Effect of temperature on AFB1, AFB2, AFG2 and T-2 mycotoxins' decomposition in sunflower oil under the irradiation of ultraviolet light

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Abstract. After developing the decontamination method with UV light and establishing the specific analytical procedure with multiple extraction and HPLC, a method was developed to determine the effect of temperature on AFB1, AFB2, AFG2 and T-2 mycotoxins' decomposition in sunflower oil. This paper presents an experimental study concerning the decontamination of mycotoxins in sunflower oil with a new type of photoreactor; the aim of this study was to determine the influence of temperature during the photochemical process. Experiments were conducted at different temperatures, observing the mycotoxin concentration decrease. Our study on the decontamination process shows the relevance of temperature effect; data confirm the differences between AFB1, AFB2, AFG2 and T-2 mycotoxin behaviour. In the photochemical conditions used, obtained mathematical models and specific data can be used to determine the conditions needed by the evolved refining process. Comparing the proposed decontamination process with the classic procedure, photochemical decontamination can be used to increase the nutrient value of the sunflower oil.

Key words and phrases: mycotoxins, photodegradation, sunflower oil, HPLC.

1 Introduction

In the case of the industrial-scale production of sunflower oil, a large portion of mycotoxins, contained previously in oilseeds, is transferred due to the specific solubility in triglycerides. The main manufacturing process uses cold or warm pressing, solvent extraction and later refining, but these stages do not lower the mycotoxin concentrations. As a consequence, the product may become undesirable, usually transferring to bio-fuels. The photochemical decontamination process may be advantageous if added to the end of the refining process, because the obtained product has a higher nutrient value. In contrast with this, other decontamination methods are not convenient due to the minimal intervention principle. In the recent years, several methods have been developed to determine the mycotoxin content of foods, but decontamination process was not considered available (*Hussein-Brasel*, 2001). Reducing or removing mycotoxin concentration from sunflower oil is a food engineering interest because mycotoxins have a multitude of negative health effects on mammals (*Richard*, 2007). Previous studies were conducted to determine the influence of the initial peroxide index of sunflower oil (*Agachi-Gombos*, 2010), the initial concentration of mycotoxins and the influence of bentonite on suspension (*Gombos-Agachi*, 2010).

Scientific publications contain very little useful information and kinetic data on the thermal stability of mycotoxins. In the contaminated sunflower oil's photochemical treatment process is expected that temperature may have small influence on the decontamination process (*Lippolis et al.*, 2008). Taking into account the multitude of contained chemical species, we consider useful to determine the influence of temperature and to find any favourable temperature of the photodegradation of mycotoxins in this composition matrix.

Finding temperature influence on sunflower oil decontamination has two major purposes: to reduce the concentration of mycotoxins, to determine the influence of each mycotoxin decontamination temperature investigated to achieve more efficient decontamination (*Sheppard*, 2008). Later, the sunflower oil refining processes have to use those values of temperatures in the industrial photochemical treatment.

Experimental part

In order to determine temperature effect on mycotoxin decontamination, we performed 4 series of experiments for each mycotoxin, conducted at different temperatures, that is, at 20, 30, 40 and 50 °C. The initial concentration of

mycotoxins was established based on scientific literature (*Sheppard*, 2008), temperature range was chosen based on the need to use small temperature changes, as the sunflower oil temperature at the end of the classical refining process is 25–28 °C. Due to economic reasons, significant temperature changes are not desirable since they would involve massive heat transfer equipments and energy costs. Figure 1 shows the schematic diagram of the experimental photoreactor system.
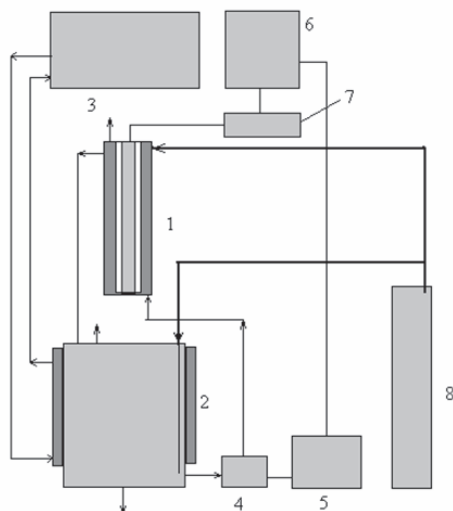

Figure 1: Schematic diagram of the experimental photoreactor system 1 – Plug-flow photoreactor (PFR); 2 – Buffer vessel; 3 – Ultrathermostat; 4 – Adjustable flow pump; 5 – Controller; 6 – Power switch unit; 7 – UV source power control unit; 8 – CO_2 cylinder

Reaction mass samples were collected from the photoreactor's effluent flow, which samples were extracted with methanol in five steps; the extracts were purified and concentrated, later analysed with Varian Star HPLC, using Varian Starn Chromatography Workstation Version 6.00 software, Supelcosil LC 18 column, 0,9 ml/min flow, eluent mixture of water, methanol and acetonitrile (130: 70: 40), excitation at 365 nm, emission at 435 nm, without derivatization (*Turner et al.*, 2009). Data statistical analysis allows observations in more details; for this purpose, experimental data values were processed in Statistica 6.0 software environment, using the Distance-Weighted Least Squares Fitting (DWLSF) method.

2 Results and discussion

Observed AFB1 $(c/c_{0\ \mathrm{AFB1}})$, AFB2 $(c/c_{0\ \mathrm{AFB2}})$, AFG2 $(c/c_{0\ \mathrm{AFG2}})$ and $\mathrm{T}-2$ $(c/c_{0\ \mathrm{T}-2})$ relative concentration values depending on irradiation time (t, minutes) at 20, 30, 40 and 50 °C operating temperatures (corresponding to initial peroxide index value $\mathrm{IP}_0 = 1$) are presented in figures 2, 3, 4 and 5.
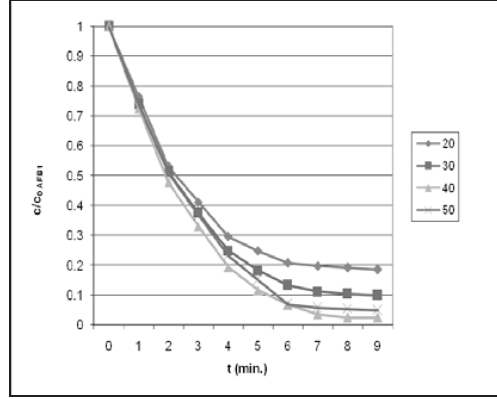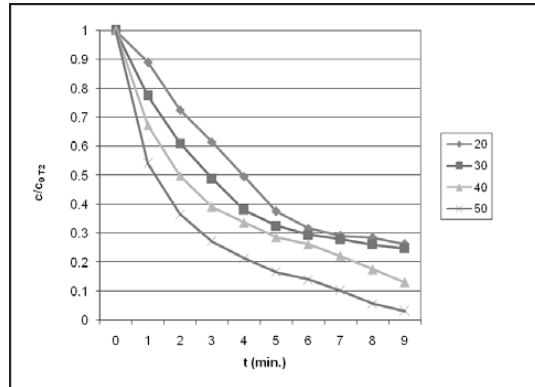

Figure 2: AFB1($c/c_{0\ \mathrm{AFB1}}$) **relative concentration depending on irradiation time (t, minutes) at 20, 30, 40 and 50 °C** ($\mathrm{IP}_0 = 1, c_{0\ \mathrm{AFB1}} = 2$ μg/kg)
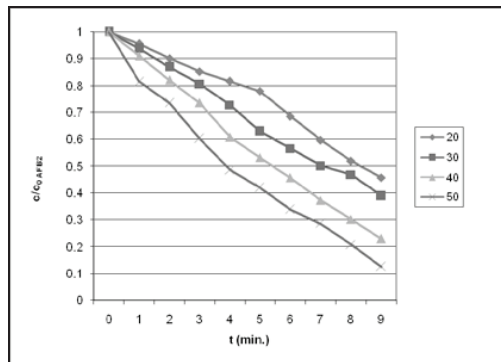
Figure 3: AFB2($c/c_{0\ \mathrm{AFB2}}$) **relative concentration depending on irradiation time (t, minutes) at 20, 30, 40 and 50 °C** ($\mathrm{IP}_0 = 1, c_{0\ \mathrm{AFB2}} = 2$ μg/kg)
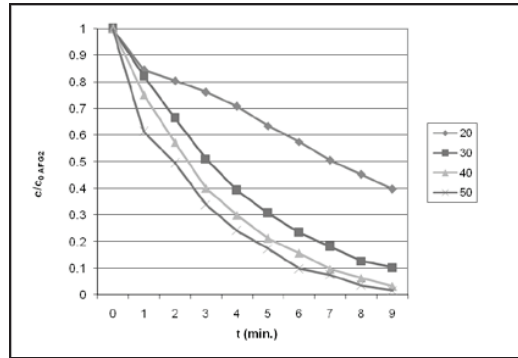
Figure 4: $AFG2(c/c_{0\ AFG2})$ **relative concentration depending on irradiation time (t, minutes) at 20, 30, 40 and 50 °C** $(IP_0 = 1, c_{0\ AFG2} = 2$ **µg/kg)**

Figure 5: Relative concentration of $T-2(c/c_{0\ T-2})$ **depending on irradiation time (t, minutes) at 20, 30, 40 and 50 °C** $(IP_0 = 1, c_{0\ T2} = 2$ **µg/kg)**

Variations of $c/c_{0\,AFB1}$ function of irradiation time at 20, 30, 40 and 50 °C show a relatively poor sensitivity of degradation rate. However, the overall temperature increase has a favourable effect on AFB1 photodegradation. At relatively low UV irradiation periods (up to 3 minutes), the maximum slopes of the curves are relatively similar, and then they decrease. Significant data were collected at 40 and 50 °C; at 50 °C, the value of $c/c_{0\,AFB1}$ is more favourable than at 40 °C. The polynomial equations of $c/c_{0\,AFB1}$ function of irradiating time t are:

$$- \text{ at } 20\,°C: \quad y = -0.001x^3 + 0.04x^2 - 0.374x + 1.342 \ (R^2 = 0.998); \quad (1)$$

$$- \text{ at } 30\,°C: \quad y = -0.001x^3 + 0.037x^2 - 0.374x + 1.34 \ (R^2 = 0.999); \quad (2)$$

$$- \text{ at } 40\,°C: \quad y = -0.001x^3 + 0.039x^2 - 0.395x + 1.36 \ (R^2 = 0.999); \quad (3)$$

$$- \text{ at } 50\,°C: \quad y = 0.03x^2 - 0.35x + 1.32 \ (R^2 = 0.999). \quad (4)$$

Based on the graph (Fig. 2), it is obvious that the favourable temperature range is 20-5 °C; a faster AFB1 photodegradation in sunflower oil is at 41 °C. Taking into account that reaction mass temperature rises inside the photoreactor, typically 0.5–1.5 °C, the favourable initial reaction mass temperature is 40 °C, depending on residence time and irradiative intensity of the UV source. Variations of $c/c_{0\,AFB2}$ indicate a relatively low sensitivity by temperature, but $c/c_{0\,AFB2}$ increase at higher temperatures. Clearly, increasing temperature has favourable effect on decreasing $c/c_{0\,AFB2}$ value, but data indicates nonlinear variations, particularly on 2–5-minute irradiation times, at 40 and 50 °C. The polynomial equations, which describe the variation of $c/c_{0\ AFB2}$ function of irradiation time t, are:

$$- \text{ at } 20\,°C: \quad y = -0.002x^2 - 0.032x + 1.028 \ (R^2 = 0.994); \quad (5)$$

$$- \text{ at } 30\,°C: \quad y = -0.006x^2 - 0.043x + 1.05 \ (R^2 = 0.997); \quad (6)$$

$$- \text{ at } 40\,°C: \quad y = 0.02x^3 + 0.018x^2 - 0.041x + 1.056 \ (R2 = 0.999); \quad (7)$$

$$- \text{ at } 50\,°C: \quad y = 0.016x^2 - 0.199x + 1.178 \ (R^2 = 0.997). \quad (8)$$

Figure 4 shows low sensitivity of decay rate; the relative concentration decreases at 30, 40 and 50 °C, but differently from 20°C, which indicate even lower sensitivity. The polynomial equations of $c/c_{0\,AFG2}$ dependence on irradiation time t are:

$$- \text{ at } 20\,°C: \quad y = -0.008x^3 + 0.069x^2 - 0.277x + 1.207 \ (R^2 = 0.996); \quad (9)$$

$$- \text{ at } 30\,°C: \quad y = -0.014x^2 - 0.229x + 1.219 \ (R^2 = 0.999); \quad (10)$$

$$- \text{ at } 40\,°C: \quad y = -0.001x^3 + 0.031x^2 - 0.328x + 1.297 \ (R^2 = 0.999); \quad (11)$$

$$- \text{ at } 50\,°C: \quad y = -0.012x^3 + 0.12x^2 - 0.607x + 1.482 \ (R^2 = 0.999). \quad (12)$$

Figure 5 shows a slightly different sensitivity of $c/c_{0\,T-2}$ by temperature than other (previously studied) mycotoxins, probably due to the specific molecular structure of $T-2$ toxin. Polynomial equations of $c/c_{0\,T-2}$ by irradiation time t are:

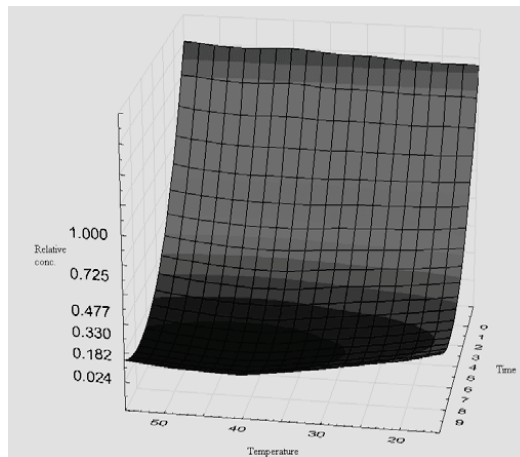$$- \text{ at } 20\,°C: \quad y = 0.006x^3 - 0.045x^2 - 0.021x + 1.061 \ (R^2 = 0.998); \quad (13)$$

$$- \text{ at } 30\,°C: \quad y = -0.001x^3 + 0.033x^2 - 0.313x + 1.281 \ (R^2 = 0.999); \quad (14)$$

$$- \text{ at } 40\,^\circ\text{C}: \ y = -0.011x^3 + 0.123x^2 - 0.613x + 1.497 \ (R^2 = 0.999); \quad (15)$$

$$- \text{ at } 50\,^\circ\text{C}: \ y = -0.021x^3 + 0.209x^2 - 0.908x + 1.708 \ (R^2 = 0.997). \quad (16)$$

Figure 6 illustrates the obtained AFB1 photodegradation's concentration-time-temperature relations with this fitting method.
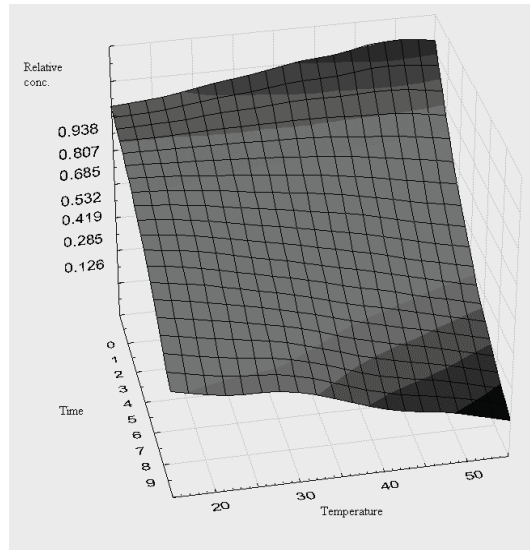

Figure 6: Reduced AFB1 concentration dependence by temperature and irradiation time, using DWLSF method $(IP_0 = 1, c_{0\,AFB1} = 2 \ \mu\text{g/kg})$

Figure 7 shows the obtained time-temperature-concentration relations for AFB2 photodegradation, using DWLSF method.

AFB2 photodegradation rate increases at higher temperatures; the highest photodegradation rate of AFB2 is at $50\,^\circ\text{C}$. Experimental data were not collected at higher temperatures because it is not favourable to use excessive sunflower oil temperatures. Taking into account the reaction mass temperature rise inside the photoreactor, typically 0.5–$1.5\,^\circ\text{C}$, the reaction mass initial temperature has to be $49\,^\circ\text{C}$ or even more, depending on residence time and the irradiation intensity. Figure 8 shows AFG2 time-temperature-concentration relations, using DWLSF method.

Based on Figure 8, AFG2 photodegradation rate increases at higher temperatures; the maximum observed rate is at $50\,^\circ\text{C}$. Taking into account reaction mass temperature rise inside the photoreactor, typically 0.5–$1.5\,^\circ\text{C}$, the initial temperature may be $49\,^\circ\text{C}$ or even more, depending on residence time and the irradiation intensity of the UV light source. Figure 9 illustrates AFG2 time-temperature-concentration relation, using DWLSF fitting method.
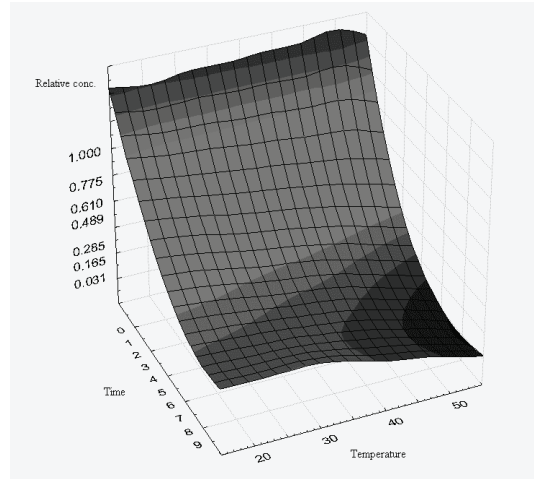
Figure 7: Reduced AFB2 **concentration dependence by temperature and irradiation time, using DWLSF method** ($IP_0 = 1, c_{0\,AFB2} = 2$ μg/kg)
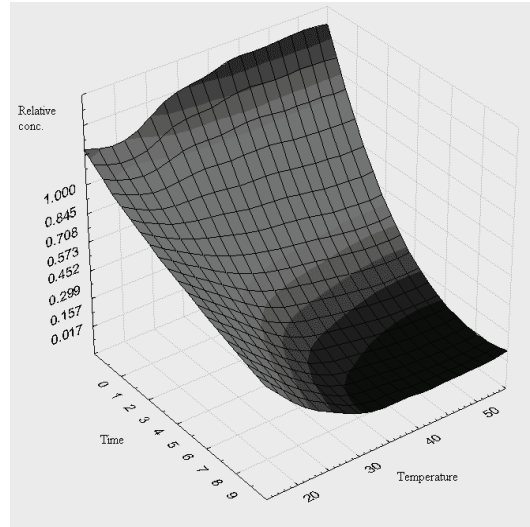
Figure 8: Reduced AFG2 **concentration dependence by temperature and irradiation time, using DWLSF method** ($IP_0 = 1, c_{0\,AFB2} = 2$ μg/kg)

Figure 9: Reduced $\mathsf{T}-2$ concentration dependence by temperature and irradiation time, using DWLSF method (IP0 = 1, $c_{0\,T2}$ = 2 μg/kg)

Based on the graph, it can be concluded that photodegradation rate of $\mathsf{T}-2$ toxin increases at higher temperatures; $\mathsf{T}-2$ toxin's higher photodegradation rate is at $50\,°C$. Taking into account the reaction mass temperature rise inside the photoreactor, typically 0.5–$1.5\,°C$, in this case, the reaction mass initial temperature may be $49\,°C$ or even more, depending on residence time and irradiation intensity of UV source. The generalized equations – which describe the studied mycotoxin (MT) concentrations' depleting during the photochemical process by UV radiation and in function of temperature –, using Statistica 6.0 software package, are:

$$\text{AFB1}: c_{AFB1} = 1.187 - 0.2252t - 0.135T + 0.0169t^2 - 0.0006tT + 0.0002T^2; \tag{17}$$

$$\text{AFB2}: c_{AFB2} = 1.0445 - 0.0485t - 0.014T + 0.0012t^2 - 0.0011tT - 6.975E - 5T^2; \tag{18}$$

$$\text{AFB2}: c_{AFB2} = 1.7109 - 0.1408t - 0.0392T + 0.0097t^2 - 0.001tT + 0.0005T^2; \tag{19}$$

$$\mathsf{T}-2; c_{T-2} = 1.079 - 0.1974t + 0.0008T + 0.0129t^2 + 4.5455E - 6tT - 0.0001T^2. \tag{20}$$

3 Conclusions

Based on the experimental data on investigated mycotoxins, by comparing experimental data, we may notice some differences and similarities regarding the photochemical behaviour. The highest sensitivity to the effect of increased processing temperature occurs for $\mathsf{T}-2$ toxin, followed by AFG2, AFB2 and

finally AFB1. showing the lowest sensitivity. It was observed that the effect of temperature in the photodegradation process may be connected with the behaviour of other chemical species which are present in the sunflower oil. From these experimental data on the effect of temperature, it can be concluded that the most effective decontamination process, the inlet temperature of the contaminated sunflower oil in the photoreactor should be adjusted, depending on the mycotoxin contamination. Increased temperature has a positive effect, except for AFB1. for which has been identified $41\,^\circ$C, this being more favourable at 20–$50\,^\circ$C. In the photochemical conditions used, obtained mathematical models and specific data can be used to determine the conditions needed by the evolved refining process. Comparing the proposed decontamination process with the classic procedure, photochemical decontamination can be used to increase the nutrient value of the sunflower oil.

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