

Magnetic nanostructured agents for the mitigation of mycotoxins and cyanotoxins in the food chain

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ABSTRACT

Natural toxins, such as mycotoxins and cyanotoxins, can contaminate food and feed, leading to toxicity in humans and animals. This study focused on using nine magnetic nanostructured agents to remove the main types of toxins. Initially, the efficacy of these materials was evaluated in water solutions, revealing that composites with sizes below 3 μm , containing magnetite, activated carbon, esterified pectin, and sodium alginate, removed up to 90% of mycotoxins and cyanotoxins with an adsorption of 873 ng/g. The application of the nanostructures was then assessed in beer, milk, Distillers Dried Grains with Solubles and water contaminated with cyanobacteria. The presence of matrix slightly decreases the adsorption capacity for some toxins. The maximum toxin removal capacity was calculated with cyanotoxins, composites achieved a removal of up to 0.12 mg/g, while nanocomposites (15 μm) reached 36.6 mg/g. Therefore, these findings point out the potential for using nanotechnology in addressing natural toxins contamination.

1. Introduction

Humans and animals are continuously exposed to various natural toxins. These compounds are produced by living organisms such as plants, bacteria, fungi or dinoflagellates, and may pose risks to public health (Nwaji et al., 2022).

Fungi produce a diverse array of secondary metabolites with various biological activities. Among these, mycotoxins are small molecules that provoke toxic responses in humans and vertebrate animals. They are responsible for various health issues, including gastrointestinal, vascular, and kidney disorders, as well as cancer (Dey et al., 2023). The most extensively studied mycotoxins are regulated in the European Union (EU), and include aflatoxins, ochratoxin A (OTA), fumonisins, zearalenone (ZEN), and trichothecenes such as deoxynivalenol (DON), T-2 toxin, and HT-2 toxin. Technological treatments commonly employed in food production often have no effect on mycotoxins,

leading to a carry-over through the food chain. As a result, mycotoxins can be present in processed foods and beverages, including beer, milk, juice, and flours (Pandey, Samota, Kumar, Silva, & Dubey, 2023).

Certain species of cyanobacteria produce cyanotoxins, which are released in large quantities during harmful algal blooms and cause intoxications in both humans and animals. A provisional Tolerable Daily Intake (TDI) has been set for some cyanotoxins, including microcystin LR, (MC-LR), cylindrospermopsin (CYN), and anatoxin-a (ATX-A), by the World Health Organization (WHO), which considered cyanotoxins as an emerging health issue. In addition, the EU has adopted a provisional guideline value of 1 $\mu\text{g/L}$ for MC-LR in drinking water (Abdallah, Van Hassel, Andjelkovic, Wilmotte, & Rajkovic, 2021). In addition, humans may be exposed to cyanobacteria through the ingestion of food including crops irrigated by contaminated water, seafood, aquatic products and freshwater fish (Mutoti, Gumbo, & Jideani, 2022).

Several strategies have been developed to mitigate the effect that

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natural toxins have on the food chain. When dealing with cyanobacterial blooms, techniques like coagulation, sand filtration, or membrane filtration can be applied to eliminate cyanobacterial cells together with their associated intracellular toxins. The removal of dissolved or extracellular cyanotoxins, however, is more difficult (Kulabhusan & Campbell, 2024).

Nanotechnology has also been proposed as a tool to eliminate mycotoxins from liquid matrices like beer. Nonetheless, the agrifood industry is still applying traditional approaches to deal with mycotoxin contamination. Our previous research has shown the effectiveness of various nanomaterials in eliminating mycotoxins, cyanotoxins and marine toxins (González-Jartín et al., 2019, 2020). The primary objective of this new study is to develop novel magnetic nanostructures that further enhance the efficacy of previous ones. We aim to study their application in real matrices, specifically milk, beer, Distillers Dried Grains with Solubles (DDGs), and water contaminated with cyanobacteria.

2. Materials and methods

2.1. Chemicals and reagents

Water was purified using a Millipore Milli-Q Plus system (Millipore, Bedford, MA). Anhydrous MgSO_4 , NaCl, methanol, acetonitrile, and glacial acetic acid (100%) were provided by Panreac Química S.A. (Barcelona, Spain). Ultrafree-MC Durapore membrane centrifugal filters with a pore size of 0.22 μm were sourced from Millipore (Billerica, MA). Formic acid was procured from Merck (Madrid, Spain), C18 from Macherey-Nagel (Düren, Germany), and ammonium formate from Fluka (Buchs, Switzerland).

Standards including DON, ZEN, FB_1 , and roquefortine C (RC) were

acquired from Sigma (Madrid, Spain), while certified reference materials of OTA, AFB_1 , AFB_2 , AFG_1 , AFG_2 , MC-LR, MC-RR, MC-LY, MC-LF, nodularin (NOD), CYN and ATX-A were obtained from Cifga (Lugo, Spain). Aflatoxin M_1 (AFM_1), deepoxy-deoxynivalenol (DOM-1), hydrolyzed fumonisin B_1 (Hydro- FB_1), T-2 toxin, beauvericin (BEA), enniatin A (ENNA), enniatin A_1 (ENNA_1), enniatin B (ENNB), enniatin B_1 (B_1), sterigmatocystin (STC), mycophenolic acid (MPA), alternariol (AOH) and alternariol methyl ether (AME) were from Romer Labs (Tulln, Austria).

2.2. Magnetic nanostructured agents

The developed magnetic nanostructured agents were synthesized via wet chemical procedures as detailed elsewhere (de Castro Alves et al., 2019; de Castro Alves, Yáñez-Vilar, Piñeiro-Redondo, & Rivas, 2020; Wang et al., 2011). A total of one medium-size and ten large-sized samples were prepared, each with different ratios of adsorptive components.

The medium-sized magnetic nanocomposite, named as M7, exhibited a diameter of approximately 15 μm (Fig. 1A), and was composed by a mixture of Fe_3O_4 (20%), bentonite (30%), activated carbon (35%) and aluminum hydroxide microparticles (15%) (Table 1). The large-sized samples, named as L3 and L10–L18, consisted of macroscopic spheres (Fig. 1B), composed of different combinations of biopolymers (alginate, esterified pectin, chitosan, nanocellulose), activated and ordered mesoporous carbon (Table 1).

Structurally and morphological characterizations of all samples was conducted by scanning electron microscopy (SEM) using a JEOL JEM-1011 microscope operating at 100 kV. Magnetization of all samples was analyzed using a vibrating sample magnetometer (VSM) with an

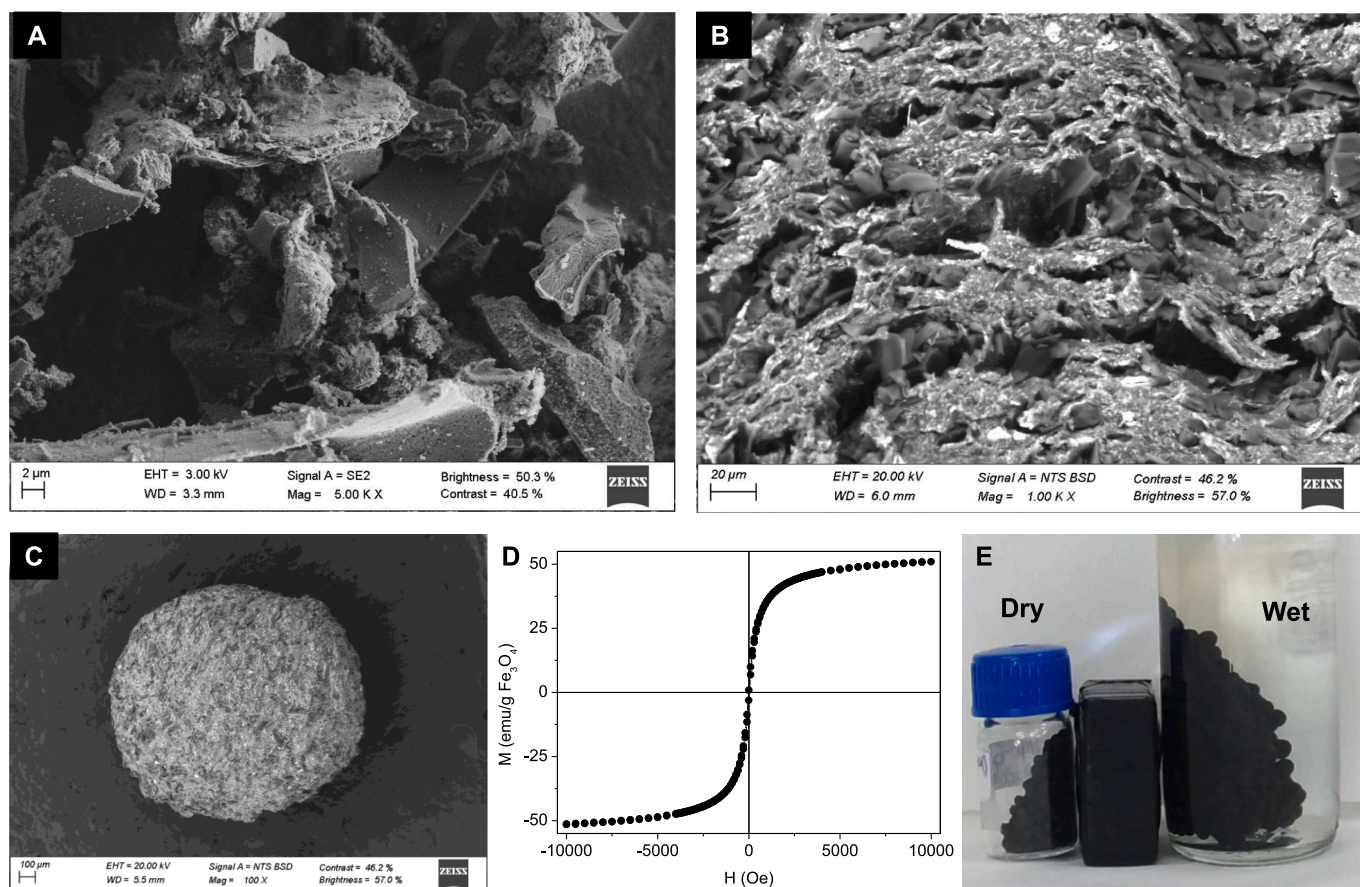


Fig. 1. Particles employed in detoxification studies. Scanning electron microscopy (SEM) images showcasing the microstructure of M7 (A) and the surface interconnected pores of L11 (B), along with the external surface of L11 (C). Magnetization curve of sample L11 (D). Digital images of wet and dry L11 beads (E).

Table 1

Composition of M and L particles used in the detoxification experiments.

	Composition
M7	Fe ₃ O ₄ @Al ₂ O ₃ @Bentonite@AC
L3	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @AC
L10	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @ES@AC
L11	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @ES@AC
L12	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @ES@AC
L13	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @ES@CS
L14	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @ES@CS
L15	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @CMK-3
L16	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @ES@CMK-3
L17	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @TOCNF@CMK-3
L18	Fe ₃ O ₄ @NaC ₆ H ₇ O ₆ @TOCNF

AC = activated carbon, EP = Esterified pectin, CS = chitosan; CMK-3 = ordered mesoporous carbon; TOCNF = 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibers (TOCNF).

applied field between −10,000 and 10,000 Oe, and working at room temperature.

2.3. Adsorption assays

2.3.1. Mycotoxin adsorption from water solutions

To assess the initial adsorption capacity of the developed particles, the same protocol previously defined was employed (González-Jartín et al., 2019). As shown in Fig. S1, in this experiment, 2 mL of multi-toxin solutions were utilized, comprising DON at 12.5 µg/L, ZEN, FB₁ and OTA at 50 µg/L, and aflatoxins (B₁, B₂, G₁, and G₂) at 1.75 µg/L. Solution were treated using 10 spheres of each particle type (5 particles/mL), these experiments were carried out in triplicate. The average weights of the particles were as follows: 30.5 mg (L10), 29.06 mg (L11), 37.04 mg (L12), 30.35 mg (L13), 27.29 mg (L14), 25.01 mg (L15), 28.84 mg (L16), 39.05 mg (L17), and 70.09 mg (L18). One aliquot of 120 µL was taken from each solution before the addition of particles. Then, aliquots of the same volume were obtained after 30, 90 and 180 min of incubation in agitation at 250 rpm. A control (a solution without the addition of adsorbent) underwent the same procedure to evaluate any potential toxin losses during the assay. In all cases, aliquots were filtered through a 0.22 µm centrifugal filter. Subsequently, a volume of 100 µL of the resultant filtrate was transferred to deactivated glass vials, evaporated to dryness using a centrifugal evaporator, and then reconstituted with an equal volume of an acetonitrile-water-acetic acid mixture (49/50/1 v/v/v). Finally, toxin concentrations were determined using ultra-performance liquid chromatography - tandem mass spectrometer (UHPLC-MS/MS) according to a method earlier developed (González-Jartín et al., 2019). The adsorption percentage was calculated for each toxin using Eq. 1, $\text{adsorption (\%)} = \frac{(C_0 - C_{eq}) * 100}{C_0}$ which relates the concentration of the toxin before the addition of the particles (C₀) to the residual amount of mycotoxin after treatment (C_{eq}). The quantity of toxin adsorbed per unit of adsorbent was then determined using Eq. 2, $Q_e = \frac{(C_0 - C_{eq}) * V}{m}$ where the term Q_e represents the µg of toxin adsorbed per mg of adsorbent. In these equations, C₀ and C_{eq} are in µg/L, V denotes the volume of the solution (L), and m indicates the mass of the sorbent (mg).

2.3.2. Beer detoxification

Beer wort samples (2 mL) were spiked with mycotoxins at different concentrations: 100 µg/L of DON, 60 µg/L of ZEN, OTA, and FB₁, along with 4 µg/L of aflatoxins. Contaminated samples were then treated with 3.5 particles/mL. The evaluation of toxin levels involved comparing untreated control samples with those treated for 180 min using a protocol adapted from an established method (González-Jartín et al., 2019), with minor adjustments. The same experiment was conducted using different amounts of spheres 7.5 and 15 particles/mL.

After treatment, particles were removed from the solutions, followed by centrifugation at 4000 rpm for 10 min. The resulting supernatant was transferred to 15 mL centrifuge tubes, and the beer was subsequently dried using a centrifugal evaporator. The resulting residue was redissolved in 2 mL of 2% acetic acid, followed by the addition of 1 mL of acetonitrile. After each solvent addition step, samples were vigorously vortex mixed and sonicated in an ultrasonic bath. To carry out phase partitioning, 1 g of MgSO₄ and 0.25 g of NaCl were added. Subsequently, 400 mg of the organic phase was subjected to further cleanup using 400 mg of MgSO₄ and 100 mg of C18. Next, 200 µL of acetonitrile were evaporated, and the residue was redissolved in 960 µL of a mixture of acetonitrile, water, and acetic acid at a ratio of 49:50:1 v/v/v. The samples were then analyzed using UHPLC-MS/MS. The extraction and analysis procedure had been validated for the analysis of mycotoxins in beer (González-Jartín, Alfonso, et al., 2019).

2.3.3. Milk detoxification

Initially, 2 mL of milk were contaminated with DON and ZEN at 12.5 µg/L, FB₁ and OTA at 25 µg/L, and with aflatoxins (B₁, B₂, G₁, and G₂) at 1.5 µg/L. Solutions were treated by using 5 particles/mL, in triplicate, for each particle type: namely, L12, L15, and L18. Additionally, another experiment was conducted using the same amount of L12 and L15 particles, but milk was contaminated at 5 µg/L with AFM₁, DOM-1, h-FB₁, ROQ C, T-2 toxin, BEA, ENNSs, STG, MPA, AOH, and AME.

Following a 180-min treatment period, the nanostructured particles were separated from the solutions. Subsequently, 1.25 mL were transferred to new tubes and extracted with 1.25 mL of 0.5% formic acid in acetonitrile. After vortex mixing, 1.2 g of MgSO₄ and 0.15 g of NaCl were added to induce phase partitioning. The supernatant (1 mL of acetonitrile) was then subjected to further treatment with 428 mg of MgSO₄ and 142 mg of C18, following which samples were analyzed using a method validated for that purpose (González-Jartín et al., 2021).

2.3.4. DDGs detoxification and analysis

DDGs were collected from a feed factory and a thoroughly homogenized sample was used to prepare a dispersion at 20% in water. The experiment was conducted in triplicate, employing 5 spheres/mL of L3, L12, L15, and L18 particles, which were incubated with the samples (400 mg of DDG in 2 mL of water) for 480 min under continuous agitation at 200 rpm. The effectiveness of the treatment was evaluated by comparing toxin levels in control samples with those treated. One additional experiment was carried out using 2.5, 5, 10, and 20 L18 spheres/mL.

Subsequently, a protocol previously validated for DDG analysis was employed with minor modifications (González-Jartín, Alfonso, Sainz, Vieytes and Botana, 2021). After recovering the nanostructured particles, 2 mL of acetonitrile containing 2% acetic acid were added to each tube. After vortex mixing, 0.8 mg of MgSO₄ and 0.2 mg of NaCl were added to induce phase partitioning. Following this, 100 µL of acetonitrile were dried and reconstituted with 800 µL of acetonitrile/water/acetic acid (49:50:1 v/v/v), filtered and analyzed.

2.3.5. Freshwater toxins detoxification and analysis

Initially, the adsorption capacity of the nanostructures was evaluated in water solutions contaminated with cyanotoxins. Specifically, solutions contained 25 µg/L of MC-LR, MC-RR, NOD, MC-LY, MC-LF, and CYN, along with 12.5 µg/L of ATX-A. Solutions (2 mL) were treated with different concentrations of M7 nanostructures (50, 113, and 225 mg/L) or particles L3, L12, and L5 (1, 2.5, and 5 particles/mL).

Before the addition of adsorbents, 120 µL aliquots were obtained from each solution. Subsequently, aliquots of the same volume were obtained after 30, 90, and 180 min of incubation with particles under agitation at 250 rpm.

Furthermore, we investigated the adsorption capacity of M7 and L12 nanostructures in a *Microcystis aeruginosa* culture. One strain was cultured in distilled water enriched with GFWS medium at 19 °C and

contained 60 µg/L of MC-LR and traces of other microcystins. The assessment involved using different particle concentrations ranging from 0.8 to 226 mg/L of M7 structures and from 7 to 297 g/L of L12. Sample treatment and analysis were conducted using an established method (González-Jartín et al., 2020).

2.3.6. Statistics

Data are presented as mean $\pm$ standard deviation (SD) of three independent experiments. To assess mycotoxin adsorption in DDGs, differences between control and treated samples were analyzed using Two-way ANOVA followed by Tukey's multiple comparison tests with GraphPad Prism 8 software. Statistical significance was established at * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$.

3. Results and discussion

The food chain is susceptible to numerous hazards, with chemical contaminants posing a significant risk. To mitigate the effects of these compounds, nanotechnology is being increasingly studied. In this sense, our previous research has proven the effectiveness of various magnetic nanocomposites of different sizes and compositions in eliminating mycotoxins, while a specific nanostructure proved effective in adsorbing cyanotoxins and marine toxins (González-Jartín et al., 2019, 2020). In the current work, novel nanostructured agents were developed to enhance removal efficiency. These agents were tested across various real-world scenarios, including beer and milk production, DDGs manufacturing, and water treatment for cyanobacteria contamination.

All detoxification experiments were conducted in triplicate, and the magnetic nanostructured agents were removed from the solutions using a Neodymium Iron Boron (NdFeB) magnet. The analysis of the toxin content in each matrix was studied using previously validated methods, and controls (solution without adsorbent addition) underwent the same procedure to assess any non-specific loss of toxins.

3.1. Mycotoxin adsorption from water

To compare the effectiveness of the new magnetic nanostructured agents, we followed the procedure detailed in previous experiments (González-Jartín et al., 2019). In each trial, 5 spheres/mL were incubated with toxin solutions for 180 min, appropriate controls underwent identical processes. The efficacy of each particle type in toxin elimination is shown in Table S1 and Fig. 2.

Particles L10, L11, and L12, comprising magnetite, AC in variable

amounts (ranging from 16 to 28%), esterified pectin, and alginate, demonstrated high efficiency in removing OTA, ZEN, FB₁, and aflatoxins, with reduction higher than 85% (Fig. 2 A). AC is a widely used adsorption material which is able to attach toxins through various physicochemical interactions, such as van der Waals forces, hydrogen bonding, and π - π interactions. For instance, it was demonstrated the π - π interaction between ZEN and AC (Hu et al., 2023). Although chitosan and pectin are polysaccharides that contains abundant carboxyl, hydroxyl and highly reactive amino groups that function as coordination and reaction sites, they are less efficient than AC for the removal of contaminants (Abbasi Pirouz, Selamat, Zafar Iqbal, Samsudin, & N., 2020). For instance, particles L13 and L14, sharing the same composition as L12 but with chitosan replacing AC, and pectin replacing esterified pectin in the case of L14, exhibited a halved adsorption capacity probably due to the absence of carbonaceous materials (Fig. 2 B). OTA adsorption notably decreased from 90% with L10–12 particles to <40% with chitosan particles (L13 and L14). In addition, the efficacy of esterified pectin (L13) in removing AFs was significantly greater, reaching 60%, compared to the 25% efficacy observed with pectin (L14).

Regarding the composition of the nanostructured agents, nearly complete exclusion of AC was achieved with L15, primarily formulated from magnetite with esterified pectin and only 0.5% of mesoporous carbon CMK-3. These particles maintained the adsorption efficiency showed by L10–12. This type of ordered mesoporous carbon presents a high specific surface area, large pore volume, and a higher proportion of mesopores, in contrast with commercial AC, which is primarily composed of micropores. Therefore, one reason for this high adsorption capacity can be attributed to the presence of a higher proportion of mesopores, which may lead to increased adsorption due to the interconnected channels characteristic of the carbon structure (de Castro-Alves et al., 2024). In addition, reducing the amount of CMK-3 by half in L16 while increasing the quantity of esterified pectin led to a notable decrease in the adsorption of all mycotoxins, suggesting that high amounts of this biopolymer may obstruct accessible binding sites for magnetite and CMK-3.

Subsequently, the potential substitution of pectin with transparent tempo oxidized cellulose nanofibril (TOCNF) was evaluated. Employing large quantities of this polysaccharide nanomaterial, as in L17, resulted in low toxin removal rates, especially for DON and OTA. The same pattern had been observed in particles L13 and 14 with a 27% of chitosan, which can be attributed to the structural similarities between chitosan and cellulose, where the hydroxyl groups in cellulose are

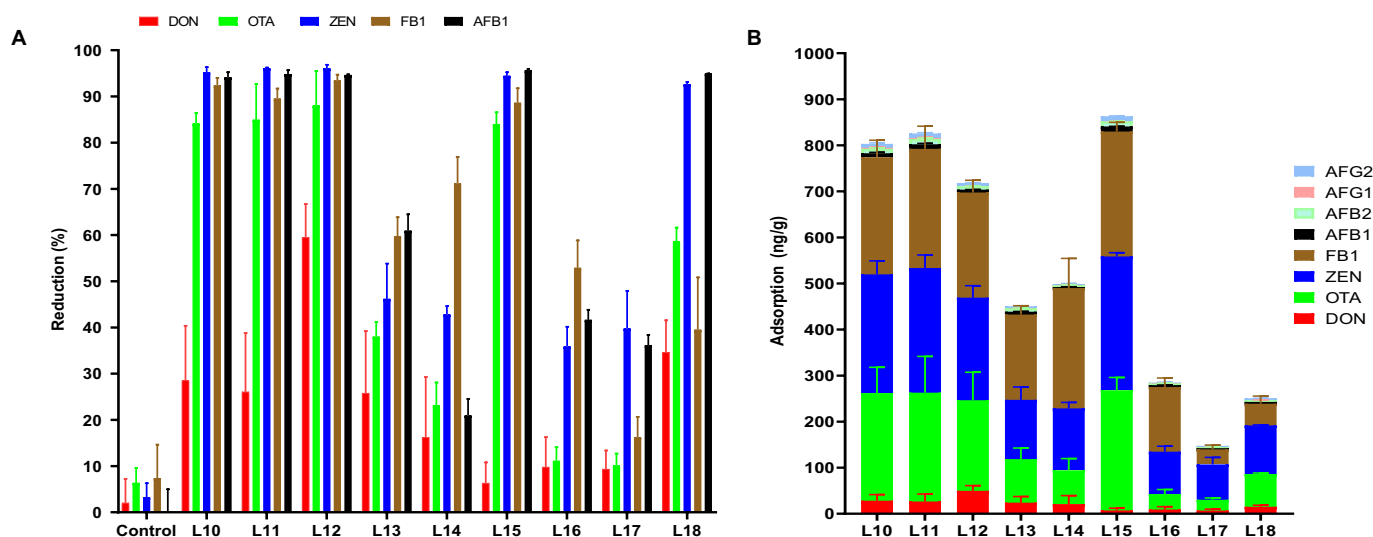


Fig. 2. Capacity of magnetic nanostructured particles to adsorb mycotoxins from water. Percentage of mycotoxins removed from solutions containing DON at 12.5 µg/L, ZEN and FB₁ at 50 µg/L, and aflatoxins at 1.75 µg/L by 10 L particles (A), and data from (A) expressed as ng of toxin adsorbed per gram of particles (B).

replaced by amino groups in chitosan at the carbon-2 position (da Silva Alves, Healy, Pinto, Cadaval Jr., & Breslin, 2021). However, using a balanced combination with magnetite and low amounts of sodium alginate and CMK-3 allowed the elimination of ZEN and aflatoxins at levels comparable to L12 composites, while intermediate reductions were observed for OTA and FB₁. Notably, L18 exhibited the second highest reduction for DON after particles L12. DON is a hydrophilic mycotoxin notoriously difficult to eliminate as most of the binding agents employed for mycotoxin decontamination are ineffective for this compound; however, the new developed particles L12 and L17 show promising results improving the elimination rates previously reached by other adsorbents (González-Jartín et al., 2019; Vila-Donat, Marín, Sanchez, & Ramos, 2018).

Despite L12 had shown the highest removal capacities for all toxins (Fig. 2 A), the particles exhibiting the highest Q_e were L15, achieving a removal efficiency of 873 ng/g (Fig. 2 B). This result can be attributed to the weight disparity among particle types, with L15 being the lightest at 25.01 mg per particle, while L12 was heavier at 37.04 mg per composite.

The effect of contact time in mycotoxin adsorption was also investigated (Fig. S2). The pseudo-first order and pseudo-second-order kinetic model parameters are summarized in Table S2. The pseudo-second-order kinetic model was found to best fit the experimental data in terms of the coefficient of correlation and the agreement between the calculated and experimental Q_e values. Hence, surface adsorption, mass transfer, and intragranular diffusion are likely to take place during the adsorption process (Liu et al., 2022).

Overall, the new nanostructured materials achieve a significant increase in adsorption capacity compared to the earlier developed particles that attained a maximum adsorption of 598 ng/g (González-Jartín et al., 2019). Another study using magnetic attapulgite composites reached a maximum adsorption of 52 µg/g (Ji & Xie, 2021). However, the adsorption of the present study has been calculated using a fixed amount of adsorbent and toxin, without reaching the maximum adsorption capacity (as indicated below). Additionally, the high-water retention capacity of the particles contributes to their substantial weight (25–70 mg), making it challenging to compare the results with non-hydrated adsorbents. However, most of previous studies have been carried out in aqueous solution or phosphate buffer, therefore, it is probable that the results may not be comparable across different food products (Ma, Cai, Mao, Yu, & Li, 2021). To assess the potential application of the developed particles in real scenarios, their adsorption capacity was evaluated across various matrices.

3.2. Beer detoxification

The performance of several particles was evaluated in beer wort. Beer is one of the most widely consumed beverages worldwide. This product is susceptible to mycotoxin contamination since it is made with barley, which is usually affected by DON (González-Jartín, Alfonso, et al., 2019). The level of contamination of the beer used in the experiment was determined based on the frequency and typical levels detected in Europe. Aflatoxins are found infrequently, with an average concentration in positive samples of 1.5 µg/L. Consequently, a contamination level of 4 µg/L was selected. On the other hand, the toxin most frequently detected, especially in German beer, is DON, with an average concentration of 48 µg/L. Thus, the beer was contaminated at a level of 100 µg/L with DON. Other mycotoxins, such as FB₁, are also present in beer, albeit in highly variable concentrations across different countries. Therefore, an intermediate contamination level of 60 µg/L was established for ZEN, OTA, and FB₁ (Schabo, Alvarenga, Schaffner, & Magnani, 2021). Particles L12 were employed due to their high efficiency in removing these contaminants (Fig. 2 A). Additionally, particles L10 and L11, sharing a similar composition, were tested, along with L13 and L14, where AC was avoided to reduce potential nutrient losses since AC is an unspecific adsorbent, and therefore essential nutrients may be also adsorbed (Vila-Donat et al., 2018).

In water experiments, a concentration of 5 particles/mL was used, while in beer three different amounts were evaluated: 3.5, 7.5, and 15 particles/mL. In general, the adsorption capacity is slightly diminished in the presence of a matrix, although the degree of reduction varies depending on the toxin. For instance, when considering L12, we found that the adsorption of AFB₁ and OTA remains notably high. Specifically, the reduction of AFB₁ in water was 94%, whereas in beer, it only decreased to around 77% (inferred from the adsorption at concentrations of 3.5 and 7.5 particles/mL) (Table S2). Similarly, the adsorption of OTA was only reduced by 16%. Conversely, FB₁ exhibited a significant decrease in adsorption, from 93% of reduction in water to 37% in beer; with intermediate values observed for ZEN. This pattern was, in general, consistent across other particles; however, L13 displayed a complete loss of its removal capacity for ZEN.

As shown in Fig. 3, L13 particles reached their maximum adsorption capacity at 204 ng/g since the amount of adsorbed toxin per gram of particle was constant at the three studied concentrations, while particles L10–12 were significantly below the saturation since reducing their number causes an important increase in the adsorption capacity (Fig. 2). Consequently, a Q_e exceeding 850 ng/g was achieved by L11 particles when 3.5 composites per mL were used improving previous results.

3.3. Milk detoxification

Dairy products, including milk, are susceptible to mycotoxin contamination that proceeds from a carry-over from animal feed. One example is AFB₁, which contaminates feedstuffs; upon ingestion, it is metabolized into aflatoxin M₁ (AFM₁), and subsequently excreted in milk. To prevent intoxication, European legislation has set a maximum level of 0.05 µg/kg for AFM₁ in dairy milk and milk used in dairy product manufacturing (Iqbal, Jinap, Pirouz, & Ahmad Faizal, 2015). While this toxin is only occasionally detected in the EU, it is expected an increase due to climate change. Moreover, it is a frequent problem in countries with warmer climates like those from sub-Saharan Africa (Akinyemi, Braun, Windisch, Warth, & Ezekiel, 2022). On the other hand, other mycotoxins not regulated in milk such as FBs, OTA, ZEN, T-2 toxin, ROQC, ENNs, and BEA have recently been detected in this matrix (González-Jartín et al., 2021). The composition of milk differs greatly from that of beer, primarily due to its fat content. Therefore, new experiments were done to assess the efficacy of nanostructured materials in this matrix. Composites L12, L15, and L18 were chosen since demonstrated high aflatoxin elimination rates in water experiments (Fig. 2). Initially, we evaluated the elimination of previously studied toxins with a concentration similar to that employed in water solutions. In the case of aflatoxins, the concentration of the combined four toxins would exceed the EU's maximum allowed level in milk by 120 times. Fig. 4 A shows toxin levels in control samples versus samples treated with particles. Under these conditions, particles L12 and L15 eliminated nearly all aflatoxins. For instance, treatment with L12 reduced AFB₁ levels to only 0.02 µg/L. However, in the case of the more hydrophilic toxin, DON, only particles L12 and L18 demonstrated a slight effectiveness, albeit with a reduced capacity in milk compared to water experiments. Results for more lipophilic toxins like FB₁, OTA, or ZEN are less favorable in milk. Only L12 particles maintain the elimination of FB₁ and ZEN at levels close to 50%. Therefore, using the suggested technique to remove toxins may be difficult due to the presence of lipids in the matrix. Nonetheless, it is effective for the elimination of the most hazardous toxins found in dairy products.

In the subsequent experiment, toxins commonly detected in milk, such as AFM₁ and T-2 toxin, as well as emerging toxins like BEA and ENNs, were included. Emerging mycotoxins are compounds that are neither routinely determined nor legislatively regulated; however, evidence of their occurrence is rapidly increasing (Gruber-Dorninger, Novak, Nagl, & Berthiller, 2017). Mycotoxins are typically detected at low concentrations in milk; therefore, chronic ingestion by children, especially in regions where AFM₁ is frequently detected, is the major

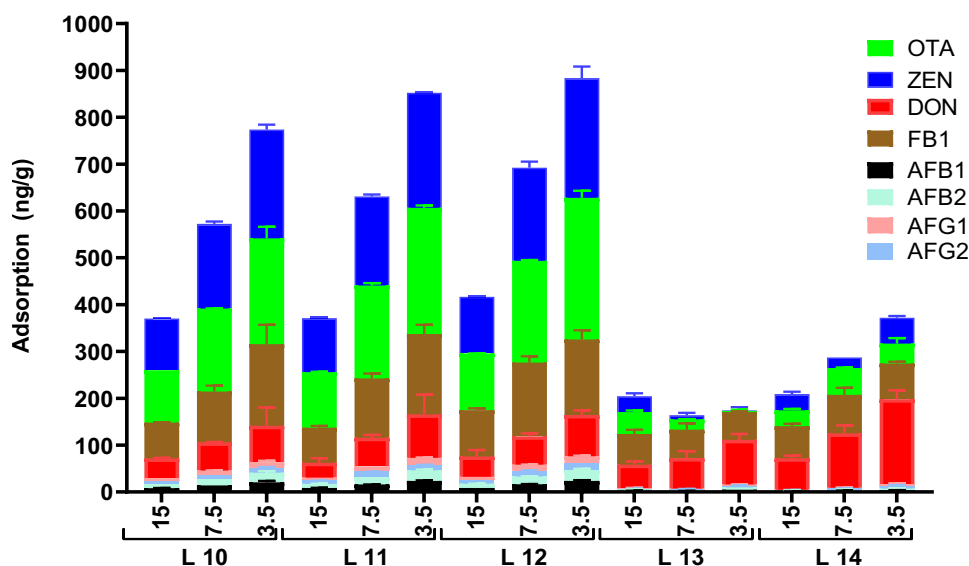


Fig. 3. Mycotoxin adsorption in beer. Data is expressed as ng of toxin adsorbed per gram of particles when 3.5, 7.5, and 15 composites were employed per milliliter of beer wort.

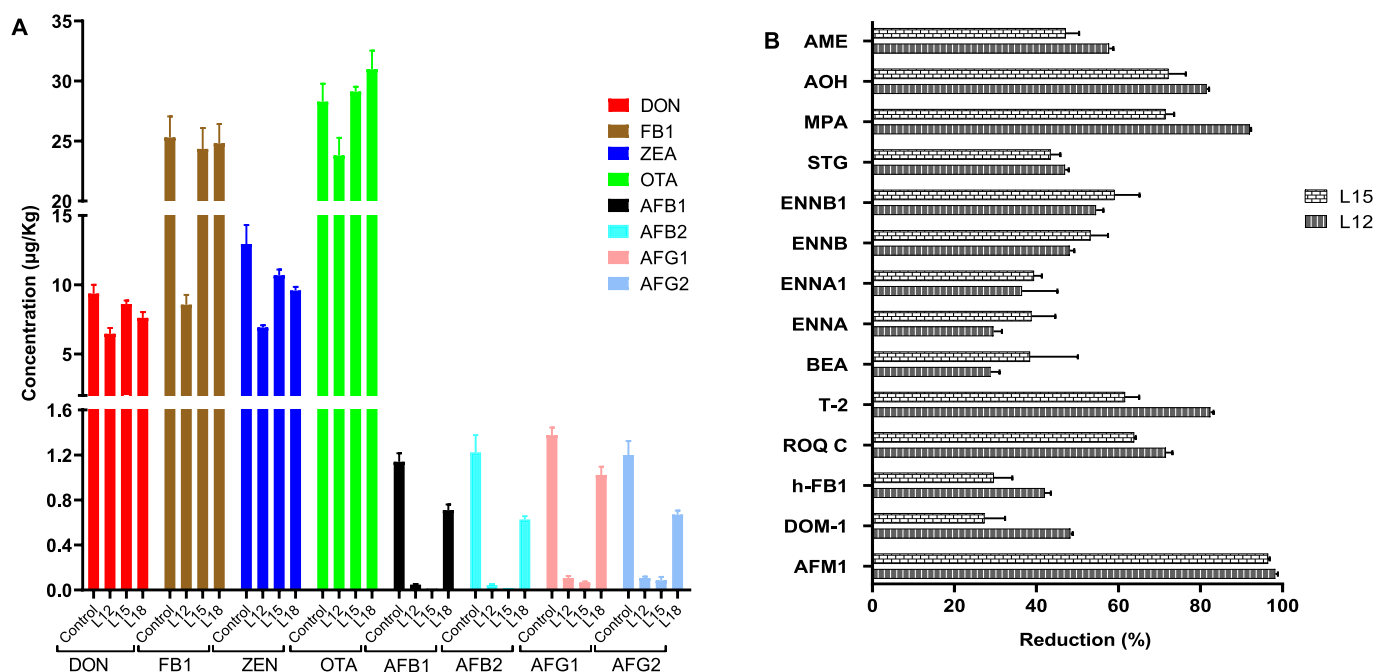


Fig. 4. Mycotoxin adsorption in milk. Toxin levels (µg/kg) in milk before (control) and after treatment with 5 particles/mL of L12, L15, and L18 composites (A), percentage of mycotoxin adsorption from milk contaminated with 5 µg/mL of several toxins after 180 min treatment with the same amount of L15 and L12 composites (B).

concern (Akinyemi et al., 2022). In this case, the milk was spiked with 5 µg/L, which is significantly higher than the typical levels detected in this matrix (Leite, Freitas, Barbosa, & Ramos, 2023); and treated with L12 and L15 particles since have showed promising results in the previous assessment.

As expected, in both cases we obtained high reductions of AFM₁, achieving a minimum elimination of 96% (Fig. 4 B). Modified forms of DON (type A trichothecene) followed a similar pattern to their primary toxin, with L12 exhibiting a greater reduction (46%) compared to L15 (27%). Similarly, T-2 toxin, a type B trichothecene, showed higher reduction when treated with L12. Enniatins are commonly found in various matrices, albeit at very low concentrations. Their elimination with the tested particles could be challenging, since the observed

reductions ranged from 28% to 59%, likely due to their highly lipophilic nature. However, the elimination of other emerging toxins such as MPA or AOH is feasible, particularly with L12 composites, which showed reductions close to 90%.

Previous attempts have been made to mitigate the presence of mycotoxins in milk. One study assessed the efficacy of clay bentonite, date pit, and chitosan nanoparticles in detoxifying milk contaminated with 0.15 ng/mL of AFM₁ and 0.96 ng/mL of OTA. The nanoparticles were found to eliminate <12% of both toxins. In contrast, clay bentonite (100 mg/mL) was the most effective adsorbent with reductions of up to 68% (Abdelnaby, Abdelaleem, Elshewy, Mansour, & Ibrahim, 2022). Another study reported that kaolinite and smectite exhibit a maximum adsorption capacity for AFM₁ at 0.079 mol/kg, as calculated from Langmuir

equations (Carraro et al., 2014). It was also proposed the use of *L. rhamnosus* biofilm to remove AFM₁ (0.1 µg/L) achieving a reduction of up to 65% (Nahle et al., 2022). One final strategy could involve using *Saccharomyces cerevisiae* at a concentration of 10¹⁰ cfu/mL. When incubated at 37 °C for 24 h, this treatment has shown reductions of 90% in AFM₁ levels when milk was spiked at 0.5 µg/mL (Fakhrabadipour, Khajehrahimi, Haghdoost, Anvar, & Tala, 2023). Therefore, L2 or L15 particles exhibit similar or greater reductions compared to previously proposed additives, while also minimizing treatment time. Thus, they could serve as promising options in the treatment of contaminated milk, particularly with aflatoxins. However, it is necessary to assess whether these particles may affect any of the nutrients present in this dairy product.

3.4. DDGs detoxification

DDGs, a by-product of the ethanol industry, serve as a key component in animal feed production. However, they are also an important source of mycotoxin contamination (González-Jartín et al., 2021). The nanostructures could be applied within the industrial processes involved in DDG production, since these products are dispersed in water at different stages. During the fermentation step, the whole stillage typically contains between 5 and 20% solids (Cekmecelioglu & Demirci, 2019). To mimic these conditions, commercial DDGs were dispersed in water, and aliquots were treated with nanomaterials for 8 h. In this case, L12, identified as the most effective in prior tests, was used together with nanocellulose particles (L18), which have demonstrated efficacy in aflatoxin elimination, the only group of mycotoxins regulated in animal feed. Additionally, nanocellulose particles have shown notable efficacy in reducing DON, one of the most commonly detected mycotoxin in DDGs together with FBs (González-Jartín et al., 2021). Additionally, L3, comprising alginate and AC, were employed since had exhibited promising results in mycotoxin removal from beer (González-Jartín et al., 2019). In this study, samples were found to be naturally contaminated with AFB₁, ZEN, BEA, DON, fumonisins, and traces of ENNs, obviating the necessity for artificial spiking. Initially, dispersions were treated with 5 particles/mL, and toxin reduction was determined relative to control samples. Comparable reductions across most toxins were observed with all particles. Notably, significant reductions were observed for fumonisins, and it was particularly noteworthy the adsorption of DON by L18 particles (Fig. 5 A). Consequently, these particles were selected for further investigation using different particle

amounts.

Mycotoxin concentration in control and treated samples is shown in Fig. S3. The results were consistent when the same particle concentration (Fig 5 B) was used, while doubling the particle quantity resulted in a proportional increase in aflatoxin elimination and an overall increase in reduction for the other toxins. Notably, employing 20 particles per mL allowed for the elimination of up to 45% of DON and approximately 30% of aflatoxins and fumonisins. This is the first reported effective measure to mitigate mycotoxins in DDGs. Therefore, introducing nanotechnology into the fabrication process of these ethanol industry by-products would result in safer feedstuffs, increasing their added value.

3.5. Freshwater toxins detoxification

The presence of contaminants in water represents a worldwide public health issue. Cyanotoxins are the largest group of toxins that most frequently appear in freshwater. Although there are some reports about acute intoxication with cyanotoxins, the major concern is associated with the prolonged ingestion of water or food contaminated with MCs, specifically MC-LR, which causes liver and colorectal cancer (Roegner, Brenna, González-Sapienza, & Puschner, 2014). Previous research shown that multicore magnetite coated with carbon NPs (average diameter of D = 400 nm) were effective for the adsorption of cyclic peptides, MCs and NOD, while only low amounts of the alkaloids ATX-a and CYN were eliminated from solutions (González-Jartín et al., 2020).

To enhance previous cyanotoxin elimination data, three of the most effective particles for mycotoxins, namely L3, L12, and L15, were tested, along with the particle M7 that had previously shown good results (González-Jartín et al., 2019). This composite measuring approximately 15 µm in diameter was formed by a mixture of magnetite, bentonite, AC, and aluminum hydroxide microparticles.

Initially, the efficacy of nanostructures in adsorbing cyanotoxins was evaluated in a water solution comprising a mixture of MCs (LR, RR, LY, and LF), NOD, and CYN, each at a concentration of 25 µg/L, alongside 12.5 µg/L of ATX-A. Given that ATX-A is less frequently detected in European waters and typically found in low amounts, a low contamination level was used. Meanwhile, other toxins, particularly MCs, are more commonly found. Thus, a total concentration of 100 µg/L was employed since the solution contained 25 µg/L of each analog. This concentration far exceeds the maximum of 1 µg/L of MC-LR in drinking water, as set by the Drinking Water Directive (EU) 2020/2184, and

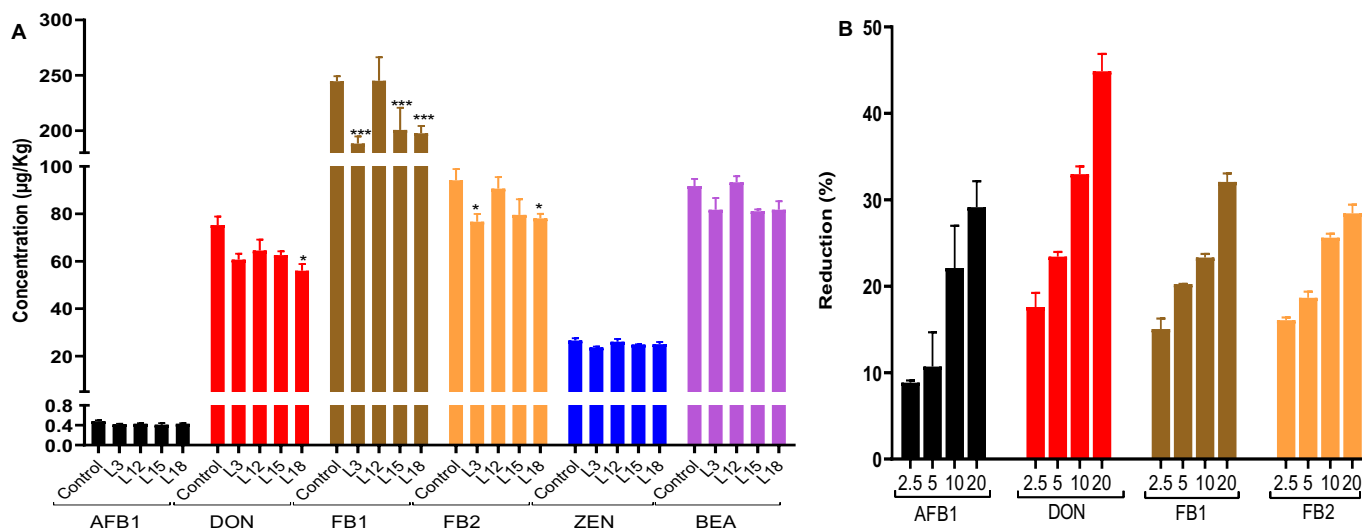


Fig. 5. Mycotoxin adsorption in DDGs. Toxin levels (µg/kg) in samples before (control) and after treatment with 5 particles/mL of L3, L12, L15, and L18 composites (A), percentage of mycotoxin adsorption after using 2.5, 5, 10 and 20 L18 particles/mL (B). Statistical differences between treatments and control were determined by ANOVA Turkey's multiple comparison test. Results were considered significant at * $p \leq 0.05$, and *** $p \leq 0.001$.

surpasses levels usually reported in surface freshwater (Filatova, Picardo, Núñez, & Farré, 2020). Since a time-dependent adsorption was observed for mycotoxins, solutions were treated with M7 nanostructures (225 mg/L) or particles L3, L12, and L5 (5 particles/mL) for 30, 60, and 180 min. M7 composited adsorbed toxin in the first 30 min of treatment while larger size particles need at least 60 min to reach the maximum adsorption (Fig. S4). Therefore, this time was used to evaluate the adsorption using different concentrations of M7 nanostructures (50, 113, and 225 mg/L) or particles L3, L12, and L5 (1, 2.5, and 5 particles/mL). The utilization of higher quantities of particles led to significant reductions in most cyanotoxins (Fig. 6). Specifically, with M7 and L12 particles, removal rates exceeding 70% were achieved for ATX-A and CYN, while the removal rate for MC-LR reached 90%. Particles L3 and L15 shown removal rates of over 70% for MCs, whereas for ATX-A and CYN ranged between 20% and 50%. Consequently, the data obtained with these new particles markedly enhance previous results, rising the adsorption capacity up to 3252 ng/g for large size particles (L12) and 1689 µg/g for smaller particles (M7).

Furthermore, we investigated the adsorption capacity of M7 and L2 nanostructures in a *Microcystis aeruginosa* culture that contained 60 µg/L of MC-LR and traces of other microcystins. The assessment involved using different particle concentrations ranging from 0.8 to 226 mg/L M7 materials and from 0.25 to 10 L12 particles/mL. Thus, the maximum adsorption capacities in the culture were calculated with the experimental data shown in Fig. 7. Specifically, each gram of L12 composites eliminated 120 µg of MC-LR (Qe 0.12 mg/g), while M7 achieved an elimination of 36,610 µg (Qe 36.6 mg/g). The adsorption capacities for MC-LR of various adsorbents was recently review (Zeng & Kan, 2021). The maximum adsorption capacity of M7 surpassed that of other reported adsorbents, such as iron oxide nanoparticles, commercial AC like Norit and Calgon, wood chips biochar or iron activated biochars. The observed adsorption is only surpassed by giant reed biochar prepared at pyrolysis temperatures of 500–600 °C, with Qe of up to 42 mg/g. Although L2 exhibits a lower Qe due to its higher weight it still outperforms certain materials such as kaolinite and illite, and falls within the range of giant reed biochar (Zeng & Kan, 2021). The adsorption is also higher when is compared with magnetic metal-organic framework that had shown a Qe of 6.1 mg/g for MC-RR (Liu et al., 2023). Another proposed strategy for cyanotoxin elimination involves the use of photocatalysts. Current methods allow for the elimination of between 1 and 5 mg/L of toxin using between 1 and 2 mg/L of TiO₂ or graphite-based photocatalysts after treatments lasting up to 9 h. In addition, these methods generate degradation products that could potentially be toxic (Guo, Li, Zhang, & Zhang, 2018; Wang et al., 2022). Consequently, M7 composites exhibit significant potential for the effective treatment of cyanotoxins from water.

3.6. Applicability and challenges

Despite several nanomaterials have been proposed as toxin adsorbents, most adsorption studies have focused on aqueous or buffered solutions (Ma et al., 2021). Hence, this study primarily aims to assess the performance of various nanostructured agents in real-world scenarios. As it was shown, we have proven the efficacy of different nanostructures to remove toxins from beverages including beer and milk. Previous studies have also tested some nanostructures in liquid matrices (Abdelnaby et al., 2022; González-Jartín et al., 2019; Ma et al., 2021). Although this technology shows promise in laboratory studies, further research is needed to facilitate its real-world application. Integrating this technology into production processes presents a significant challenge. However, in liquid matrices, implementation could be relatively straightforward by utilizing nanomaterial-enhanced membranes in filtration steps (Wahab et al., 2024). The application of nanotechnology for detoxifying solid raw materials remains largely unexplored due to challenges such as the recovery of nanostructures after the detoxification. Despite these, our research demonstrates their potential in reducing mycotoxin contamination in solid matrices when their manufacturing involves a dispersion like in the case of DDGs. However, industry adoption presents greater complexities compared to liquid matrices, since it is necessary to modify manufacturing processes to enhance particle-material contact and facilitate nanostructure recovery post-detoxification. Various strategies are employed in drinking water treatment plants (DWTPs), with AC being the predominant adsorbent. However, the necessity for high doses of carbon-based adsorbents (10,000 mg/L) to remove cyanotoxins results in the generation of significant volumes of exhausted carbon (Kulabhusan & Campbell, 2024). Consequently, there is a growing demand for alternative adsorbents, particularly those that are environmentally friendly. The use of 225 mg/L of M7 particles proves effective in removing substantial quantities of cyanotoxins, thereby diminishing the requirement for large quantities of adsorbent. Moreover, after the detoxification process, these particles can be easily recovered using a magnet.

One crucial aspect to consider is the potential loss of nutrients due to unspecific adsorption. For example, the use of AC can lead to the unintended adsorption of vitamins and minerals (Vila-Donat et al., 2018). Similarly, the use of clay bentonite can slightly impact the nutritional profile of milk by sequestering milk proteins, while date pit and chitosan nanoparticles have minimal effects on the chemical composition of this beverage (Abdelnaby et al., 2022). The influence of copper benzene-1,3,5-tricarboxylate metal-organic frameworks on oil quality was also investigated. While these materials can decrease resveratrol content, other parameters such as acid value, peroxide value, fatty acid composition, and vitamin E content remain unaffected (Ma et al., 2021).

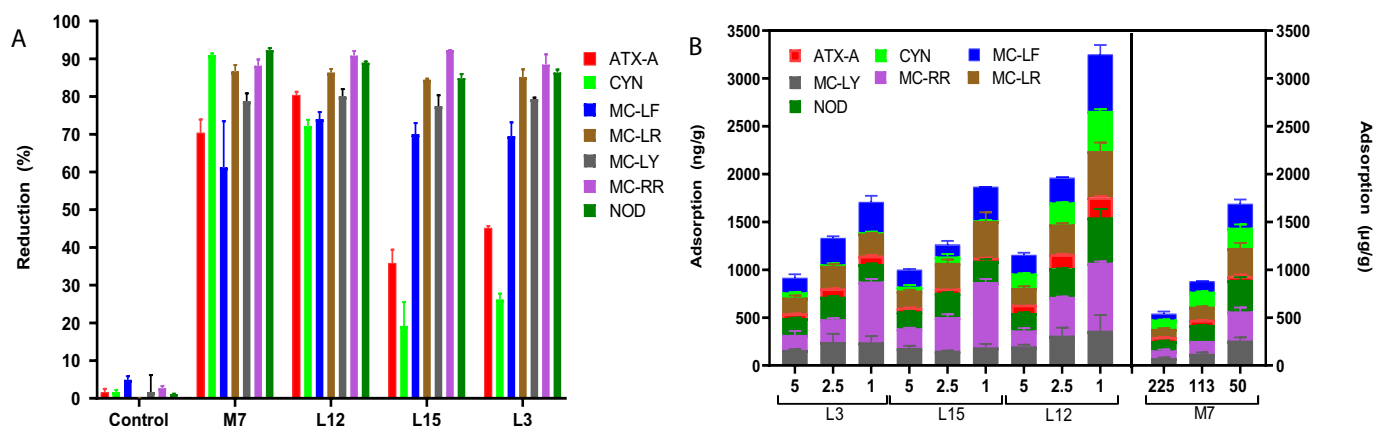


Fig. 6. Capacity of magnetic nanostructured particles to adsorb cyanotoxins from water. Percentage of toxins removed from solutions containing 12.5 µg/L of ATX-A and 25 µg/L of MCs, NOD, and CYN by 5 L3, L12, and L5 particles/mL or 225 mg/L of M7 nanostructures (A), and toxin adsorbed per gram of particles after treatment with L3, L12, and L5 particles (1, 2.5, and 5 spheres/mL) or M7 (50, 113, or 225 mg/mL) nanostructures.

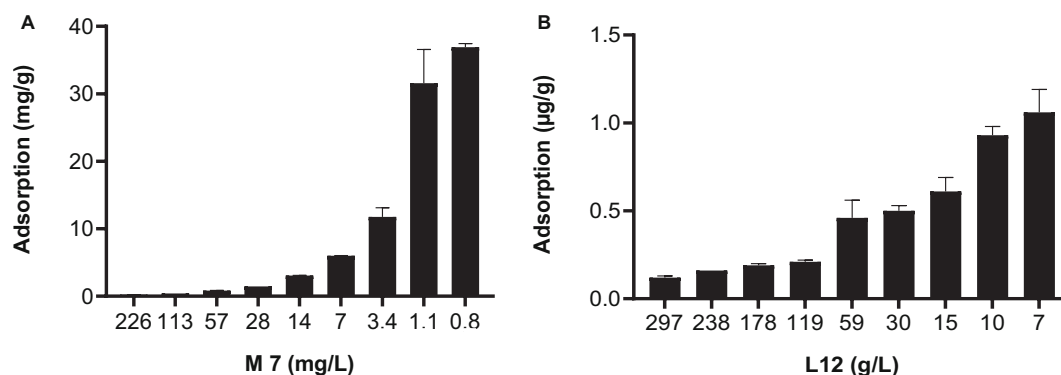


Fig. 7. MC-LR adsorption using different amounts of particles. Adsorption (expressed as mg/g) by M7 structures used in concentration ranging from 0.8 to 226 mg/L (A) adsorption (expressed as µg/g) by L12 composites used in concentration ranging from 7 to 297 g/L (B).

Therefore, although the nanotechnology could be a useful tool in food and water processing, several considerations must be addressed before implementing this technology. Firstly, it is essential to determine whether its application is feasible within the current manufacturing process or if modifications are necessary. Secondly, identifying the optimal point in the production process to integrate the technology is crucial. Lastly, assessing any potential alterations in nutritional value or organoleptic characteristics is essential for ensuring consumer acceptance and product quality.

4. Conclusion

Particles comprising magnetite, AC, esterified pectin, and alginate demonstrated high efficiency in removing OTA, ZEN, FB₁, and aflatoxins, with reductions close to 100%. TOCNF particles allowed the elimination of ZEN and aflatoxins to levels comparable to L12 composites, showing the second-highest reduction for DON. The proposed particles are also effective for the elimination of cyanotoxins, reaching a maximum of 36.6 mg/g. Despite their high efficiency, these magnetic nanostructured agents face limitations as presence of matrix, as in the case of milk or beer, slightly reduces the ability to eliminate toxins. Therefore, these findings indicate the potential for using nanotechnology to address natural toxin contamination. Future research should focus on evaluating any potential impacts on the nutritional quality of treated products which could be a major limitation. Additionally, exploring the integration of these nanostructures with existing water and food processing systems is needed to prove their applicability and effectiveness.

CRediT authorship contribution statement

Jesús M. González-Jartín: Writing – original draft, Investigation, Data curation. **Lisandra de Castro Alves:** Writing – original draft, Investigation. **Y. Piñeiro:** Methodology. **Amparo Alfonso:** Methodology. **Rebeca Alvarino:** Investigation. **Manuel González Gomez:** Investigation. **Mercedes R. Vieytes:** Visualization. **J. Rivas:** Supervision, Resources. **Luis M. Botana:** Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2024.140004>.

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