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Adsorbents selection for aflatoxins removal in bovine milks

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ABSTRACT

This work deals with the aflatoxins M1 detoxification of bovine milk by adsorption processes. Several types of natural and industrial sorbents have been analyzed by considering their effects on the quality of the treated milk and their removal efficiencies.

Treated milk characterization tests in terms of organic acids, lactose, chlorides, pH and protein contents show a moderate alteration of the milk properties proportionally with the sorbent dosage. On the other hand, experimental evidences reveal that the highest removal efficiencies ($\eta > 90\%$ for AFMs = 0.5 μg/kg) have been obtained for the activated carbons due to the concurrent effects of high surface area, sufficiently wide micropore size and higher affinity between the AFM molecules and the aromatic structure of the carbons. Also the bentonite shows significant removal efficiency, combined with lower side effects on the treated milk.

Therefore, this preliminary analysis shows that an optimization of sorbent dosage should be considered to account for both a reliable detoxification of the milk and for assuring the acceptability of the treated milk in light of its direct reuse for human consumption or as raw material for dairy products.

1. Introduction

Mycotoxins are secondary metabolites of some organisms of the fungus family and they contaminate a wide range of crop plants and fruits before or after harvest. As suggested by their own name, which literally means "fungus poisons", some of them are highly toxic, causing severe diseases and sometimes the death both in humans and in farm animals (Hatch et al., 1982).

Mycotoxins may reach humans by direct ingestion of contaminated crops, by eating foods (oil, wine, peanut butter, nut paste, etc) deriving from contaminated commodities, and by consumption of meat and dairy products coming from infected animals. In fact, mycotoxins present elevated chemical stability and they resist to decomposition during typical industrial and household food preparation treatments. Furthermore, they resist to animal digestion processes and they are partially accumulated in tissues and excreted with milk after metabolization.

According to the FAO more than 25% of the world agricultural production is contaminated by mycotoxins. This result in economic losses estimated at $923 million annually in the US grain industry alone. Similarly, the large world consumption of foods as milk (619 Mtonne/year in 2004), oil (around 88 Mtonne/year in 2000) and wine (277 Mhl/year in 2005), makes the presence of mycotoxins in liquid products a severe problem for alimentary industry.

Most countries have adopted severe regulations to limit the exposure to mycotoxins, having strong impact on food and animal crop trade. The presence of mycotoxins is unavoidable. Therefore, testing of raw materials and products is required to keep our food and feed safe.

Aflatoxins are among the most dangerous mycotoxins. They are present in several crops as a result of their contamination by *Aspergillus flavus* and *Aspergillus parasiticus* ascomicetic fungi.

There are 18 different types of mycotoxins, among which the most diffuse are the B1, B2, G1, G2, M1 and M2.

The last two compounds derive from the metabolization of B1 and B2 that occurs in the liver of animals due to the consumption of contaminated foods. They are accumulated in the tissues and, if possible, they are excreted through milks (Ellis et al., 1991; Ismail and Rustom, 1997; Yiannikouris and Jouny, 2002). The chemical structures of M1 and M2 aflatoxins (named in the following AFM1 and AFM2 or, all together, as AFMs) are reported in Fig. 1.

All the aflatoxins are highly stable to thermal treatment (they are thermally degraded only above 240 °C) and have a slightly acid character. The presence of AFMs in milks leads to the contamination of dairy products, as they are not eliminated by the typical processes of food industries as well as by food cooking. Ottaviani (1991) showed that AFMs are mainly present in the milk serum (~46.5%) and in the casein (~48.5%) while only a minor portion is contained in the fat fraction (~5%).

European Union has defined the maximum level of AFM1 and AFM2 in milk by means of the CE 2174/2003 Regulation. For the case of milks for human consumption, the highest allowed

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Nomenclature

c	AFMs concentration in solution at equilibrium (μg/kg)	m/V	sorbent dosage (g/Kg)
c_0	AFMs initial concentration in solution (μg/kg)	T	temperature (°C)
η	removal efficiency	t	adsorption time (h)

concentration is of 0.05 μg/kg while for children's foods it is as low as 0.025 μg/kg.

Techniques to reduce aflatoxins concentration in liquid foods include prevention strategies to reduce the fungal contamination before harvest, decontamination methods to select only the uncontaminated commodities and detoxification procedures aiming to deplete the mycotoxin content of foods by means of physical, chemical or biological treatments.

The main drawback of decontamination processes is related to the intrinsic complexity of recognizing and separating the contaminated crops from the uncontaminated ones. Nowadays, there are no automatic methods for the rapid detection and separation of aflatoxins–contaminating crops. Indeed, while for small-scale productions a manual selection can be reasonably adopted, for large-scale productions the manual selection becomes almost inapplicable. For this reason, the detoxification of contaminated liquid foods appears to be much more reliable than the decontamination of the original raw materials.

Detoxification treatments (e.g. Piva et al., 1995) should be technically and economically reliable, and should meet the criteria listed by the FAO/WHO/UNEP Conference on Mycotoxins held in Nairobi, Kenya in 1997. According to these criteria the ideal process: (a) destroys or inactivates the toxin, (b) does not produce toxic or carcinogenic products in the finished product, (c) destroys fungal spores and mycelia that could proliferate and produce the toxin, (d) preserves the nutritive value and acceptability of the product, and (e) does not significantly alter important technological properties of the product.

In line of principle, the adsorption treatments seem to intrinsically achieve some of these criteria as they are usually cost effective, they exclude the formation of secondary contaminants and they are proven to have high removal efficiency for AFB–AFG removal from aqueous and organic solutions. Furthermore, a peculiar feature of adsorption processes is their ability to auto-adapt to inflow pollutant content. This feature is of the greatest relevance for the high variability of aflatoxin concentrations in natural contaminated milks.

Variety of adsorbent materials like activated carbons and clays has been shown to capture *B* and *G* aflatoxins in aqueous solutions (e.g. Galvano et al., 1995; Daković et al., 2000, 2005; Diaz et al., 2002; Phillips et al., 1988). More details on the experimental conditions and the obtained results are reported in Table 1, showing that adsorption treatment usually allows a very high removal of aflatoxins from water. Furthermore, activated carbons and phosphosilicate clay are currently used as alimentary integrator for grazing animals as they bind aflatoxins in their intestinal apparatus reducing the occurrence of pathologies and contamination of milk (Hatch et al., 1982; Galvano et al., 1996; Nageswara Rao and Chopra, 2001; Diaz et al., 2004).

An early study by Applebaum and Marth (1982) pointed out that the adsorption on bentonite of AFMs from naturally contaminated milk allows a removal efficiency ranging from 65% to 89% by increasing solid loading from 5 to 20 g/kg. Batch experimental tests have been carried out at 25 °C and shows that the protein content of the treated milk is around the 95% of the original material.

This study aims to verify the reliability of adsorption process as a method for milk detoxification by experimental comparison of several conventional and unconventional sorbents. Lab-scale tests consist in the screening of the sorbent removal efficiencies for different kinds of activated carbons, zeolites, clinoptilolite, bentonite and char and are carried out on bovine milk artificially contaminated with AFM1 standard solutions. The treated milk is eventually analyzed in order to test the sorbents effects on its nutritional properties.

2. Experimental analysis

2.1. Materials

2.1.1. Milk

The sample milk is obtained from an UHT whole milk produced in the northern area of the Caserta province, in Italy, artificially contaminated with standard AFM1 standard solution (Supelco reagent grade 46319-U) to obtain a mycotoxin content of 0.5 μg/kg. Standard solutions are former dilute 1:100 in methanol and then added to the milk sample.

2.1.2. Adsorbents

Adsorption equilibrium tests have been carried out with nine different sorbents, four carbonaceous materials, three commercial zeolites and two minerals. As regards the carbons, experiments are carried out with three type of activated carbons: Filtrasorb 400 (Calgon Carbon), Aquacarb 207EA (Sutcliffe Carbon) and GCN1240 (Norit). These are non-impregnated granular activated carbons commonly used for water treatments. They are characterized by a high specific area, mainly related to their microporosity,

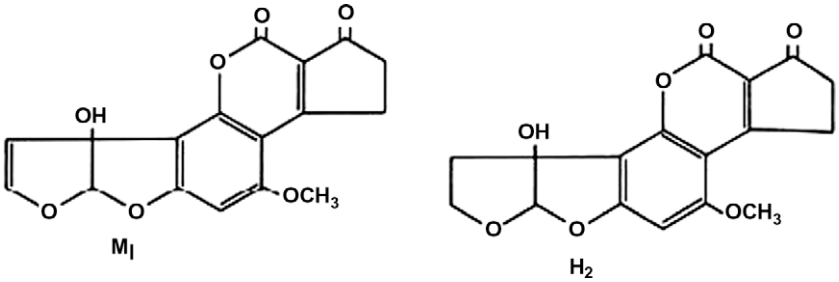

Fig. 1. Chemical structure of AFM1 and AFM2.