

## Review Article

# Application of Smart Sensors for Monitoring Spoilage of Aquatic Foods

Vinothini Vaz Motcham, Madhan Kathavarayan, Hema Anjappan, Kesavan Devarayan\*

College of Fisheries Engineering, Tamil Nadu Dr.J.Jayalalithaa Fisheries University, Nagapattinam, Tamil Nadu – 611 002, India

**Abstract**

Freshness is a key factor for any aqua food. However, determination of freshness is rather difficult due to influence of time and handling. Alternatively, spoilage can be used as a measure to indicate whether an aquatic food is 'consumable' or 'non-consumable'. Several researches demonstrated different invasive as well as non-invasive techniques for determination of fish spoilage. However, most of these techniques are expensive and laborious. A simple visual indication of the spoilage by color changing materials is more beneficial for efficient monitoring of packaged fish spoilage. In this view, present article critically reviews preceding researches on the development of halochromic sensors for monitoring aqua food spoilage and gives suggestions for prospective improvement of these sensors.

**Keywords:** Aqua food spoilage, fish spoilage sensor, nanomaterials, halochromic materials, halochromic sensor, shrimp spoilage, fish freshness

**\*Correspondence**

Author: Kesavan Devarayan  
Email: dev.kesavan@gmail.com

**Introduction**

Though there are seven senses, humans depend on visual information predominantly. This is mainly because it is presumed that representation in visual format is the best way of understanding any complex data. If one recaps the scientific inventions, for instance, telescopes, microscopes, infrared cameras, scanning electron microscopy among many others, are simple extension of our visual sense only. In contrast to other senses, the sense of sight is comparatively strong. So only it is possible for us to differentiate thousands of colors with our eyes. However, beyond the visual, there is also availability of further ways of sending signals to our senses. Rare individuals have synaesthesia i.e. the production of a sensation relating to one sense of the body by stimulating another sense of the body. Likewise in the world of science, many scientists, inventors and technologists made sincere attempts to convert one type of sensory input to a different type of sensory output. One such technology is 'smart sensors' or 'electronic noses' that detects gases and converts it into a digital or visible data.

Freshness is an important quality of aqua foods. Though the terms 'freshness' and 'spoilage' are used synonymously used in practice both are technically different. For fishes, freshness is rather difficult to find. Instead, the degree of spoilage can be determined by different method. Spoilage management is a very difficult task in the food industry. Undesirable microbial contamination in the food poses a threat to consumers' health. Several traditional methods are still exists for detecting the microbial contamination. But these traditional methods were laborious, tedious, time consuming and mostly destructive. Spoilage is mostly judged by odour, color and texture in our daily life. Total volatile base nitrogen (TVB-N) is a widely used potential indicator to monitor the freshness of aqua foods. However, the TVB-N method is lengthy, time consuming and need pre-treatment of fish samples and suitable for research and laboratory levels only. Some of the amines such as trimethylamine are produced in fish immediately after its death and also its concentration increases with time. So these vapours of amines can be used to indicate the spoilage of fish rapidly without damaging the fish.

Biosensors are made using biological materials which acts as a sensing element which reacts with the analytes resulting in detectable physical or chemical change. Hence the biosensors offer a major advantage in detecting this spoilage immediately without destruction. The inherent specificity over target and sensitivity makes them ideal to use in food industry widely. But the application of the biosensors has to meet its standard analytical technique in terms of performance, cost and reliability.

**Nanomaterials in biosensors**

The development of biosensors for quality control in food industry is a key field for nanomaterial science and nanobiotechnology. The integration of nanomaterial with biosensors exhibits higher stability, sensitivity and selectivity. By using nanomaterial, the sensing capacity of the biosensors can be increased. Nanomaterial such as magnetic nanoparticles, carbon nanotubes, nanorods, nanowires, quantum dots and nanochannels can be used. These

nanomaterials can be used in electrical biosensor offering very high ability of charge transfer that makes them ideal for reaching lower detection limits and higher sensitive values. Enormous improvements in quality control, food safety and traceability have been evolved in food industry by the usage of nanobiosensors. The nanobiosensors can be used in various processes in food industry like starting from raw material preparation to monitoring of storage conditions. So these nanobiosensors can be served as a tool for quality and process control to ensure food safety.

Biosensors are mainly used in three broad categories in the analysis of food, to control food safety, food quality and for accurate analysis. Food product analysis generally concentrates on detecting the undesirable impurities in the food, such as biological toxins, food allergens, antibiotic residues, pesticides and pathogenic microbes. Few biosensors could verify the nutritional gain of the food product and analysis of authenticity for traceability while giving details about the imitation and adulteration of the food product. As per the information published by the recent literatures, electrochemical biosensors are mostly used in food safety instead of quality and validity analysis. Conventional techniques to detect pathogenic or mycotoxic microorganisms, antibiotics or pesticides could be in post-production only. This constraint is surely solved by the usage of biosensing techniques that permits the testing of food items at all stages of production from raw materials selection to the product on the shelf, proceeding in an effective means of safeguarding the safety of food. By implementing advanced biosensing tools minimum voluminous samples can be analysed directly, hence avoiding the requirement of laborious, tedious, time consuming and very exorbitant sample pre-treatment steps. An important prerequisite used in traditional techniques for analyzing the food is the sample homogenization process that could arise many complications because of the usage of organic acids and antimicrobial compounds present in fruits and vegetables. The effect of these organic compounds during sample homogenization process can retard the indication of specific compounds and impurities that have potential mortal effects on consumers. This drawback is overcome by the biosensors as they need very little or no sample preparation.

Speedy inspection is an extra beneficial feature of biosensors. Biosensors provide a good replacement and permits minimum detection times, from many days to hours or even minutes. In addition to that, *in situ* detection facilities provide enhanced motility of analytical tools such as handy or mobile, which commonly involves minimum skill to operate and also provides the chance for real time analysis unification in food processing set-ups.

Several attempts were made by the researchers for monitoring spoilage of food products. A brief review on the literature available on sensors for monitoring spoilage of aquatic food is given here (Table 1).

### **Halochromic sensors for monitoring spoilage of aquatic food**

Halochromism represents a material that changes its color when there is a change in pH. The word 'chromic' includes the materials that could change colors reversibly with the existence of certain factor. The factor here mentioned is pH and the pH indicators have this quality. Halochromic materials are suitable to use in environments where pH changes takes place often. Halochromic materials detect the changes in the acidity of substances, for example detection of corrosion in metals. Halochromism is exhibited by synthetic dyes mostly. But, the use of synthetic dyes can lead to detrimental effects on the human health and environment. Instead of synthetic dyes, naturally extracted pigments from plant tissues can be utilized. But, natural pigments exhibit lower stability towards pH, oxidation, temperature and light.

### **Biosensor for monitoring freshness of silver carp**

An important application of the halochromic sensor can be used to evaluate freshness of the fishery products. Keeping this in mind, Zhai et al. [1], fabricated a new colorimetric sensor which is prepared by starch/PVA films that is integrated with anthocyanins extracted from Roselle flowers (*Hibiscus sabdariffa L.*). Initially, the author extracted the anthocyanins from the flowers of Roselle. By casting/solvent evaporation method, the natural pigments were immobilized into the starch/PVA. It was noted that the color of the fabricated films were steady at room temperature for 14 days and at refrigeration. This sensor was used to evaluate the freshness of silver carp (*Hypophthalmichthys molitrix*) under refrigerated condition. The fabricated colorimetric sensor changes its color on generation of total volatile amines from fish over time. This thin film sensor can be used as a smart packaging sensor.

### **Curcumin sensor for shrimp spoilage detection**

Kuswandi et al. [2], investigated about the monitoring of shrimp spoilage in real time using on-package sticker sensor prepared by natural dye of curcumin. This sticker sensor was developed to detect total volatile amine based nitrogen specifically. The extracted curcumin was immobilized by optical method onto bacterial cellulose membrane. Hence the sensor was edible and suitable for food products. This curcumin sensor changes its color due to its increase of pH in the packed shrimp product. The color of this sensor changed from yellow to orange and then to reddish orange,

indicates the complete spoilage which can be visually seen. The color change was measured quantitatively by analyzing the color in photoshop software. Finally curcumin based sticker sensor was successfully used and it is used in real time monitoring of spoilage of shrimp.

### ***Colorimetric method to estimate histamine***

Patange et al. [3], developed an easy and quick method to determine the histamine in the fish. Mostly histamine is present in the family of *scombridae* and it is a good detector for temperature abuse and also it indicates whether the fish was handled properly or not. The reaction and response between the imidazole ring and p-phenyldiazonium sulfonate forms the basic rule of this quantitative colorimetric method to estimate the amount of histamine. The range of detection was 1mg/100g for this assay. A reference color scale based on the concentration was provided to indicate the defect. This color scale was important so that the presence of histamine and its concentration can be visually identified and the spectrophotometer was not required to estimate the histamine. This assay does not need any tedious laborious process and it is suitable for analyzing histamine in daily life.

Contrary to other amines that are evolved from microbial mortification of fish, histamine is non-destroyable by cooking and non-volatile at ambient conditions. Therefore, histamine can be used as a helpful indicator. Researches about colorimetric arrays involve multiple step extraction and purification of histamine by chromatography. Patange et al. [3], described a method for verification of histamine available in tuna which needs multiple steps. The histamine extraction from tuna needs treatment with several reagents. At last the extract is dealt with p-phenyldiazonium sulfonate for developing reddish pink color. Still, the color change was narrow and non-distinguishable for human eye. Oguri et al [4], evaluated a suitable halochromic indicator called 2, 3-naphthalenedicarboxaldehyde to sense the histamine.

### ***Colorimetric sensor arrays***

Usually, the use of halochromic sensors to evaluate the spoilage is limited as they can't be able to discover the low concentration total volatile amines. But the fish releases volatile amines at lower concentrations during the initial stage of the spoilage. Thus it is important to develop a sensor which can be able to detect volatile amines at lower concentrations at initial stage of spoilage. In this regard, Suslick [5], developed a very simple colorimetric sensor array composed of four different chemically interactive dyes to identify the volatile amines. In response to avoid the error due to humidity, hydrophobic dyes and substrates were used. Amines such as trimethylamine, diisopropylamine, dipropylamine, diethylamine, pyridine, homopiperidine, piperidine, pyrrolidine, cyclohexylamine, n-octylamine, n-hexylamine, n-butylamine were studied. The results showed that the developed colorimeter sensor array worked well even below 1 ppm with differentiation between isomeric amines.

Similarly, Zhonglin et al. [6] fabricated a novel based halochromic sensor array composed of six halochromic dyes. Cobalt and zinc complexes of porphyrin compounds were considered as chemically responsive dyes. The developed array has a sampling system consists of flow controller, sensor array integrated with digital camera which has a connection to a computer. This halochromic sensor array was used to detect six types of health affiliated trimethylamines.

In an attempt, Xiao-wei et al. [7], discovered a TiO<sub>2</sub> based nanoporous colorimetric sensor array to detect the trimethylamine. To prepare the mixture eight chemoresponsive dyes were used. The dye blend was coated on a nanoporous film developed from TiO<sub>2</sub> and examined for its ability of sensing. The developed sensor was observed for color changes upon exposure to TMA. The RGB values were calculated using the computational program to understand the sensor limits.

Pacquit et al. [8], developed a spoilage indicator to monitor the fish spoilage based on an immobilized pH responsive dye (Bromocresol green). Most of the sensitive reagent in spoilage indicator is a chemical reagent dye. These indicators are unsafe to consume because the reagent used could be lethal for humans. So for the consumer safety purpose, the indicators are clearly labelled as "Do Not Consume".

### **Redox - hydrogel based biosensors**

Quality maintenance of fishery products is the major requirement of the food industry. Classical methods such as chromatographic techniques are used to for the biogenic amines analysis. However this technique of chromatography often requires sample pretreatment, well trained operators, lengthy time and expensive operational costs which makes these methods not suitable for daily usage. So an optical biosensor was designed and used for the fish sample analysis kept under different conditions.

Mihaela Niculescu et al. [9], detailed about the development of amperometric biosensors to determine the biogenic amines and their application in determining the freshness index of the fishery products. The developed redox - hydrogel based biosensors were used to evaluate the content of total amines in fish which is kept for 10 days at various surroundings and the biosensors were assessed based on its stability and selectivity.

### **Visual methods and devices to detect fish spoilage**

Wallach et al [10], described about the methodologies and tools used to detect the microbial contamination in the food product visually. In this method the spoilage indicator device was placed with the food product in fluid contact. The spoilage indicator was observed to analyze whether any detectable change has occurred. The developed spoilage indicator provided a color change upon reactant molecule reaction which can be a visual indication of spoilage. This indicator can be safely placed in a package without contaminating the food. Different indicator materials such as Bromocresol blue, Bromocresol green, Bromocresol purple were used in this study.

### **Myoglobin based spoilage indicator**

Maria et al. [11], described about the myoglobin based spoilage indicator designed for the poultry meat that was packed with modified atmosphere. This indicator was designed to detect the presence of hydrogen sulphide that was evolved during storage of the packed meat. This indicator makes some color change during detection that can be visually seen by the customers. This visual indication helps the customers to know whether the packed poultry meat gets spoiled or not. The indicator was made from the Agarose gel which is mixed with sodium phosphate of pH 6.8.

### **TMA vapour probe to determine fish freshness**

Generally odour is used to determine the fish freshness in routine life, but still a widely used index was total volatile based nitrogen. Changzhi Zhao et al. [12], described about the fish quality and its freshness. A trimethylamine (TMA) vapour probe was developed to determine the fish freshness assay because TMA is a volatile amine immediately produced in the fish after its death and its increase in concentration indicates the lowering of fish freshness. This TMA vapour probe was based on chitosan membrane which was encapsulated on piezoelectric crystal with pimelic acid. This TMA probe has an exponential response to the concentration of TMA ranges from 5 to 200ppm. The observed results using this TMA vapour probe was consistent.

### **Colorimetric array for the detection of amines**

Molecular recognition depends on the potentiality to distinguish in terms of analyte chemical properties. Rakow et al. [13], reported about the expanded use of colorimetric array detector. This detector was highly responsive and more critical in the amines distinction. Four different families of chemically selective dyes were integrated into this array of colorimetric sensor to a probe of chemical properties space. Reactions to a set of analytes were obtained and it was recognized by this sensor array. This colorimetric array was composed of Metalloporphyrins, free-base porphyrins, pH indicators and solvatochromic dyes.

### **Polythiophene based sensor**

Toby Nelson et al. [14], described about the single conjugated polymer that is cross reactive which can give multiple responses to identify and differentiate 22 amines that are similar in structure. Statistical analysis of this polythiophene provided excellent accurate classification in highly competitive aqueous media.

### **Lactic acid based TTIs**

Chahattuche et al. [15], discussed about the time-temperature indicator (TTI) which works with the interaction of lactic acid to monitor the food product quality. Usually time -temperature indicator provides a visual summary of products temperature history which records the effect of temperature and time. Based on lactic acid, four TTIs were developed with various substrate concentrations. Changes in color were monitored with the reaction and diffusion with lactic acid. A permanent color change was occurred in a chemical chromatic indicator (green to red) and it was due to pH reduction. The characterized temperature range of these TTIs was 4 – 45°C which gives activation energy ( $E_a$ ) of 50 kJ mol<sup>-1</sup>. For each TTI, the mathematical model was established which relates between change of color, time and temperature. The difference between the  $E_a$  values of TTIs and food quality losses were lesser than 40 kJ

mol<sup>-1</sup>. So the developed TTIs were considered as good one to monitor the food quality loss. However these TTIs cannot include wide variety of food quality losses, they could be used to monitor the food quality of fruits and vegetables along with time-temperature history.

**Table 1** Summary of applications of sensors for monitoring spoilage of aqua foods

Application	Sensing element	No. of sensors	Software used	Ref. no.
Fish freshness	Redox-hydrogel based biosensors	1	-	9
Microbial spoilage in the food	Bromocresol blue, bromo-cresol green, bromocresol purple	3	-	10
Spoilage in poultry meat	Agarose gel+sodium phosphate	1	-	11
Determination of the fish freshness by using TMA vapour probe	Chitosan membrane + piezoelectric crystal with pimelic acid	1	-	13
Colorimetric array to determine amines for evaluating fish freshness	Metalloporphyrins, Free-base porphyrins, pH indicator, solvatochromic dyes	4	-	3
Colorimetric method to estimate histamine in <i>scombridae</i> family	Imidazole ring and p-phenyldiazonium sulfonate	1	-	14
Determination of amines to evaluate food freshness	Polythiophene	1	-	15
Time-temperature indicator	Based on lactic acid	4	-	6
Colorimetric sensor for fish freshness	Dimethylamine, triethylamine, Diisopropylamine, aniline, cyclohexylamine, pyridine	1	-	16
Electrochemical detection of xanthine in fish meat	Xanthine oxidase/ carboxylated multiwalled carbon nanotubes/ polyaniline/pt electrode	1	-	17
Fluorometric sensor for biogenic amines detection	Carboxylic acid modified tetraphenylethenes	1	-	18
Colorimetric sensor array to evaluate fish freshness.	Chemically reactive dyes	1	-	2
Curcumin sensor to detect shrimp spoilage	Curcumin	1	-	19
Amperometric determination of xanthine in fish flesh	Zinc oxide nanoparticle/ chitosan/multiwalled carbon nanotube	1	-	21
Determination of xanthine in meat by nanoparticles biosensor	Xanthine oxidase	1	-	22
Colorimetric indicator to detect skinless chicken breast spoilage	Bromocresol green and phenol red/bromothymol blue and methyl red	1	-	23
Chromogenic sensor to detect spoilage in turkey	16 sensing materials	1	photoshop	24
Colorimetric sensor to determine pork freshness	Spinach, red raddish, winter jasmine, black rice	4	-	25
Time-temperature indicator to monitor pasteurized milk	Red cabbage(anthocyanins)	1	CIELab	26
Indicator sensor to monitor meat quality	Bromophenol blue	1	-	27
Nanoparticles to monitor meat quality	FePt nanoparticles	1	-	28
Colorimetric indicator to monitor food freshness	Red cabbage extract(anthocyanins)	1	-	29
Colorimetric plastic film indicator to monitor food quality	Aerosol hydrophilic silica, bromophenol blue	1	-	30
Tilapia fish freshness	Gelatin	1	Gwayddion	31
Rainbow trout freshness	Alizarin	1	-	32
Monitoring pH changes in saliva	Anthocyanin from red cabbage	1	CIELab and Photoshop	33 34 35

### **Xanthine based electrochemical biosensor**

Rooma Devi et al. [16], discussed about the presence of xanthine by electrochemical detection based on xanthine oxidase in fish meat. A xanthine based electrochemical biosensor was fabricated using a working electrode that is composed of xanthine oxidase/carboxylated multiwalled carbon nanotubes/polyaniline/Pt electrode, standard reference electrode with Ag/AgCl and auxiliary electrode with Pt wire. These all electrodes were connected through a potentiostat. The characterization of enzymatic electrode was done by electrochemical impedance spectroscopy (EIS), Fourier Transform Infrared Spectrophotometry (FTIR) and scanning electron microscopy (SEM). The developed biosensor displayed a linear and optimum response. The biosensor losses half of its initial activity over the period of 100 days after its 200 uses.

### **Fluorometric sensor for biogenic amines detection**

Mitsutaka Nakamura et al. [17], evaluated about the fluorometric sensor to detect and identify the biogenic amines. Mixtures of carboxylic acid modified tetraphenylethenes were prepared and the biogenic amines show a blue emission when aggregated. This sensor worked as a “turn on” fluorescent sensor when reacted with amines. The degree of fluorescence was used to distinguish the amines. This fluorescent sensor was used to identify 10 different amines accurately.

### **Colorimetric sensor array to evaluate fish freshness**

Xingyi Huang et al. [18], described about the novel technique for quick verification of fish freshness using colorimetric method. Nine chemically reactive dyes were taken based on their sensitivity towards volatile compounds that will occur during the fish spoilage. The array of colorimetric sensor was prepared by impregnated the dyes on a reverse phase silica gel. Fish spoilage was observed every 24 hours for continuous seven days. A color change was obtained for each and every sample by distinguishing the sensor images taken before and after upon exposure to the odour sample. The digitalized data which represents a color change were analysed by principal component analysis.

### **Amperometric determination of xanthine**

Rooma Devi et al. [19], discussed about the amperometric determination of presence of xanthine in fish flesh by xanthine oxidase bound compound film. Xanthine oxidase was trapped on a composite film of nanoparticle of zinc oxide/carboxylated multiwalled carbon nanotube/ chitosan/polyaniline. This composite film was electrodeposited on the platinum electrode surface. A xanthine based biosensor was prepared and it was used as a working electrode, reference electrode was prepared by Ag/AgCl and auxiliary electrode by platinum wire. These electrodes were connected through a potentiostat. This biosensor displayed an accurate response with a detection limit of 0.1  $\mu\text{M}$  when pH is 7 and temperature is 35 $^{\circ}\text{C}$ . To determine the xanthine in fish flesh, the enzyme electrode was employed during storage. The initial activity will be lost by 30% after 80 uses when stored at 4 $^{\circ}\text{C}$ .

### **Determination of yellow croaker freshness**

Jin Zhao et al. [20], discussed about the various methods to determine the freshness of yellow croaker (*Pseudosciaena crocea*) fillets when it was stored in chilled storage. The physiochemical properties such as thiobarbituric acid (TBA), k value, pH, color, texture profile analysis and microbiological properties such as transcriptomics, sensory attributes, total viable count (TVC) and some functional properties of proteins were evaluated during 0, 5, 10, 15, and 20 days of storage. This study also determines the effect of time on fish muscle during storage by gel electrophoresis. The parameters such as color, TPA, pH, k value TVC, transcripts coding for cathepsin were considered as the suitable indicators to evaluate the yellow croaker freshness during chilled storage which was under vacuum packaging.

### **Nanoparticles based biosensor for xanthine determination**

Rooma Devi et al. [21], discussed about the method to determine the presence of xanthine in meat by amperometric biosensor which was composed of nanoparticles of silver/cysteine modified Au electrode. Xanthine oxidase was immobilized onto silver nanoparticles which is citrate capped that was deposited on Au electrode surface. These can be done by self assembled monolayers of cysteine. The developed sensor was used to measure the amount of xanthine in fish, pork, chicken and beef meat. The biosensor displayed an accurate response at pH 7.0 and 35 $^{\circ}\text{C}$  within 5s when

polarized at 0.5 V. The detection limit is 0.15  $\mu\text{M}$ . The 20% initial activity of the enzyme electrode was lost over 60 days after its 180 uses, stored at 4°C.

### **Colorimetric indicator to detect chicken spoilage**

Chompoonoot Rukchon et al. [22], discussed about the spoilage indicator development to monitor the spoilage of skinless chicken. An indicator based on colorimetric mixed pH dye for smart packaging in the form of chemical barcode was developed to monitor spoilage of skinless chicken breast. This spoilage indicator has two groups of dyes which is pH responsive; one is combination of bromothymol blue and methyl red while other is a combination of Bromocresol green and phenol red. The degree of the spoilage was measured by the increase in the amount of  $\text{CO}_2$ . Characterization of two groups of dyes were analysed in response to  $\text{CO}_2$ . The spoilage indicator changes its color according to the microbial growth patterns. Thus the spoilage is monitored in real time.

### **Chromogenic sensor for turkey**

Yolanda Salinas et al. [23], fabricated a chromogenic sensor array to determine the freshness quality of marinated turkey under modified atmospheric packaging. The sensor array had 16 sensing materials that are synthesized by the combination of three various inorganic support and 13 indicators. Commodity tool such as digital camera and photoshop were used to analyze the color changes. The data was obtained for each sampling day. Statistical analysis classifies the sample as “fresh”, “not fresh” and “not edible”. Along with these, sensorial and microbiological tests were done. From this study, a shelf life period of 38 days was determined at 4°C.

### **Colorimetric sensor for pork freshness**

Huang et al. [24], determined the spoilage of pork by developing colorimetric gas sensor prepared by natural pigments. This gas sensor was developed from the extracts of four natural pigments. The four natural pigments were spinach, red radish, winter jasmine and black rice. A color change was obtained before and after upon exposure to the odour of the pork flesh. In this, HPLC was used to distinguish biogenic amines. Putrescine and cadaverine is used to calculate the biogenic amine index (BAI). As a result, it was found that the extract of black rice was at most responsive among all of the extracts due to the very good interaction between the hydroxyl groups and carbonyl groups of anthocyanins that is present in the black rice with amines developed during spoilage.

### **TTI from red cabbage**

Valdir et al. [25], developed a TTI using PVA chitosan polymer that is doped with anthocyanins to monitor the quality of food by detecting the changes in pH during storage. This TTI was developed from chitosan, PVA and the anthocyanins that were extracted from red cabbage (*Brassica oleracea var. capitata*). The characterization of developed TTI was done by TG-DSC, FT-IR, UV-Vis and swelling index. CIELab scale was used to measure the color difference upon exposure to various pH values. Stress /strain tests were used to evaluate the mechanical properties of TTIs. This TTI can be used in intelligent food packaging. In this article, the TTI was used to monitor the pasteurized milk which gives the color change when there occurs a change in chemical composition of food.

### **Sensor to monitor meat quality**

Vivek et al. [26], developed a real time on package indicator sensor to monitor the meat quality. The indicator sensor response was compared with the quality parameters at room temperature. This sensor was made by filter paper and bromophenol blue as indicator carrier and indicator solution respectively. This indicator solution was coated onto indicator carrier by centrifugation. Now the developed sensor was placed inside the package where the buffalo meat was packed. The color change of the sensor was observed and it was compared with the quality parameters of meat to evaluate the meat quality during its storage period. From the result of this work, the sensor displayed a color change from yellow to blue during the 24 hour storage period with ambient temperature. Thus the shelf life and the meat quality can be evaluated by observing the color change.

### **Nanotechnology for meat quality**

Pradeep et al. [27], discussed about the nanotechnology that would be a futuristic tool to improve the meat quality and food safety in the industry. Metal nanoparticles that is FePt nanoparticles were prepared by mixing two pre-cursor

liquids. The pre-cursor liquids were ferric acetyl acetonate and platinum acetyl acetonate in polyol solution of sodium hydroxide at high temperatures. Nanocarriers were prepared by emulsion-solvent evaporation technique, double emulsion and evaporation method, salting out method.

### **Image processing to evaluate fish freshness**

Malay et al. [28], described about an image processing technique to evaluate fish freshness and quality. This method is fully automatic, non-invasive and efficient for tissue segmentation and freshness of the fish sample. Using cluster-based method, the fish gill tissues were automatically segmented and its features were extracted strategically. First, second and third level decomposition were performed and the coefficient have been obtained at each and every level to determine the freshness of fish sample. The results obtained from the experiment are used to indicate the monotonic variation pattern of the coefficients and these coefficients used to indicate the freshness of the fish. The difference in the image featured with the retention time gave a strategic framework in order to assess the fish freshness. Image analysis is a non-invasive and harmless method to evaluate data based on digital image and the color difference is used to calculate the fish freshness. The author provides 3 freshness ranges. They are FR1, FR2 and FR3, where FR1 is most fresh, FR2 is moderate fresh and FR3 is least fresh. The author has done these experiments for 4 types of fishes with 3 replications. The image of the fish was photographed for 6 days continuously. RGB values and segmented ROI were evaluated and the coefficients were calculated to label the freshness range. As a future view of this work, a barcode reader might be developed using this data for checking process in supermarket where large volume of fish is an issue.

### **Edible sensors**

Yulia et al. [29], developed an inexpensive, edible sensor which was completely made from food derived product such as red cabbage and pectin. As this sensor was fully made from edible materials, it is safe to use inside the package. This sensor acts as colorimetric indicator to monitor the food freshness. The sensor showed a color change when it started to react with the gaseous amines. The sensor film was made from pectin matrix where red cabbage extract is trapped in it to serve as a colorimetric indicator. Anthocyanins from the red cabbage act as an amine sensing element of this film because anthocyanins change its color when exposed to pH changes. This edible sensor shows a remarkable sensitivity towards gaseous amines and the film displays a visual color change even upon exposure to as little as 1ppm of amines. These edible films displayed a color change dramatically from purple to yellow when it is exposed to gaseous amines.

### **Colorimetric plastic film indicator**

Nathan et al. [30], developed a simple, inexpensive colorimetric film indicator to monitor the fish spoilage based on volatile nitrogen compounds. The TVB-N pigment was prepared with materials such as aerosil hydrophilic silica, bromophenol blue. A bright yellow colored pigment was obtained which responds to the ammonia or volatile amines which changes bright yellow to blue color. The TVB-n indicator was prepared with BPB coated hydrophilic silica pigment that is blended with LDPE powder. Then the powder was pelletized using extruder. A clear yellow colored plastic film was obtained. This indicator film changes its color from yellow to blue in reaction with trimethyl amine. These films were characterized using a UV-vis spectrophotometer. All digitalized photographic images were taken and digital image analysis was done to get RGB values. This TVB-N plastic film spoilage indicator was tested at two different temperatures (22 and 24°C). The 25mm diameter disc of TVB-N indicator was stuck inside the lid of the package of cod fish. Photographs were taken every hour continuously for 3 days. A clear color change from yellow to blue is observed. Digital image analysis was done for the photographs to get RGB values. The same experiment were also conducted at 4°C and noted that the film changes its color completely at 5<sup>th</sup> day. In future, this food spoilage indicator can be widely used in industry if it is combined with color analysis app in mobile phone or simply a color matching card.

### **Optical gas sensor for tilapia fish**

Ana et al. [31], developed a single optical gas sensor to monitor microbial spoilage of tilapia fish. This gas sensing method works on the principle of single gas reactive gel material that was connected to an optical electronic nose. The optical sensor was prepared by hybrid gel which is composed of gelatin. A transparent uniform film with thickness 36 μm was prepared. This film was characterized by polarizing optical microscope, scanning electron microscope, X-ray spectroscopy. Gwyddion software was used to process the images. A gas sensor device consists of two closed

compartments separated by a door that is one for the fish samples to be kept and the other for the sensor. Each sampling cycle lasted for 20 minutes 5 minutes exposed to the volatiles generated by the fish and the remaining 15 min was for the recovery where the fresh air is allowed inside the chamber space. The temperature of 21°C was maintained throughout the process. Generation of conductance signals by the optical sensor was plotted against the time and its relative amplitude. The bacterial colonies were counted by plate count method and the results were given as log CFU/g. The fish becomes unsafe for human consumption when it reaches beyond 6-7 log CFU/g.

### **Cellulose Acetate nanofibres containing Alizarin as a halochromic sensor**

Zahra Aghaei et al. [32], developed a sensor based on halochromism that was prepared using cellulose Acetate Nanofibres containing Alizarin to monitor the contamination of rainbow trout. The materials needed to prepare this sensor were cellulose acetate, acetone and N, N-dimethylacetamide and Alizarin. Electrospinning solution was prepared by using acetone which was a binary solvent. This 'on package' sensor changed its color visually with the evolution of total volatile basic nitrogen and with the increase of product's pH value. The fillets of rainbow trout were stored at 4°C for 12 days. The color of the film does not change for 48 hours, but a very light brick color was obtained on the sensor after the fourth day and this gradually became dark on the sixth day, which represents the accurate pH changes. On 12<sup>th</sup> day, the color of this sensor changed towards violet.

### **Prospective and Conclusions**

Generally, the spoilage of raw fish is determined by sensory evaluation such as change in its appearance, color of eyes and gills, odour and texture. But this sensory evaluation is not possible in the case of packaged fishes. Total volatile amines come out of fishes is a best indicator of spoilage. Several sensors involving invasive (or) non-invasive techniques were demonstrated for detection of spoilage in fishes. However, most of them involve toxic chemicals, expensive instruments and tedious laboratory procedures. Halochromic materials are potential candidates for monitoring spoilage since these sensors change their color depending on the concentration of the TVB-N evolved from the packaged fishes.

Most of the halochromic materials are synthetic dyes, which have detrimental effects on human health. It should be noted that it is highly possible that the spoilage sensor could get in contact with the packaged fish during transportation. Therefore, the materials used in the fabrication of sensor must be biocompatible and non-toxic. In view of this, halochromic material of natural origin would be preferable. Unlike agricultural food products, aqua foods contain higher moisture content. Since the spoilage monitoring of the packaged fishes occurs in a closed system, the effect of the moisture on the performance of the sensor should be the major concern. This can be overcome by introduction of suitable non-contaminating and biocompatible moisture adsorbent.

### **Acknowledgements**

The authors are thankful to the Tamil Nadu Dr.J.Jayalalithaa Fisheries University, Nagapattinam for financial support under Junior Teacher Research Fellowship (TNJFU/JTRF/CoFE/DK/2019).

### **References**

- [1] Zhai, X., J. Shi, X. Zou, S. Wang, C. Jiang, J. ZhanG, X. Huang, W. Zhang, M. Holmes. (2017). Novel colorimetric films based on starch/polyvinyl alcohol incorporated with roselle anthocyanins for fish freshness monitoring. *Food Hydrocoll*, 69:308-317.
- [2] Bambang, K., Jayus, T.S. Larasati, A. Abdullah, L.Y. Heng. (2012). Real-Time Monitoring of shrimp spoilage using on-package sticker sensor based on natural dye of curcumin. *Food Anal. Methods*, 881-889.
- [3] Patange, S.B., M.K. Mukundan, K. Ashok Kumar. (2005). A simple and rapid method for colorimetric determination of histamine in fish flesh. *Food Control*, 16:465-472.
- [4] Oguri, S., A. Mizusawa, M. Kamada. (2006). A new method of histamine colorimetry using 2,3-naphthalenedicarboxaldehyde on a silica gel column cartridge. *Anal. Chim. Acta*, 558:326-331.
- [5] Suslick, K.S. (2012). Synesthesia in science and technology: more than making theunseen visible. *Curr. Opin. Chem. Biol.*, 16:557-563
- [6] Zhonglin, T., J. Yang, J. Yu, B. Cui. (2010). A colorimetric sensor for qualitative discrimination and quantitative detection of volatile amines. *Sensors*, 10:6463-6476.

- [7] Xiaowei, H., L. Zhi-hua, Z. Xiao-bo, S. Ji-yong, M. Han-ping, Z. Jie-Wen, H. Li-min, M. Holme. (2016). Detection of meat borne trimethylamine based on nanoporous colorimetric sensor arrays. *Food Cem*, 197:930-936.
- [8] Pacquit, A., K. T. Lau, H. McLaughlin, J. Frisby, B. Quilty, D. Diamond. (2006). Development of a volatile amine sensor for the monitoring of fish spoilage. *Talanta*, 69:515-520.
- [9] Mihaela, N., C. Nistor, I. F. bort, P. Pec, B. Mattiasson, E. C. Regi. (2000). Redox hydrogel-based amperometric bienzyme electrodes for fish freshness monitoring, *Analytical Chemistry*. 72:1591-1597.
- [10] Donald, F. H., W. Hollis, NH. (2002). Methods and devices for detecting microbial spoilage in food products. US Patent, 6495368 B1.
- [11] Maria, S., E. Hurme, K.L. Kala, T. Luoma, H.L. Alakomi, R. Ahvenainen. (2002). Myoglobin-based indicators for the evaluation of freshness of unmarinated broiler cuts. *Innovative Food Science and Emerging Technologies*, 3:279-288.
- [12] Changzhi, Z., Y. Pan, L. Ma, Z. Tang, G. Zhao, L. Wang. (2002). Assay of fish freshness using trimethylamine vapor probe based on a sensitive membrane on piezoelectric quartz crystal. *Sensors and Actuators B*, 81:218-222.
- [13] Neal, A. R., A. Sen, M. C. Janzen, J. B. Ponder, K.S. Suslick. (2005). Molecular recognition and discrimination of amines with a colorimetric array. *Angewandte Chemie*, 44: 4528-4532.
- [14] Marc, S. M., T.L. Nelson, C.O. Sullivan, J.J. Lavigne. (2007). A food freshness sensor using the multistate response from analyte-induced aggregation of a cross-reactive poly (thiophene). *Organic letters*, 9:3217-3220.
- [15] Chahattuche, W., V. Hongtrakul, P. Suppakul. (2010). Development and characterization of a prototype of a lactic acid-based time-temperature indicator for monitoring food product quality. *Journal of Food Engineering*, 100:427-434.
- [16] Rooma, D., S. Yadav, C.S. Pundir. (2011). Electrochemical detection of xanthine in fish meat by xanthine oxidase immobilized on carboxylated multiwalled carbon nanotubes polyaniline composite film. *Biochemical Engineering Journal*, 59:148-153.
- [17] Mitsutaka, N., T. Sanji, M. Tanaka. (2011). Fluorometric sensing of biogenic amines with aggregation-induced emission-active tetraphenylethenes. *Chemistry –A european journal*, 17:5344–5349.
- [18] Xingyi, H., J. Xin, J. Zhao. (2011). A novel technique for rapid evaluation of fish freshness using colorimetric sensor array. *Journal of Food Engineering*, 105: 632-637.
- [19] Rooma, D., S. Yadav, C.S. Pundir. (2012). Amperometric determination of xanthine in fish meat by zinc oxide nanoparticle/chitosan/multiwalled carbon nanotube/polyaniline composite film bound xanthine oxidase. *Analyst*, 137:754-759.
- [20] Jin, Z., J. Li, J. Wang, L. Weijin. (2012). Applying different methods to evaluate the freshness of large yellow croaker (*pseudosciaena crocea*) fillets during chilled storage. *Journal of agricultural and food chemistry*, 60: 11387-11394.
- [21] Rooma, D., B. Batra, S. Lata, S. Yadav, C.S. Pundir. (2013). A method for determination of xanthine in meat by amperometric biosensor based on silver nanoparticles/cysteine modified Au electrode. *Process Biochemistry*, 48:242-249.
- [22] Chompoonoot, R., A. Nopwinyuwong, S. Trevanich, T. Jinkarn, P. Suppakul (2014). Development of a food spoilage indicator for monitoring freshness of skinless chicken breast. *Talanta*, 130:547-554.
- [23] Yolanda, S., J. V. Ros-Lis, J. L. Vivancos, R. M. Manez, S. Aucejo, N. Herranz,
- [24] Lorente, E. Garcia. (2014). A chromogenic sensor array for boiled marinated turkey freshness Monitoring. *Sensors and Actuators B Chemical*, 190:326-333.
- [25] Huang, X., Z. Xiao-bo, S. Ji-yong, G. Yanin, Z. Jie-wen, Z. Jianchun, H. Limin. (2014). Determination of pork spoilage by colorimetric gas sensor array based on natural pigments. *Food Chemistry*, 145:549-554.
- [26] Valdir, A. P. J., I. N. Q. De Arrudaa, R. Stefania. (2014). Active chitosan/PVA films with anthocyanins from brassica oleraceae (red cabbage) as time-temperature indicators for application in intelligent food packaging. *Food hydrocolloids*, 43:180-188.
- [27] Vivek, S., G. Kandeepan, M. R. Vishnuraj. (2015). Development of on package indicator sensor for real-time monitoring of meat quality. *Veterinary World*, 8:393.
- [28] Pradeep, K. S., G. Jairath, S. S. Ahlawat. (2015). Nanotechnology is a future tool to improve quality and safety in meat industry. *J Food Sci Technol*. 53:1739-1749.
- [29] Malay, K. D., A. Issac, N. Minhas, B. Sarkar. (2016). Image processing based method to assess fish quality and freshness. *Journal of Food Engineering*, 177:1-9.
- [30] Yulia, D., E. R. Janecek, J. V. Joset, F. Stellacci. (2017). Edible Sensors for Meat and Seafood Freshness. *Sensors and Actuators B*, 23745.

- [31] Nathan, W., D. Yusufu, A. Mills. (2018). Colorimetric plastic film indicator for the detection of the volatile basic nitrogen compounds associated with fish spoilage. *Talanta*, 194:830-836.
- [32] Ana, T. S. S., D. F. Maffei, S. Palma, R. W. C. Li, B. D. G. M. Franco, A. C. A. Roque, J. Gruber. (2018). Tilapia fish microbial spoilage monitored by a single optical gas sensor. *Food Control*, 89:72-76.
- [33] Zahra, A., B. Emadzadeh, B. Ghorani<sup>1</sup>, R. Kadkhodae. (2018), Cellulose acetate nanofibres containing alizarin as a halochromic sensor for the qualitative assessment of rainbow trout fish spoilage. *Food and Bioprocess Technology*, 11:1087-1095.
- [34] Kesavan, D., B-S Kim, (2015). Reversible and universal pH sensing cellulose nanofibers for health monitor. *Sensors and Actuators - B - Chemical*, 209: 281-286.
- [35] Byoung-Suhk, K., D. Kesavan. (2017). Dying methode of cellulose nanofiber by vegetable dye. South Korean Patent No. 10-1751819-0000.

© 2019, by the Authors. The articles published from this journal are distributed to the public under “**Creative Commons Attribution License**” (<http://creativecommons.org/licenses/by/3.0/>). Therefore, upon proper citation of the original work, all the articles can be used without any restriction or can be distributed in any medium in any form.

#### Publication History

Received	10.06.2019
Revised	27.08.2019
Accepted	28.08.2019
Online	30.08.2019