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DEVELOPMENT OF A PH-RESPONSIVE BIOPOLYMER FILM BASED ON SILK FIBROIN AND *HIBISCUS SABDARIFFA* EXTRACT FOR SMART FOOD PACKAGING

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Abstract
Fish is among the most perishable food products, highlighting the need for simple and reliable approaches to freshness assessment. In this study, a biopolymer material for colorimetric monitoring of fish quality was developed using a pH-sensitive extract of *Hibiscus sabdariffa*. The anthocyanin-rich extract exhibited a pronounced color response within the pH range associated with fish spoilage, which was confirmed by UV–Vis spectroscopic analysis. In addition, the extract showed notable antioxidant activity as determined by a radical scavenging assay, supporting its multifunctional character. Agar-based films were selected as a biodegradable matrix; however, their strong sensitivity to moisture limits practical application on wet food surfaces. To address this issue, silk fibroin was incorporated into the polymer matrix. The resulting composite films displayed reduced swelling and enhanced mechanical stability compared to pure agar films, as evidenced by mechanical testing. These improvements enable stable performance under humid conditions relevant to food storage. Overall, the developed agar–silk fibroin biopolymer system provides a promising platform for smart packaging materials capable of real-time, visual freshness monitoring of fish products while maintaining environmental sustainability.
Keywords
Smart packaging, silk fibroin, *Hibiscus sabdariffa*, pH-indicator.

РАЗРАБОТКА PH-ЧУВСТВИТЕЛЬНОЙ БИОПОЛИМЕРНОЙ ПЛЕНКИ НА ОСНОВЕ ФИБРОИНА ШЕЛКА И ЭКСТРАКТА *HIBISCUS SABDARIFFA* ДЛЯ УМНОЙ УПАКОВКИ ПИЩЕВЫХ ПРОДУКТОВ

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Работа выполнена в рамках проекта РНФ №24-76-10093 «Разработка оптически активных индикаторов для умной упаковки пищевых продуктов».

Аннотация
Рыбная продукция относится к числу наиболее скоропортящихся пищевых продуктов, что обусловливает актуальность разработки простых и наглядных методов контроля её свежести. В данной работе предложен биополимерный материал для колориметрического мониторинга качества рыбы на основе pH-чувствительного экстракта *Hibiscus sabdariffa*. Экстракт, богатый антоцианами, демонстрирует выраженное изменение цвета в диапазоне pH, характерном для процессов порчи, что подтверждено спектрофотометрическими исследованиями в УФ–видимой области. Дополнительно показана высокая антиоксидантная активность экстракта, оценённая с использованием радикал-поглощающего теста, что подчёркивает его функциональный потенциал. В качестве полимерной матрицы использованы агаровые плёнки, однако их высокая

влагочувствительность ограничивает применение при контакте с влажными продуктами. Для повышения стабильности в матрицу введён фиброин шелка. Модифицированные плёнки характеризуются сниженным набуханием и улучшенными механическими свойствами по сравнению с чистым агаром, что подтверждено механическими испытаниями. Разработанный композитный материал рассматривается как перспективная основа для создания экологически безопасной умной упаковки, обеспечивающей визуальный контроль свежести рыбной продукции в реальном времени.
Ключевые слова
Умная упаковка, фиброин шелка, *Hibiscus sabdariffa*, pH-индикатор.

Fish is the perishable food product due to its high moisture content, rich composition of proteins and unsaturated lipids, which together become suitable conditions for rapid microbial spoilage, enzymatic degradation, and oxidative rancidity. Approximately two-thirds of the total fish biomass is discarded as waste around the world, contributing to environmental concerns and economic losses. Intelligent packaging solutions that enable real-time monitoring of freshness offer a promising approach to reduce waste by providing more accurate quality assessment than simple expiration dates [1]. Food spoilage in protein-rich products, such as fish, is accompanied by a pH increase, making pH-sensitive colorimetric indicators a promising tool for freshness monitoring. Natural anthocyanins from *Hibiscus sabdariffa* extract can serve as safe visual indicators in smart food packaging. However, the high hydrophilicity of polysaccharide-based films limits their application on moist food surfaces. To overcome this limitation, silk fibroin is going to be incorporated into the film matrix containing *H. sabdariffa* extract to form a pH-responsive biopolymer material.

An aqueous extract of *Hibiscus sabdariffa* was obtained by cold infusion of ground dried calyces [2]. The extract has a clear pH-dependent color response, changing color from red at pH 2-4 to grey and yellow at pH 7-9. There was detected an absorption maximum at 520 nm in acidic media on the UV-Vis spectra, while another band at 600-630 nm appeared under alkaline conditions, and that confirms the pH-dependent optical response of the extract.

The antioxidant activity of the extract was evaluated using the DPPH (2,2-diphenyl-1-picrylhydrazyl) assay [3]. The extract demonstrated a DPPH inhibition of 52.22 ± 1.80%, corresponding to a Trolox Equivalent Antioxidant Capacity (TEAC) of 101.25 μmol TE/g of dry extract. Total phenolic content (TPC) was measured using the Folin-Ciocalteu method [4] and found to be 1.34 ± 0.02 mg gallic acid equivalent (GAE)/mL, which is consistent with the observed antioxidant activity.

At the beginning of material development, the film matrix was optimized based on agar-agar and glycerol without silk fibroin. Different agar-glycerol ratios were evaluated according to their properties like film thickness, solubility, swelling behavior, and mechanical properties. Tensile testing revealed a wide range of mechanical responses depending on the composition. Among the tested samples, the selected formulation (containing 1.5% agar-agar and 1% glycerol) exhibited a suitable balance between strength and flexibility, with a maximum force of 4.49 ± 0.53 N, an elongation at break of 16.6 ± 6.6%, and a Young's modulus of 1583 ± 354 MPa.

Then silk fibroin extracted from *Bombyx mori* cocoons using multi-stage processing was incorporated into the selected agar-glycerol matrix. This solution was added to the matrix at concentrations ranging from 0 to 1.25% (w/v). Agar-based films without fibroin exhibited pronounced water sensitivity and significant softening under moist conditions. The addition of silk fibroin led to a noticeable reduction in swelling and improved film integrity during exposure to water [5]. Fibroin-containing films maintained their shape and structural cohesion, indicating enhanced stability in humid environments. This behavior demonstrates that silk fibroin effectively moderates the water sensitivity of the polysaccharide matrix.

A biopolymer film system based on agar-agar and silk fibroin was successfully developed and optimized for application under moisture conditions. The aqueous extract of

Hibiscus sabdariffa demonstrated a distinct pH-dependent color response in the range relevant to fish spoilage, as well as pronounced antioxidant activity.

Stepwise optimization of the film matrix showed that agar-glycerol films require structural modification to ensure sufficient stability in wet environments. Incorporation of silk fibroin significantly improved the resistance of the films to swelling and softening, enhancing their suitability for contact with moist food products.

The obtained results can become a basis for the further development of smart packaging materials. Future work will focus on the incorporation of *Hibiscus sabdariffa* extract into the optimized silk fibroin–modified film matrix and on the evaluation of the functional performance of the resulting composite films under conditions relevant to food storage.

Literature

1. Uysal-Unalan I., Sogut E., Realini C.E., Cakmak H., Oz E., Espinosa E., Morcillo-Martín R., Oz F., Nurmi M., Cerqueira M.A., Perera K.Y., Ayhan Z., Arserim-Ucar D.K., Kanakaki C., Chrysochou P., Marcos B., Corredig M. Bioplastic packaging for fresh meat and fish: Current status and future direction on mitigating food and packaging waste // Trends in Food Science & Technology. 2024. Vol. 152, 104660. https://doi.org/10.1016/j.tifs.2024.104660.
2. Aydin G., Zorlu E.B. Characterisation and Antibacterial Properties of Novel Biodegradable Films Based on Alginate and Roselle (*Hibiscus sabdariffa* L.) Extract // Waste and Biomass Valorization. 2022. Vol. 13. P. 2991–3002. https://doi.org/10.1007/s12649-022-01710-3.
3. Kebede B.H., Them R.L., Mengistu B.A. Effects of extraction solvents on phenolic contents, in vitro antioxidant, and antimicrobial activities of roselle (*Hibiscus sabdariffa* L.) Calyx // Food Chemistry Advances. 2025. Vol. 9, 101119. https://doi.org/10.1016/j.focha.2025.101119.
4. Borrás-Linares I., Fernández-Arroyo S., Arráez-Roman D., Palmeros-Suárez P.A., Del Val-Díaz R., Andrade-Gonzáles I., Fernández-Gutiérrez A., Gómez-Leyva J.F., Segura-Carretero A. Characterization of phenolic compounds, anthocyanidin, antioxidant and antimicrobial activity of 25 varieties of Mexican Roselle (*Hibiscus sabdariffa*) // Industrial Crops and Products. 2015. Vol. 69. P. 385–394. https://doi.org/10.1016/j.indcrop.2015.02.053.
5. Rockwood D., Preda R., Yücel T., Wang X., Lovett M.L., Kaplan D.L. Materials fabrication from Bombyx mori silk fibroin // Nature Protocols. 2011. Vol. 6, no. 10. P. 1612–1631. https://doi.org/10.1038/nprot.2011.379.