The role of pumpkin seed oil in slowing lipid oxidation in functional beverages and its kinetic models

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Abstract: *The article investigates the role of pumpkin seed oil as a natural inhibitor of lipid oxidation in functional plant-based beverages. The main attention is paid to the quantitative assessment of antioxidant activity and construction of kinetic models of oxidative degradation of lipids during storage. Soy milk-based emulsions with the addition of pumpkin seed oil in concentrations of 1-5% were used as a model system. Oxidation was assessed by the peroxide value (PV), thiobarbituric acid index (TBA), and tocopherol content for 28 days at 25°C. It was found that the addition of 3% pumpkin oil reduces the oxidation rate by 32% for PV and by 29% for TBA. Based on the experimental data, a first-order kinetic model with a correlation coefficient of $R^2 = 0.96$ was constructed. The induction period was increased from 8 to 14 days. The results confirm that pumpkin seed oil effectively inhibits oxidation chain reactions due to its high γ-tocopherol and carotenoid content, and the developed kinetic model allows for the shelf life prediction of functional beverages.*

Keywords: *pumpkin seed oil, lipid oxidation, functional beverages, antioxidants, peroxide value, TBA index, kinetic model, γ-tocopherol, induction period, first-order reaction, emulsion*

Introduction

Lipid oxidation is one of the most common chemical spoilage processes in the food industry. It not only degrades the taste, color, and odor of the product, but also causes the formation of toxic compounds (e.g., malondialdehyde, 4-hydroxynonenal), which are hazardous to health. Functional beverages - especially those enriched with vegetable oils, seed, or nut extracts - are particularly susceptible to oxidation because they are emulsified systems in an acidic environment and have a high surface area.

Therefore, the use of natural antioxidants in their production is a modern approach. Since artificial antioxidants (BHA, BHT) can have negative health effects, consumers and regulatory agencies are against their use.

Pumpkin seed oil is widely recognized as a rich source of powerful natural antioxidants, such as γ -tocopherol, phytosterols, carotenoids, and polyphenols. In particular, γ -tocopherol is a 5-10 times more effective free radical scavenger in the lipid phase than simple α -tocopherol . However, the mechanism by which pumpkin seed oil inhibits lipid oxidation in functional beverages, as well as the kinetics of this process, has not yet been sufficiently studied.

Kinetic models are mathematical models that allow for scientifically based predictions of product shelf life by expressing the rate of oxidation. Such models are important for industrial enterprises to control product quality, indicate the correct expiration date on labels, and comply with international standards.

The relevance of this work is that in Uzbekistan, the antioxidant effect of pumpkin seed oil has not been studied not only quantitatively, but also kinetically. Therefore, this study determines the role of pumpkin seed oil in slowing down lipid oxidation in functional beverages, proposes the optimal addition amount, and builds a first-order kinetic model.

Analysis of scientific works (with examples from European countries)

In European countries, pumpkin seed oil is produced in Austria, Germany and Slovakia as "Styrian pumpkin seed oil" and its antioxidant properties have been extensively studied. The Austrian BOKU University (Rezig et al., 2020) determined the γ -tocopherol content of pumpkin oil to be 45-60 mg/100g, which is 4 times higher than that of sunflower oil.

A study conducted at the Max Rubner Institute in Germany (Zimmermann & Walczyk, 2021) showed that the addition of pumpkin seed oil to soy-based emulsions could reduce the TBI index by 28%. They also found that the oxidation kinetics followed a first-order reaction law ($R^2 > 0.95$).

The EMPA laboratory in Switzerland (2022) introduced the concept of a lag phase and observed that this period was extended from 7 to 13 days when pumpkin seed oil was added. They also used the Arrhenius equation as a kinetic model, allowing them to predict the temperature-dependent oxidation rate.

analyzed the correlation between peroxide value and DPPH radicals and proved that pumpkin seed oil slows down not only the initial oxidation, but also the subsequent stages.

However, most studies have been conducted only in laboratory conditions, and the practical application of kinetic models under real storage conditions is not yet sufficiently developed. It is with this aspect in mind that this work was carried out.

Method for studying the kinetics of pumpkin seed oil in slowing lipid oxidation in functional beverages.

Execution procedure:

Sample preparation: 6 samples were prepared based on an emulsion made from soy milk (87% water, 10% soybean oil, 3% lecithin):

N0: 0% pumpkin seed oil (control)

N1: 1%

N2: 2%

N3: 3%

N4: 4%

N5: 5%

were stored at 25°C, in the dark, for 28 days .

Analysis frequency: Peroxide number (PS), TBK index and every 4 days The amount of γ -tocopherol is measured.

Statistical analysis: Kinetic models were built in Excel and OriginPro programs.

Peroxide number (PS):

Titration with sodium thiosulfate according to GOST 6673-76 .

Result: PS on day 28 in N0 = 6.8 meq O_2/kg; in N3 = 4.6 meq O_2/kg → 32% decrease.

TBK index:

Reaction with thiobarbituric acid, spectrophotometry at 532 nm.

Result: TBK in N3 = 0.38 mg MDA/kg; in N0 = 0.54 mg MDA/kg → 29% reduction.

γ -Tocopherol composition:

HPLC (Agilent 1260), C18 column, 292 nm.

Result: Initial = 38.2 mg/100g at N3 ; Day 28 = 24.1 mg/100g (37% loss).

Building a kinetic model:

ln(PS) vs. time was constructed based on the PS data.

For N3: $k = 0.021$ days^{-1}, $R^2 = 0.96$.

For N0: $k = 0.031$ day^{-1}, $R^2 = 0.94$.

Determining the induction period:

- ✓ The time before the sharp increase in the TBK index.
- ✓ N0: 8 days ; N3: 14 days.
- ✓ Result (percentage gains)
- ✓ Oxidation rate reduction (PS): -32%
- ✓ TBK Index Reduction: -29%
- ✓ γ -Tocopherol retention: +18% (compared to control)
- ✓ Induction period extension: +75% (8 → 14 days)
- ✓ Kinetic model accuracy rate (R^2): 0.96
- ✓ Shelf life extension: +9 days (rancidity onset time)
- ✓ Antioxidant activity (IC_{50} DPPH): 18.4 μ g/mL (3% mixture)

Results and discussion

The results of the study showed that 3% pumpkin seed oil most effectively slows down lipid oxidation in functional drinks. This amount of γ -tocopherol is present in sufficient quantities to effectively neutralize free hydroperoxide radicals.

Kinetic analysis showed that the oxidation process obeyed the first-order reaction law, which confirmed the simplicity and practicality of the model. The rate constant (k) decreased to 0.021 day^{-1} when adding 3%, which was 32% lower than the control.

In particular, the induction period of 14 days means that the product is stable for the first 2 weeks, which is important for the industry. At 4-5%, the antioxidant effect decreases due to the oxidative properties of pumpkin seed oil itself (pro-oxidant effect).

Also, the 37% loss of γ -tocopherol over 28 days indicates that it is actively involved, confirming its function as an indispensable antioxidant.

The developed kinetic model can predict the PS or TBK value at any time, for example:

Conclusion: Pumpkin seed oil acts as an effective natural antioxidant in slowing down lipid oxidation in functional beverages. 3% is recommended as the optimal concentration, as this amount reduces the oxidation rate by 32%, with an induction period of up to 14 days.

The developed first-order kinetic model (R^2 = 0.96) allows for scientifically based prediction of product shelf life. This is of great importance for industrial enterprises in quality control, labeling expiration dates, and international certification processes. In the future, it is possible to further enhance the effect of pumpkin seed oil by synergistically adding it with other natural antioxidants (ascorbic acid, rosmarinic acid). In the conditions of Uzbekistan, such an approach is promising for the production of export-oriented, “healthy” and “sustainable” functional drinks.

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