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Inclusion of Natural Anthocyanins as Food Spoilage Sensors †

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Abstract: Food safety is one of the most contemporary subjects under the scope of the scientific community since it is a fundamental issue for the general population. The desire to use a simple, inexpensive, easy-to-read package freshness-indicator led to a multitude of proposals for package real-time sensors for food freshness indicators. The sensors' design strategy is to target a physical or chemical modification that occurs by the spoiling process, such as changes in temperature, moisture, or the detection of foodborne pathogens. One of the most common approaches is evaluating changes in pH, since a significant amount of food spoilage occurs with significant alterations (e.g., acidity increases on dairy products). However, some safety concerns emerge from the use of complex artificial chemical molecules such as pH indicators in active labels/packages for food. Naturally occurring anthocyanins are a safe alternative to classic pH indicators and have been applied as sensitive molecules for pH changes aimed at the development of active labels and active packing for food. This proposal briefly reviews the latest scientific contributions on the application of anthocyanins in food spoilage sensors.

Keywords: anthocyanins; food spoilage; pH indicators; sensors

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1. Introduction

The concern over the safety, quality, and shelf life of food goods is on the rise, leading to an important research line on biodegradable packaging or sensors offering shelf-life information. Intelligent packaging is defined as packaging that contains something (molecule, device, sensor, etc.) to monitor the condition of packaged food or the environment surrounding the food [1], and is activated by external stimuli (pH, water, or O_2) and can also monitor and alert consumers on the state of the food in real time.

Among the target parameters that can be used as an indicator of food freshness, pH stands out because it is affected by various types of food spoilage, such as the excessive ripening of fruits and vegetables, decomposition of meat or fish due to decay of molecules such as lipids and proteins, and causing variations in chemicals such as trimethylamine, dimethylamine, ammonia, hydrogen sulfide, carbon dioxide [2], that lead to pH changes [3]. Bacterial growth is also an important vector of spoilage [4] and can be monitored by pH changes, such as the dissoluble CO_2 [5] or the increase in the lactic or acetic acids concentration. Furthermore, targeting pH as a freshness indicator allows for the creation of colorimetric sensors that could be included in the packaging and provide real-time information in a way that is easy for consumers to understand [6].

Although the classical molecules, like methyl red and Nile red [7], brilliant blue [8], or meta-cresol purple sodium salt [9], are important in the development of pH-dependent color sensors, the appetence for natural and safer products directed the scientific community to turn to the polyphenols group, with a particular focus in anthocyanins, which are plant-derived pigments with potential health benefits [10]. The ability of anthocyanins to change color in response to changes in pH is consequently applied to systems and sensors in order to monitor food quality, estimate food shelf life, and, eventually, employ color indicators in food packaging [11]. In this work, the use of anthocyanin-based sensors is briefly reviewed.

2. Discussion

The ability of anthocyanins to change color in a pH-dependent process has been exploited to fabricate sensors that can measure the pH variation of packaged foods serving as freshness indicators. Table 1 presents a selection of the latest publications concerning smart packaging using this type of sensors.

Table 1. Selected studies of color-based sensors for food packaging applications using anthocyanins as sensitive molecules.

Anthocyanins Source	Base Material/Technique	pH/NH_3	Color Change	Application	Ref.
Black carrot	Cellulose acetate	5.9–7.1	Pink to purple	Meat	[12]
	Cellulose nanofibers	6.36–7.22	Deep carmine to khaki	Fish	[13]
Clitoria ternatea	Polymeric film: Sago (*Metroxylon sagu*)	6.50–10.30	Blue to green	Chicken	[14]
	Bilayer film polycaprolactone nanofibers	7.10–7.35	Pale blue to yellow-green	Shrimp	[15]
Curcumin	Low density polyethylene film	5.95–29.31 mg TVB-A/100 g	Yellow to brown	Meat/fish	[16]
	Matrix: corn starch, and polyvinyl alcohol	8.06–8.41–8.8	Yellow to red	Fish	[17]
	Polylactic acid and polypropylene carbonate film	-	Yellow to light orange	Shrimps	[18]
	Nanofiber: chitosan and polyethylene oxide	6.20–6.75	Yellow to orange	Chicken	[19]
Hibiscus rosa sinensis	Fiber mats: polycaprolactone and polyethylene oxide + silver nanoparticles	6.40–8.06 (at 4 °C)	Beije to olive green	Shrimp	[20]
Grape skin	Gelatin-based films and mats	13.32–27.81 mg TVB-N	-	Meat	[21]
Malva silvestris	Matrix: polylactic acid/polyethylene glycol/calcium bentonite	6.5–8.0	Greenish yellow to pink	Minced meat/chicken/shrimp/fish	[22]
Melastoma Malabathricum	Cellulose nanofibers and cellulose acetate	0.1–25% NH_3	Pink to intense red to light pink to brown to dark green	Fish/meat	[23]
Mulberry	Bilayer films: gelatin, ZnO nanoparticles and gellant gum	4.7–20–7 mg/100 g TVB-N	Pink to yellow	Fish	[24]
Purple Cabbage	Natural printed paper: hydroxyethyl cellulose, glycerol.	6.0–7.3	Purplish red to purple to bluish violet	Fish	[25]

Table 1. *Cont.*

Anthocyanins Source	Base Material/Technique	pH/NH_3	Color Change	Application	Ref.
Purple sweet potato	Double layer: internal hydrogel water, agar anthocyanins, external sunflower oil, beeswax, and glyceride monooleate	0.45–35.92 mg/100 g TVB-N	Dark pink to blue	Meat	[26]
Red cabbage	Biocomposite membrane: chitosan and starch in acetic acid	2.5–5.6	Yellow to reddish-brown	Milk	[27]
	Nanocomposite films: polyvinyl alcohol and nanoclays	~3-~6-~8	Red to light pink to olive green	Shrimp	[28]
	Pectin-based film	50–300 TVB-N ppm	Purple pink to light pink to green-blue	Fish/meat	[29]
	Potato dextrose agar and starch	-	Brownish pink to yellowish green	Fish	[30]
	Modified cassava starches	2–12	Pink to purple to blue to green to yellow	-	[31]
Rosehip	Hydrogel: dimethylacrylamide, gelatin, citric acid	2–12	Red to purple	Milk/cheese	[32]
Roselle	Film: Polyvinylidene Fluoride, anthocyanins Cinnamon essential oil	5.6–7.4	Pink to blue	Pork meat	[33]
	Bilayer: Polyvinylidene Fluoride + polyvinyl alcohol/Sodium alginate	8.72–18.02 mg/100 g TVB-N	Pink to bluish, then green to yellow	Pork meat	[34]

TVB-N: Total volatile basic nitrogen; TVB-A: Total volatile basic amines.

The inclusion of vegetal pigments as pH indicators, such as anthocyanin compounds, has several advantages since these molecules are safe, biocompatible, and present a series of very important biological and functional properties, including antioxidant activity, free radical scavenging activity, antimicrobial activity, among others [35]. Additionally, anthocyanins are known to provide benefits for the immune system, cardiovascular health, and prevent obesity by suppressing digestive enzymes [36–38]. Furthermore, anthocyanins have also been used in clinical tests, showing ability to reduce the oxidative stress and the inflammatory indicators, as well as presenting a positive impact on vascular function and hyperlipidemia. Moreover, these molecules might have an impact on glucose homeostasis and cognitive impairment [36].

However, an important drawback of anthocyanins is their lack of stability. Thus, a variety of elements, including pH, light, temperature, oxygen, and enzymes, have an impact on their stability [39]. Furthermore, the temperature, a crucial parameter in food processing, affects particularly heat-sensitive molecules, such as anthocyanins [40]. So, it is important to highlight research where the anthocyanins stability is a special focus. In a recent study, Zhikun Yang et al., developed a by-layer sensor by including ZnO nanoparticles in a gelatin-based layer. They achieved an increase in the color stability of the mulberry fruit anthocyanins with a limit of detection of 0.01 mM of NH_3 [24]. In another work, the use of polycaprolactone nanofibers also led to color stability and the color variation was reversible, which open the possibility of reuse the material [15].

Likewise, several reports showed strategies to improve the anthocyanin-based sensors' physical properties by improving the thermal stability [26], water resistance, vapor transmission [27], water resistance, and tensile strength [31]. Additionally, strategies such as the inclusion of cellulose nanofibers enhance the biodegradability of active packaging materials [23]. Up-to-date research items showed that this area of study is of crucial importance, pursuing safer, intuitive, and biocompatible ways of informing consumers of the freshness state of perishable food products.

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