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THE APPLICATION OF NATURAL DYES IN FOOD FRESHNESS INDICATORS DESIGNED FOR INTELLIGENT PACKAGING

Abstract: The paper presents natural dyes i.e. curcumin, grape peel and beetroot extract which were incorporated into the compositions of food freshness indicators. The obtained indicators were assessed and compared with an artificial dye, methyl red, in relation to their capability of volatile amine monitoring. Additionally, a model of volatile amine release based on the evaporation of ammonia solution was applied in the first stage of the presented research. The response of freshness indicators was estimated by the colorimetric analyses of colour alteration and the calculation of Total Colour Difference (TCD) index values. Comparing to the methyl red dye, the grape peel extract gave a similar response with the TCD value equalled ca. 30 units. Beetroot extract did not provide a desirable colour change and the most promising composition was the indicator containing the curcumin addition. Further research was made on the freshness indicators containing only curcumin, grape peel extract or methyl red. The indicators were evaluated in relation to their response to the spoilage of raw cod flesh both in the model system (chamber with evaluated indicators) and in food packaging (plastic box). Although all examined natural dyes were able to detect food spoilage, the response comparable to the methyl red was obtained for grape peel extract in the model system and for curcumin in a real package. Both natural dyes and methyl red provided the colour changes correlated with cod flesh spoilage and characterized with TCD values equal to ca. 30 units.

Keywords: food freshness indicator, intelligent packaging, natural dye.

JEL classification: L79, L89.

WYKORZYSTANIE NATURALNYCH BARWNIKÓW WE WSKAŹNIKACH ŚWIEŻOŚCI ŻYWNOSCI PRZEZNACZONYCH DO OPAKOWAŃ INTELIGENTNYCH

Streszczenie: W artykule przedstawiona została ocena możliwości wykorzystania naturalnych barwników, kurkuminy, antocyjanów oraz czerwieni buraczanej, we wskaźnikach świeżości żywności wykrywających lotne aminy. Właściwości wyżej wymienionych substancji zostały porównane z barwnikiem syntetycznym, czerwieńią metylową. W badaniach wstępnych zastosowano model oparty na wykorzystaniu par amoniaku, który symulował wydzielanie się lotnych amin podczas psucia się żywności. Reakcje wskaźników świeżości oceniono, mierząc zmianę zabarwienia i wyliczając wskaźnik TCD (ang. *Total Colour Difference*). W porównaniu do syntetycznego barwnika antocyjany zapewniły podobną odpowiedź wskaźnika świeżości, którego przebarwienie dało wartość TCD równą ok. 30 jednostek. Czerwień buraczana nie zapewniła satysfakcjonującej zmiany barwy wskaźnika. Najbardziej obiecujące rezultaty uzyskano, stosując dodatek kurkuminy. W dalszych badaniach zastosowano wskaźnik świeżości oparty na kurkuminie, antocyjanach oraz czerwieni metylowej. Zbadano reakcję wskaźnika na psujące się świeże mięso dorsza atlantyckiego w układzie modelowym (komora z badanymi wskaźnikami) oraz w opakowaniu do żywności (pojemnik z tworzywa sztucznego). Pomimo że oba oceniane barwniki naturalne były zdolne do wykrywania psującej się żywności, to odpowiedź wskaźnika świeżości, porównywalną do tej otrzymanej dla czerwieni metylowej, uzyskano dla antocyjanów w układzie modelowym, natomiast dla kurkuminy – w opakowaniu do żywności. Zarówno naturalne barwniki, jak i czerwień metylowa zapewniły zmianę zabarwienia wskaźnika świeżości skorelowaną z procesem psucia się mięsa dorsza oraz odznaczającą się wartością wskaźnika TCD równą ok. 30 jednostek.

Słowa kluczowe: wskaźnik świeżości żywności, opakowania inteligentne, naturalne barwniki.

Introduction

The freshness and safety of fish and fishery products are essential problems bothering fish producers and distributors. These food products are especially perishable goods due to their chemical content, microbiological contamination and complexity in their processing and distribution [FAO 2014; Ryder, Iddya, and Ababouch 2014]. The quality and freshness of fish and seafood could be evaluated by many different sensory, microbiology or chemical methods [Oehlenschläger 2014]. Unfortunately many of them are usually time-con-

suming, require expensive instrumentation or employ qualified staff; therefore they cannot be used in fast indicative analyses [Parlapani et al. 2015].

Modern food safety assurance systems rely mainly on preventative actions covering the complete life cycle of food products that includes their production, distribution and post-purchase processing by final consumers [Nychas et al. 2008]. The most common solution, which is also generally accepted by consumers in self-service packaging and distribution systems, is the connection of modified atmosphere packaging (MAP) with product refrigeration [Jeremiah 2001]. However such a combination does not provide complete information about the real state of the packaged product. Only visual assessment of uncertain food could warn the consumer against the results of possible alternations of the cooling chain during product distribution or food contamination during the packaging process [Salinas et al. 2012]. Therefore there is an increasing demand for simple methods of food freshness and safety indication, which could be applied in so-called intelligent packaging. From the definition, the name of intelligent packaging is applied to the particular properties of packaging or its material, that are capable to monitor the condition of packaged items or the circumstances of storage and distribution [Kerry, O'Grady, and Hogan 2006]. Consequently intelligent packaging could comprise Time and Temperature Indicators (so-called TTI indicators) or food freshness indicators. The latter ones enable the monitoring of food freshness or ripeness that are most often recognized indirectly by the information about its best-before period.

Freshness indicators could recognize the typical chemical products of food spoilage that are emitted inside a packaging. Compounds with the characteristic smell like trimethylamine (TMA), various other nitrogenous (classified together with TMA as TVB-N) and sulphuric compounds, aldehydes, ketones and esters are released during fish spoilage by various microorganisms, that are main cause of fresh fish quality decrease [Parlapani et al. 2014]. Total Volatile Basic Nitrogen (TVB-N) level refers to volatile compounds such as TMA, dimethylamine (DMA) and ammonia (NH_3) that are products of the microbial degradation of fresh fish [Pacquit et al. 2006]. TVB-N level is used as an indicator of fish spoilage and its limits for fishery products are defined in Commission Regulation (EC) No 1022/2008 [Commission Regulation 1022/2008 of 17 Oct. 2008]. Unfortunately the reference method for the determination of TVB-N involves the long-lasting extraction of volatile bases by perchloric acid solution followed by steam distillation of the extract, collecting it in boric acid and then titration against standard HCl [Commission Decision 95/149/EC of 8 March 1995]. Alternative methods, like photometric

measurements with a flow injection analysis [Ruiz-Capillas, Gillyon, and Homer 2000], chromatography method with solid-phase micro-extraction [Bene et al. 2001] or the electrochemical method using a near-field passive volatile sensor [Bhadra et al. 2015], require specialized equipment and skilled personnel.

Freshness indicators are usually simple colorimetric chemical arrays that are able to change their colour in the presence of target volatile compounds. Pacquit's group developed a solid-state sensor based on bromocresol green to monitor TVB-N level in fish headspace and established a correlation between the dye colour and the population of *Pseudomonas* spp. (microorganisms commonly spoiling fresh fish) [Pacquit et al. 2006, 2007]. The freshness indicator contained the pH sensitive dye, which was entrapped within a polymer matrix and placed onto polyethylene terephthalate substrate. As basic spoilage volatile amines were gradually produced in the package headspace, pH level increased resulting in the indicator colour change from yellow to blue. The change was visible to the naked eye. Other fish freshness indicators capable of TVB-N detecting inside sealed fish packages are based on polyaniline (PANI) film. [Kuswandi et al. 2012a]. The polymer film responded through colour change from green to blue in the presence of basic volatile amines released during the fish spoilage period. The sensor response was correlated with bacterial growth patterns in fish samples. The freshness indicator in a form of a colorimetric food package label enabled the real-time monitoring of the condition of a fish product either at various constant temperatures or with temperature fluctuations. The form of a sticker was used for other sensor utilizing volatile amines as a food freshness index [Kuswandi et al. 2013]. The colorimetric array with a methyl red acid-base indicator was immobilized onto a bacterial cellulose membrane. The presence of basic spoilage volatiles amines produced during food spoilage caused the increase of pH in the colorimetric array which was demonstrated in a form of its colour change from red to yellow. The indicator was applied to monitor the freshness of packed chicken cuts but its operating principle could be employed for the evaluation of fishery products. The sensor outcomes were correlated with the bacterial growth characteristics observed in the food samples, so it could be an effective tool for monitoring the freshness and microbial quality of packaged food products.

Foods and their packaging could have much higher consumer tolerance, when they contained natural colouring instead of artificial ones. Natural food dyes are recognisable as more harmless and healthy. Some constructions of freshness indicators have already exploited natural dyes that could be used as

a pH indicator. Bambang Kuswandi made also an attempt to utilize curcumin as an acid-dye indicator for the construction of food freshness indicators focused on the detection of basic spoilage volatile amines. The bacterial cellulose membrane was used as a carrier sheet for the immobilization of the natural dye that changed its colour adequately to pH increase associated with the increase of TVB-N amount in spoiled food [Kuswandi et al. 2012b]. The curcumin-based indicator detected a growing amount of spoilage volatile amines in the headspace of a package containing shrimps. The curcumin colour changed from yellow to orange and further to reddish orange for the ascending TVB-N content present in the packaging headspace. The sensor response was also correlated with the increase of bacterial contamination of analysed food samples. Less advanced research results were presented for a bio-based film with anthocyanin from grape anthocyanins that were designed as an indicator of chilled pork deterioration [Golasz, da Silva, and da Silva 2013]. Pork loin samples were placed in Petri dishes containing the anthocyanin film. The films were subjected to colorimetric measurement. Pork loin samples were analysed simultaneously for the psychrotrophic microorganisms' contamination and its pH level. The bio-based film with anthocyanin was able to monitor changes in the food product during storage through visible changes in its colour. The correlation between the colour of the film and the number of spoilage microorganisms was stable at the first stage of food quality deterioration. The end point of the pork samples spoilage could not be clearly determined.

Based on the information presented above and following our interest in developing a food freshness indicator [Krysińska, Tichoniuk, and Cierpiszewski 2013; Dobrucka and Cierpiszewski 2014; Cierpiszewski 2016] we can report on a promising study of natural dye application in a chromogenic indicator, which has been applied to follow the evolution of the ageing of cod flesh. Selected natural colouring, curcumin, beetroot or grape peel extract, was introduced into the composition of the food freshness indicator. The potential of the analysed mixtures was compared with the identification of volatile amine using methyl red (artificial colouring and pH indicator). A model of volatile amine release relied on the evaporation of ammonia solution was applied in the first stage of the study. The working of individual indicators was assessed by the colorimetric analyses of their colour modification and the evaluation of Total Colour Difference (TCD) index values. Curcumin, grape peel extract and methyl red were employed in freshness indicators used to follow the ageing of cod flesh both in the reaction chamber and in food packaging (plastic box).

1. Methodology

1.1. Materials and chemicals

Sodium carboxymethyl cellulose (with average molecular weight ca. 250 000), glycerol (with purity over 99%) and methyl red (MR) used in the study were purchased from Sigma-Aldrich (Poznań, Poland). Hydrochloric acid, HCl (35% solution) and ethanol (96% solution) were from Avantor Performance Materials Poland S.A. (Gliwice, Poland). Natural dyes, curcumin (90% ethanol solution) (E100), beetroot extract (69–72°Bx) (E162), grape peel extract (40±6°Bx) (E163) were obtained from Ipra Polska Ltd. (Nowy Sącz, Poland). The stock solutions of natural dyes were made using distilled water in the proportion 1:10. All other solutions were also prepared using distilled water.

The reaction chamber with circular forms (16.2 mm diameter) used for freshness indicator preparation and testing was made from transparent polystyrene (PS). The cell culture flasks were purchased from Bionovo (Legnica, Poland). Boxes with 500 ml volume, made from oriented polystyrene (OPS), and foil for sealing, made from the composite of polyethylene terephthalate and cast polypropylene (PET/CPP), were obtained from Bagstar (Warszawa, Poland). The boxes were applied for testing selected freshness indicators in real food packaging with a cod flesh sample.

1.2. Preparation of the freshness indicator

The stock solutions of natural dyes were freshly prepared as 10% (v/v) solutions of its original extracts or solution, and they were stored in lightproof flasks before use. Methyl red was applied as a 3% (w/v) stock solution in 50% (v/v) ethanol solution. Freshness indicator preparation began with the dissolution of carboxyethyl cellulose (3% w/v) in distilled water at the temperature of 40°C. Then the mixture was enriched with 1% (w/v) glycerol, 3% (v/v) solution of natural dye or methyl red stock solution and 0.01% (m/v) HCl solution. The homogenous mixture of a particular freshness indicator was degassed in an ultrasound bath for 1 minute. 0.7 ml portion of the mixture was placed into a circular form (16.2 mm diameter) and left to dry at room temperature for 20 hours. Freshness indicators placed onto foil for sealing packages (PET/CPP foil) were left to dry for 16 hours.

1.3. Model research with ammonia solution

A prepared and dried freshness indicator placed in the reaction chamber (cell culture flask) was used for the preliminary study of the pH indicator reaction (colour change of natural or synthetic dye) to the presence of volatile amine. As a model of TVB-N level increase the evaporation of 5% (m/v) ammonia aqueous solution was used [Pacquit et al. 2006; Heising et al. 2012; Kuswandi et al. 2012a]. For each two analysed freshness indicators a portion of 0.5 ml 5% (v/v) ammonia solution was introduced into the reaction chamber, which was further closed tight with a glass plate (1 mm thick) and monitored at room temperature. The volume of the chamber was ca. 100 cm³. The indicator response (colour change) after the addition of the NH₃ solution and the chamber being closed was monitored by taking photos with a digital camera (Canon PowerShot S3 IS) with the same settings for all of the measurements. The experiment was repeated three times for each of the analysed freshness indicators.

The colour of a particular freshness indicator was evaluated using GIMP 2.8 graphic software [The GIMP Team 2015] and WorkWithColor colour converter [WorkWithColor 2015]. The average colour of the freshness indicator was measured in the RGB colour model and converted into the CIE L*a*b* colour model. The colour changes were measured in regards to the appearance of the dried freshness indicator before interaction with ammonia vapour. In order to describe the range of colour difference a Total Colour Difference (TCD) index was calculated according to the following equation [Nopwinyuwong, Trevanich and Suppakul 2010; Golasz, da Silva, and da Silva 2013]:

$$\text{TCD value} = \left[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2 \right]^{1/2},$$

where:

ΔL , Δa , Δb – differences in L , a and b – parameters between the colours description in CIE L*a*b* model of evaluated and reference freshness indicators.

TCD index values above 5.0 referred to noticeable colour changes. The TCD index equalled 12.0 or more characterised colour changes that were visible to the naked eye [Nopwinyuwong, Trevanich, and Suppakul 2010].

1.4. Indicator response to fish flesh spoilage

Dried freshness indicators present in the reaction chamber were applied to monitor fish flesh spoilage. A set of evaluated indicators were closed in the chamber with a fresh cod flesh sample (25 g weight) and stored at room temperature for 20 hours. The response of the particular freshness indicator was recorded by taking photos with a digital camera, evaluation of its average colour and calculation of TCD index values. The whole research procedure was the same as described in Section 1.3. Each indicator was analysed three times and the final research results were an average from the three independent measurements.

The study of the freshness indicators' performance and working in real food product packaging was performed by its positioning onto a plastic foil for packaging sealing made from the composite of polyethylene terephthalate and cast polypropylene (PET/PPP). The fresh cod flesh sample (100 g weight) was placed into a plastic box with a 500 ml volume made from oriented polystyrene (OPS) and sealed with the PET/PPP foil containing analysed indicators immobilized from its inner side. The packed fish sample was stored at room temperature for 22 hours. The changes of the freshness indicator colour were monitored by taking the photos and analysing them according to the procedure described in Section 2.3. Each indicator was examined three times.

2. Results and discussion

2.1. Model research with ammonia solution

The main element of the freshness indicator, responsive to volatile basic (or acidic) products of food spoilage, is a pH indicator dissolved in the sensor composition, whose reaction is observable and correlated with packed product quality and freshness deterioration. Although the quite successful application of some artificial pH indicator in such colorimetric arrays [Pacquit et al. 2006, 2007; Kuswandi et al. 2012b, 2013; Morsy et al. 2016] there are requests for alternative compounds which ensure a more precise response of an indicator or are more acceptable for food consumers. In our study the selected natural dyes, curcumin (E100), beetroot and grape peel extracts (E162 and E163, respectively), were considered as an effective pH indicator for fish freshness sensors. All of the chosen dyes are approved as food additives; therefore they have E numbers, which are given for substances that are permitted to be used as food additives within the European Union and Switzerland. The natural dyes due to their physicochemical properties are able to change colour as a result of

the ambient pH modification for example from neutral or acidic to a basic one. Their properties were compared in the study with the artificial pH indicator, methyl red, whose solution has a red colour in the acidic pH range and yellow in the basic one. Each one from the analysed colouring was implemented in the fish freshness indicator performed according to the procedure described in Section 1.2. The obtained freshness sensors were tested in a model research with ammonia solution (Section 1.3). The response of the particular indicator for ammonia vapour imitating volatile basic food spoilage products was presented in the form of the TCD index values in Tables 1 and 2.

Table 1. Response of freshness indicators based on methyl red dye or on natural dye, grape peel extract, for the presence of vaporized ammonia

Interaction with NH ₃	Freshness indicator with artificial dye – methyl red					
	0 sec.	10 sec.	3 min.	10 min.	20 min.	30 min.
TCD value	–	3.0 ± 1.1	12.6 ± 0.9	30.3 ± 1.2	31.6 ± 1.5	31.8 ± 1.1
	Freshness indicator with natural dye – grape peel extract					
TCD value	–	8.7 ± 1.2	21.5 ± 0.8	33.4 ± 1.1	34.8 ± 1.4	34.2 ± 1.1

The grape peel extract revealed a similar response of the freshness indicator in comparison to the artificial pH indicator, methyl red. Both compositions were characterized with the TCD index equalled ca. 30 (Table 1). The maximal values of the total colour difference index were obtained after a ten minute interaction of indicators with ammonia vapour. Beetroot extract did not provide the required colour change of the freshness indicator based on it (Table 2). Its colour change was nearly observable and the indicator seemed to be an unchangeable reddish colour through the whole experiment.

The most promising indicator turned out to be the composition including the curcumin addition. This freshness indicator changed its colour from yellow to dark brown (with TCD about 60) during the interaction with the vaporised ammonia solution (Table 2).

Table 2. Response of the freshness indicator based on beetroot extract or curcumin for the presence of vaporized ammonia

Interaction with NH ₃	Freshness indicator with artificial dye – beetroot extract					
	0 sec.	10 sec.	3 min.	10 min.	20 min.	30 min.
TCD value	–	3.6 ± 1.1	4.1 ± 0.6	5.6 ± 0.7	9.4 ± 1.0	10.6 ± 1.0
	Freshness indicator with natural dye – curcumin					
TCD value	–	2.5 ± 0.8	33.4 ± 1.1	56.0 ± 1.5	59.8 ± 2.3	59.5 ± 2.0

The application of curcumin as a pH indicator resulted in a clear colour alteration of the indicator in the presence of target volatile compounds. Nevertheless, the addition of HCl to the indicator mixture worsened its homogeneity and the solubility of curcumin. For the further experiments with the natural dye as a component of the freshness indicator the HCl addition was omitted. The indicator compositions containing curcumin or grape peel extract were typed to be used for monitoring the freshness of real fish flesh and to compare their response with the work of the methyl red colorimetric sensor and with the sensory changes of the food product.

2.2. Freshness indicator response to fish flesh spoilage in model conditions

Selected pH indicators were employed in the *in vitro* test with cod flesh samples. Freshness sensors containing curcumin, grape peel extract or methyl red were placed into the reaction chamber together with the fresh cod flesh sample and stored at room temperature for 20 hours (Figure). The indicators' response (in the form of the TCD index values after the storage period) when the fish samples started to smell unpleasant is presented in Table 3. The first symptoms of cod flesh spoilage appeared after 12 hours of storage at room temperature in a closed reaction chamber.

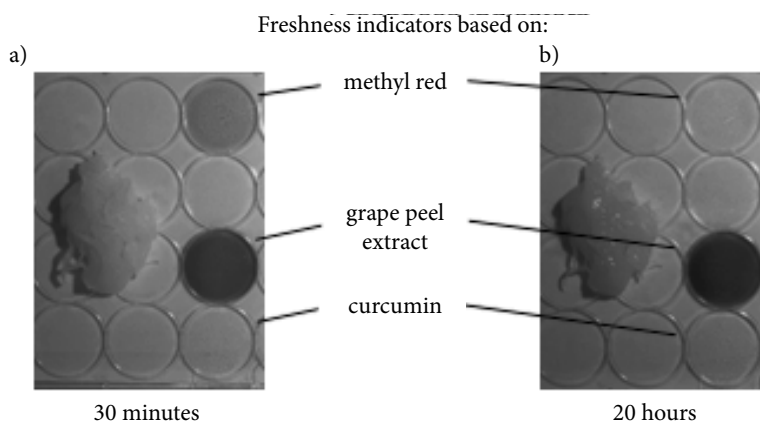


Figure 1. Reaction chamber with a sample of raw cod flesh and freshness indicators containing methyl red, grape peel extract, curcumin after 30 minutes (a) and 20 hours of interaction (b)

Taking into consideration the noticeable beginning of fish spoilage after 12 hours of its storage, the first indicator that reacted to changing its colour

was the sensor containing curcumin. Its response was fast and resulted in the satisfactory measurements of TCD index values confirming the visibility of the indicator action. The freshness sensor containing curcumin changed its colour from yellow to orange during the whole experiment.

The indicators based on grape peel extract and methyl red responded a little bit slower but the final colour change and measured TCD index values (equalled almost 30) were more promising for the two sensors' compositions (Table 3). One drawback of the grape peel extract application in the freshness sensor was not very attractive to start with and the final colours of the indicator – dark brick red and dark brown-claret, respectively. Nevertheless, the difference in the freshness indicator colour at the beginning and at the end of the experiment was easy to notice and the obtained TCD values were comparable to the response of the indicator based on methyl red.

Both natural dyes, curcumin and grape peel extract, provided a satisfactory response (colour change) of the indicators, that was correlated with the deterioration of the quality and freshness of the cod flesh samples. The activity of the grape peel extract measured by the TCD index values increasing during the experiment was comparable to the reactivity of the freshness indicator based on artificial dye, and methyl red. The model experiments were performed to ensure optimal conditions for monitoring indicator changes and to exclude other factors that could influence the observed indicator colours.

Table 3. Response of the freshness indicator based on methyl red dye, grape peel extract or curcumin for the presence of perishable cod flesh in the reaction chamber

Interaction with fish flesh	Freshness indicator with artificial dye – methyl red					
	0.5 hour	12 hours	14 hours	16 hours	18 hours	20 hours
TCD value	3.6 ± 0.3	5.1 ± 0.9	6.8 ± 0.5	12.5 ± 0.5	21.25 ± 1.5	29.8 ± 0.5
	Freshness indicator with natural dye – grape peel extract					
TCD value	3.1 ± 0.7	3.9 ± 0.6	6.9 ± 0.3	10.0 ± 0.6	16.0 ± 0.7	29.6 ± 0.2
	Freshness indicator with natural dye – curcumin					
TCD value	2.6 ± 1.0	10.8 ± 2.2	16.8 ± 0.6	18.3 ± 0.3	23.3 ± 0.8	23.4 ± 0.8

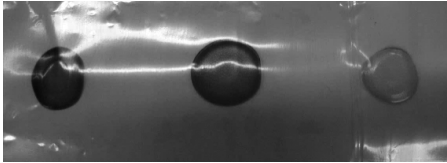
2.3. Indicators' response to fish spoilage in real food packaging

Selected freshness indicators containing methyl red or one of the natural dyes, grape peel extract or curcumin, were applied to examine its response to a food sample (cod flesh) in real food packaging. A set of three analysed freshness indicators were immobilized on the inner side of the foil for sealing the plastic packages (Figure 2). The foil was highly transparent and was performed from

a composite of polyethylene terephthalate and cast polypropylene (PET/CPP). The fresh cod flesh sample (100 g weight) was inserted into the plastic box (500 ml volume) made from oriented polystyrene (OPS) and sealed with the PET/CPP foil containing the tested indicators immobilized from its inner side. The packed fish sample was stored at room temperature for 22 hours. The changes of the freshness indicator colour were monitored by taking photos and analysing them by calculating the TCD index values for a particular indicator.

The box made from OPS plastic and sealed with PET/OPP foil was more hermetic than the reaction chamber applied in previous experiments. The indicator colour changes were observed before any significant deterioration of the fish sample quality. The least significant but observable colour changes were recorded for the freshness indicator based on the grape peel extract. Its colours changed from dark brick red and dark claret, which was accompanied by the increase of the TCD index values up to about 16 units (Table 4).

a)



b)



Figure 2. Freshness indicators containing grape peel extract (right side), methyl red (central position) or curcumin (left side) immobilised on PET/CPP foil (a) and inside the food packaging (OPS plastic box) (b)

Table 4. Response of the freshness indicator based on methyl red dye, grape peel extract or curcumin for the presence of perishable cod flesh in real packaging

Interaction with fish flesh	Freshness indicator with artificial dye – methyl red					
	14 hours	15 hours	16 hours	18 hours	20 hours	22 hours
TCD value	19.7 ± 1.4	23.1 ± 0.5	30.4 ± 0.4	32.6 ± 2.3	32.0 ± 1.0	32.8 ± 1.4
	Freshness indicator with natural dye – grape peel extract					
TCD value	12.0 ± 1.4	13.9 ± 1.5	16.8 ± 1.6	16.6 ± 2.0	15.1 ± 1.1	15.7 ± 0.7
	Freshness indicator with natural dye – curcumin					
TCD value	19.5 ± 1.0	22.2 ± 1.2	26.7 ± 0.9	26,8 ± 1.3	26.1 ± 6.7	26.3 ± 5.7

The freshness indicator containing curcumin natural dye presented a clear change of colours during the storage of the packed fish. It was light yellow at the beginning of the experiment and it became a more and more intense orange as the food spoilage progressed. The response of this indicator expressed in the evaluated TCD index values equalled ca. 26 units and was a little lower than the TCD values measured for the indicator with methyl red (Table 4). Curcumin provided the sensor colour change from light yellow to orange. The indicator based on methyl red altered its colours from raspberry red to light straw yellow. Noticeable was also the stability of the changed colours in the case of both freshness indicators.

Conclusions

The presented colorimetric sensors were tested in relation to the applied pH indicator, in relation to their ability to monitor the deterioration of cod flesh quality and freshness. Three selected natural dyes, curcumin, beetroot and grape peel extract, were examined and compared as a pH indicator with methyl red (an artificial colouring). The model research with ammonia vapour as a substitute of volatile basic food spoilage products excluded the application of beetroot extract as a pH indicator because of the unsatisfactory response of the analytical array based on it. The other two analysed natural dyes, curcumin and grape peel extract, exhibited sensitivity to volatile basic fish spoilage products similar to the response of the pH artificial indicator, methyl red. Both of them could be incorporated in effective food freshness indicators for intelligent packaging. Especially curcumin provided clearly observable changes of indicator colour from yellow to orange during the deterioration of the packed fish (cod flesh) quality and freshness.

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