SERS is preferred for quick, high-sensitivity screening, LC-MS/MS is best for confirmatory and regulatory analysis, and biosensors work well for portable, real-time monitoring. Therefore, the most dependable and thorough analytical framework for mycotoxin detection in complex food systems is provided by combining fast screening methods with LC-MS/MS validation. **Table 4** presents comparison of various detection methods.

Table 5. Comparison of detection methods based on performance, limitations, and application potential.

Detection method	Pros	Cons	Applicability
LC-MS/MS (liquid chromatography-mass spectrometry)	Minimal sample preparation, highly sensitive and specific, capable of analyzing several mycotoxins at once	Expensive, complicated, requiring highly qualified specialists, and requiring a lot of maintenance	Regulatory compliance and confirmatory analysis
Biosensors	Quick and instantaneous findings, portability and user-friendliness, and field-testing potential	Calibration drift, matrix interference, and limited stability	Early warning systems and field monitoring

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6.6 Advanced tools for transformation pathway elucidation

Due to its high mass accuracy and capacity for retrospective data interpretation, high-resolution mass spectrometry (HRMS), specifically LC-QTOF-MS and LC-Orbitrap-MS, are presently the mainstay for non-targeted screening and identification of unknown transformation products.[237] In complex matrices like grains and edible oils, an extra separation dimension based on collision cross section (CCS) improves isomer discrimination and increases confidence in structural annotation of co-eluting degradation products when combined with ion mobility spectrometry (IMS-HRMS).[238]

Nuclear magnetic resonance (NMR) spectroscopy continues to be an essential method for conclusive structural verification, especially in clarifying bonding changes and confirming detoxification byproducts. Still, its use is restricted because it requires a fairly high level of sample purity and concentration, making it less appropriate for examining trace levels of transformation products without previous isolation or enrichment.[239]

Techniques like LC-MS/MS-based targeted metabolomics are commonly employed to measure known degradation intermediates; however, their reliance on reference standards limits their ability to identify new or unforeseen products. On the other hand, non-targeted methods based on HRMS enable wider detection but encounter issues with data complexity, false positives, and a lack of validated spectral libraries for mycotoxin transformation products.[240] Even with progress in these fields, major challenges persist. The comprehensive requirements for sample preparation, data processing, and the need for manual spectrum interpretation in non-target analysis workflows limit throughput, while ion suppression effects may reduce sensitivity in intricate food matrices. Moreover, the combination of IMS-HRMS and NMR is not commonly found in commercial or regulatory labs because of high expenses, restricted instrument access, and an absence of established procedures. Thus, the most successful method for clarifying the mechanistic pathways of mycotoxin degradation in sophisticated detoxification systems is seen as a hybrid analytical strategy that combines LC-HRMS/IMS for screening, LC-MS/MS for quantification, and NMR for structural verification.

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7. Challenges and Future Perspectives

Progress has been made in developing innovative green technologies for mycotoxin detoxification; nonetheless, many scientific, technological, and regulatory hurdles persist that need to be addressed for broad implementation in food systems. This signifies a notable void in the existing field of green detoxification research. An honest assessment shows that closing the carbon mass balance is rarely achieved, and the toxicological assessment of transformation products (TPs) is not regularly performed in the field.

7.1 Carbon mass balance: current state of the art

The reduction of parent mycotoxin, usually quantified by a decrease in chromatographic peak area, continues to be the principal performance parameter in the majority of photocatalytic, plasma-assisted, and enzyme-mediated detoxification research. The absence of the parent poison does not inherently signify total mineralization or detoxification. In numerous instances, only a limited number of transformation products (TPs) are identified. Moreover, thorough carbon mass balance analyses are infrequently conducted. As a result, the proportion of the original carbon poison that can be reliably attributed to recognized products is frequently ambiguous, especially when employing targeted LC-MS/MS techniques. The residual carbon may exist as uncharacterized low-molecular-weight molecules, highly polar entities that evade standard detection, matrix-bound residues, or, less frequently, mineralization products like CO_2.[241]

Loi et al.[70] reported that the oxidation of AFB1 by laccase yields numerous detectable products, such as AFQ1, epi-AFQ1, AFB1-8,9-dihydrodiol, AFB1-dialdehyde, AFB2a, and AFM1. The importance of profiling transformation products (TP) goes beyond mere theoretical curiosity, as demonstrated by the observation that while AFQ1 and epi-AFQ1 are markedly less toxic than AFB1, AFM1 still possesses significant hepatocarcinogenic traits, being roughly ten times less effective than AFB1. It is also significant that the total molar yield of all detected compounds seldom surpasses 70-80% of the theoretical yield, indicating the existence of unmeasured carbon, which might encompass bioactive compounds.

7.2 Toxicological profiling: current practice vs. required standard

Most detoxification studies fail to consistently perform toxicological profiling of TPs. Existing approaches mainly utilize structural alert databases and Ames test-predictive QSAR models, like

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Derek Nexus and TIMES, for in silico assessments of genotoxicity. Furthermore, in vitro cytotoxicity tests such as MTT, neutral red, and comet assays are used to evaluate genotoxicity, and high-resolution non-targeted mass spectrometry (HRMS, Orbitrap) aids in the untargeted discovery of unforeseen products. The study by Alonso-Jauregui et al.,[242] showed that combining SOS/umu assays with structural alerts is effective for prioritizing genotoxicity, effectively differentiating genotoxic mycotoxins like AFB1 and sterigmatocystin from non-genotoxic compounds such as DON, OTA, and ZEA. Additionally, the dependability of risk assessments significantly improves when LC-MS and infrared ion spectroscopy (IRIS) are used to distinguish isomeric TP candidates prior to performing in silico toxicity assessments.[243].

7.3 Life cycle assessment (LCA) and scalability considerations of green detoxification technologies

The term "green" warrants careful consideration, particularly when analyzed through extensive life cycle data. Currently, there is a significant lack of validation for the asserted environmental advantages of detoxification systems utilizing nanozymes, metal-organic frameworks (MOFs), or photocatalysis, since comprehensive cradle-to-grave life cycle assessments for these technologies have not been published.[244] Research from current studies on nano-enabled technologies shows that aspects like material synthesis, solvent application, heat activation, catalyst immobilization, and energy demands for photocatalysis can significantly increase the total environmental footprint.[245] As a result, the lack of comprehensive assessments focused on these detox systems creates a considerable void in verifying their "green" character.[244] Based on data from nano-enabled technologies, the total environmental footprint can be greatly increased by material production, solvent consumption, heat activation, catalyst immobilization, and photocatalytic energy demand.[246] Current evidence from the comprehensive literature on nanotechnology and advanced oxidation indicates that material synthesis, solvent use, thermal activation, catalyst immobilization, reactor design, energy requirements, catalyst regeneration, and end-of-life disposal substantially influence the overall environmental impact.[247]

Additionally, scalability is often overlooked. Most published studies are conducted at laboratory or pilot scale, with sample sizes ranging from grams to kilograms, even though global grain production exceeds several billion tons annually. Cumulative energy demands, catalyst effectiveness, water consumption, material loss, and waste management are vital issues in

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sustainability at these levels. Without techno-economic analyses and thorough life cycle assessments considering industrial-scale operations, it is unclear if these technologies will maintain their environmental advantages when used at the scales required for commercial grain processing.[248]

Although these technologies are commonly labelled as "green" due to their operation under mild conditions and reduced need for harsh chemicals, this label should be considered tentative. Future research must incorporate life cycle assessments in accordance with ISO 14040/14044, techno-economic analyses, catalyst fate investigations, and the principles of Safe-and-Sustainable-by-Design. These extensive evaluations will facilitate a detailed comparison of new detoxification technologies against traditional methods such as thermal treatment, ozonation, and biological fermentation.

7.4 Technology readiness levels and scale-up constraints

A crucial assessment of the gap between laboratory proof-of-concept and industrial use is demonstrated through the assignment of Technology Readiness Levels (TRLs). Existing research suggests that the majority of photocatalytic and nano-assisted detoxification systems are still in initial phases of development. In particular, MOF-derived adsorption-photocatalysis and adsorption-biocatalysis hybrids are typically categorized within TRL 2-3, suggesting they are at the proof-of-concept phase. Conversely, semiconductor photocatalysis and magnetic nanohybrid systems are located at TRL 3-4, indicating a stage of laboratory testing. Simultaneously, cold atmospheric plasma systems have advanced, reaching TRL 4-5, as shown by multiple documented pilot-scale studies on grain treatment.[249,250] A major engineering hurdle for photocatalytic systems is the restricted light penetration in opaque particle grain structures. In grains and flour, UV/visible photons can penetrate only micrometers to millimeters deep, limiting photocatalytic action to the surface and possibly leaving internalized mycotoxins unaddressed.[249]

In addition to reactor design, challenges in its scaling up are intensified by the differences between lab testing conditions and actual grain-processing environments. Research usually employs pure mycotoxins in buffered solutions or simplified food models; however, industrial grain streams are made up of heterogeneous particulate systems that encompass dust, proteins,

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lipids, and other competing elements. Elements like mass transfer constraints, matrix shielding impacts, uneven catalyst distribution, and the erratic placement of toxins can greatly hinder detoxification effectiveness in real-world operating scenarios. Therefore, demonstrating the efficacy of these technologies at both pilot and industrial levels is crucial for advancing them beyond existing Technology Readiness Levels.[250]

7.5 Machine learning: from predictive modeling to mechanistic understanding in mycotoxin detoxification

Instead of offering complete mechanistic explanations, the majority of machine learning applications in mycotoxin prediction and nanozyme design are now mostly correlative and rely on pattern recognition from comparatively small and heterogeneous datasets.[251] For instance, hybrid deep-learning models outperform traditional mechanistic models in terms of prediction accuracy for AFB_1 contamination; nevertheless, they often serve as "black-box" predictors that do not clearly identify causative biochemical processes.[252] Nonetheless, new research is starting to connect mechanism and prediction. ML combined with DFT calculations has produced testable hypotheses in nanozyme research that link catalytic activity to particular coordination environments and surface defects. These hypotheses can be experimentally verified using spectroscopic methods.[253,254] Similar to this, catalytic degradation pathways for several mycotoxins have been suggested by AI-assisted enzyme screening in conjunction with molecular docking, and these pathways have subsequently been confirmed through experimental validation.[255] We concur that the absence of sizable standardized datasets, a lack of multi-omics and real-food operational data, inadequate FAIR data reporting, and inadequate integration of causal modeling techniques are the main obstacles to explanatory AI.

7.6 Regulatory safety and GRAS (Generally Recognized as Safe) pathway for food-grade nanomaterials

Research on engineered nanomaterials in food-contact uses have demonstrated that under certain processing and storage circumstances, nanoparticles may migrate and metal ions can be released. Different factors, such as pH levels, temperature, ionic strength, food makeup, and exposure time, significantly influence the behavior of this migration. Significantly, leaching is heavily influenced by acidic pH, temperature, and moisture, which promote processes like diffusion,

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surface erosion, and particle detachment.[256] Since there is no physical barrier preventing nanoparticle-food contact, this is especially important for nanozyme systems that are directly administered in liquid food matrices. Furthermore, under food-relevant settings, MOF-based systems may emit partially degraded organic linkers and metal ions (such as Fe^{3+}, Cu^{2+}, and Zr^{2+}), creating unresolved chronic exposure concerns.[256] Because of their slow disintegration and limited biodegradation, nanomaterials have a protracted environmental persistence, and current life cycle assessment (LCA) frameworks do not adequately characterize their environmental destiny. Safe and Sustainable by Design (SSbD) guidelines specifically acknowledge this uncertainty as a critical risk component that needs to be assessed before implementation.[245] Crucially, there are currently no GRAS approved nano- enabled photocatalytic, MOF, or nanozyme based food detoxification systems. Regulatory approval will likely require an extensive safety file that includes migration studies, toxicokinetic evaluations, genotoxicity assessments, repeated-dose toxicity studies, environmental risk evaluations, and exposure modeling in applicable usage scenarios. Clearly, the main obstacle in the actual application of these technologies is fulfilling regulatory standards rather than their catalytic effectiveness.

7.7 Industrial scalability and safety of degradation products

A significant obstacle to the industrialization of laboratory-scale detoxification systems is the discrepancy between high-efficiency bench-scale performance and real-world processing conditions, where scalability, energy demand, and product safety become crucial considerations. For the industrial-scale decontamination of grains and feed ingredients, recent studies on non-thermal dielectric barrier discharge (DBD) cold plasma systems have showed tremendous potential. These systems are suitable for continuous or semi-continuous processing environments because, under ideal conditions, they may eliminate important mycotoxins like aflatoxin B_1 and deoxynivalenol by more than 80-100%.[257] Photocatalytic and adsorption-photocatalysis systems can break down mycotoxins in edible oils and real food systems with an efficiency of 75-90%, according to similar studies on food-relevant matrices. However, performance is significantly impacted by catalyst recovery, mass transfer limitations, and matrix complexity, indicating that more engineering improvement is required for large-scale implementation.[258]

New findings indicate that the reliability of detoxification methods cannot be trusted without carefully assessing the safety of the byproducts created from degradation. Employing

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LC-MS/MS for monitoring metabolites in conjunction with in vitro tests for cytotoxicity and mutagenicity shows that partial mineralization may result in intermediate transformation products with unclear biological effects. While different photocatalytic and non-thermal techniques have demonstrated a substantial reduction in the toxicity of original mycotoxins, research suggests that the degradation products of aflatoxin, for example, could be less hazardous than the parent molecule. However, thorough toxicological validation through biochemical and cellular assessments is crucial before any real-world use.[259] Together, these findings demonstrate that future industrial adoption of green detoxification technologies must include scalable process design, catalyst reusability, and comprehensive toxicological assessment of degradation by-products in order to ensure food safety, regulatory compliance, and sustainable deployment.

A variety of photocatalytic, plasma, and nano-enabled techniques are still undergoing evaluation at laboratory or pilot scales, posing significant difficulties for scalability and application in industry. Commercialization involves creating continuous-flow reactors, plasma setups, and light-delivery systems that are affordable, energy-efficient, and suitable for current food-processing equipment. Another significant challenge is validation in complex, real-world food matrices. Most published studies utilized artificially spiked commodities or model solutions that fail to accurately reflect the variability, moisture levels, fat-protein interactions, and shielding effects present in real foods. These matrix influences can hinder process management and greatly diminish detoxification effectiveness. To guarantee robustness and reproducibility, thorough analysis across various food categories, including grains, nuts, dairy items, oils, and processed foods, is essential.

Regulatory acceptance and safety evaluation are equally significant challenges. Although the goal of green technology is to reduce secondary pollution, residual toxicity remains a concern due to the development of unknown or poorly described degradation products. Achieving high mycotoxin selectivity in complex food matrices without sacrificing nutritional quality is a major unresolved challenge. Therefore, more selective photocatalytic systems, visible light-active and surface-engineered catalysts, and integrated analytical frameworks that can concurrently monitor toxin breakdown and nutrient preservation would be needed for future industrial translation.[203, 213]

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It is crucial to conduct a thorough toxicological study that includes bioavailability assessments, chronic exposure tests, and metabolomic analysis of breakdown byproducts. To satisfy regulatory and consumer safety requirements, it is also necessary to thoroughly evaluate the possible migration, permanence, or accumulation of nanomaterials in food systems. Long-term stability, reusability, and selectivity of photocatalysts, nanozymes, and adsorbents remain challenging from a materials standpoint, especially under harsh processing conditions and frequent applications. Factors such as reduced enzyme activity, fouling from food components, and catalyst deactivation can limit operational longevity. To improve durability and specificity for target mycotoxins, advanced materials engineering techniques such as encapsulation, bioinspired catalyst design, and surface functionalization are required. In the future, integrated and hybrid detoxification platforms offer compromising options. By combining cold plasma with photocatalytic or enzymatic systems, it is possible to reduce treatment time and energy consumption while utilizing synergistic formation of reactive species. Similarly, adsorption-biocatalysis systems can be designed to minimize unwanted reactions with food ingredients by selectively capturing and regulating enzymatic transformation. These multipurpose platforms align with the principles of sustainable food processing and green chemistry.[125-129, 205]

Finally, future research should concentrate on challenges related to sustainability and the circular economy, such as the utilization of low-cost, renewable, or waste-derived materials for catalyst synthesis, energy-efficient processes powered by renewable resources, and life-cycle assessments to quantify environmental benefits. It will require interdisciplinary cooperation among materials scientists, food technologists, toxicologists, and regulatory authorities to transform next-generation green detoxification technologies from the laboratory into safe, scalable, and internationally applicable food safety solutions.

Figure 16 illustrates the interdisciplinary framework proposed in this review for sustainable mycotoxin management. The image links climate-related pollution issues with innovative green detoxification technologies, enhanced methodology for characterizing transformation products, and AI-supported predictive tools. The integration of these components results in the creation of selective, efficient, and environmentally sustainable methods to decrease mycotoxin risks in food systems.

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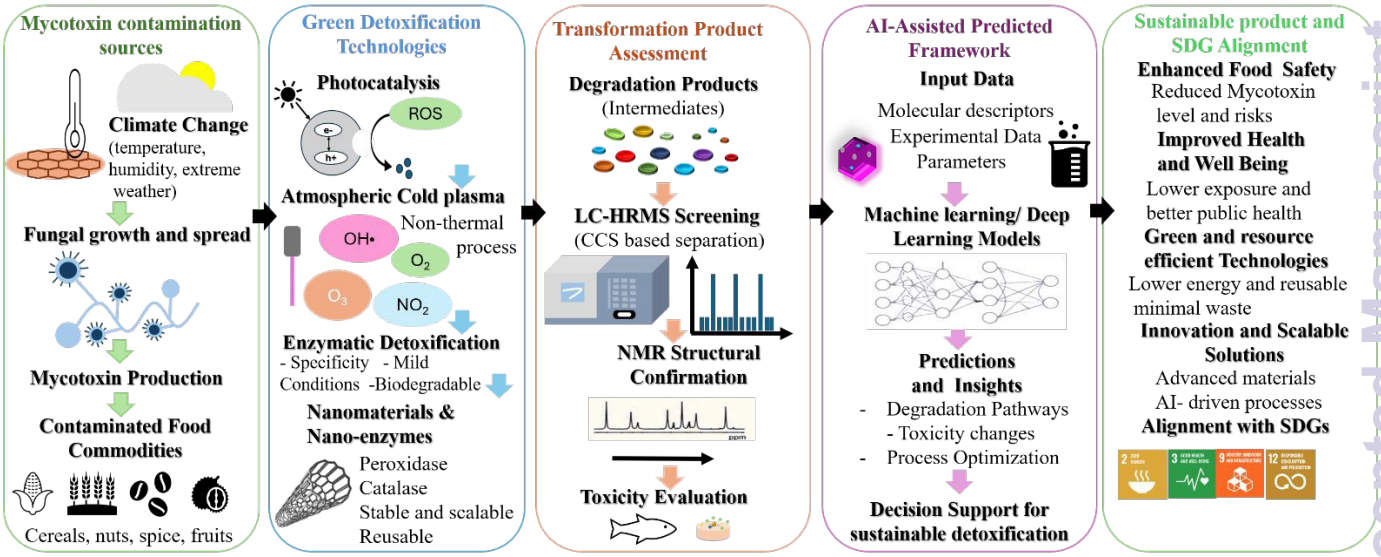

Fig. 16: Comprehensive framework for sustainable mycotoxin management employing environmentally friendly detoxification techniques, advanced analytical instruments, and AI-assisted predictive algorithms.

8. Conclusion

The detoxification of mycotoxins is undergoing significant advancement due to the emergence of next-generation green technologies that offer non-thermal and potentially more sustainable alternatives to conventional chemical and thermal procedures. Techniques such as nanoengineered photocatalysis, cold atmospheric plasma, enzymatic degradation, and adsorption-biocatalysis hybrid systems have demonstrated considerable potential in reducing mycotoxin contamination while preserving food quality and minimizing chemical residues. Their adherence to green chemistry principles, utilization of renewable energy, and sustainable food processing highlights their importance for future food safety solutions.

Despite these achievements, several substantial obstacles remain, impeding widespread implementation. Numerous methods are restricted to laboratory or pilot phases, requiring further investigation to address challenges associated with process scalability, treatment consistency,

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catalyst recovery, the intricacies of actual food matrices, and the comprehensive characterization and toxicological assessment of transformation products. Furthermore, governmental approval processes, customer acceptability, and assessments of environmental sustainability are insufficiently analyzed and may considerably influence commercial adoption, perhaps rivaling technical performance.

Future breakthroughs will depend on interdisciplinary collaboration among materials science, food engineering, analytical chemistry, toxicology, data science, and regulatory research. The utilization of advanced analytical platforms, AI-driven prediction instruments, bioinspired catalysts, and multifunctional hybrid detoxification systems may enhance the precision, efficiency, and sustainability of mycotoxin management. Considering the increasing issues presented by climate change and food security related to mycotoxin contamination, the development of scientifically validated, scalable, and environmentally sustainable detoxification technologies will be essential for creating safer and more resilient food systems.

CONFLICT OF INTEREST: Authors declare no conflict of interest.

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Declaration of data availability statement

☒ Data are available within the manuscript in the form of figures and tables. No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.