Chapter 1
Introduction

1. Introduction

Fish is highly susceptible to postmortem changes due to the complex interplay of various customers' key parameters, i.e., composition, type, source, environmental conditions, catching techniques, and storage methods, which leads to a strong struggle for clear prediction of shelf life. In fish production, India ranked 3rd largest with about 8 % share. The total fish production was increased by 7.76 % (> 12 million metric tons) in the financial year 2022 in India. This sector was previously held by the traditional practices from the past 75 years that have been revolution 22-fold in terms of fish production (Ministry of Fisheries, Animal Husbandry & Dairying, 2023). In the Indian scenario Fisheries Infrastructure Development Fund, Pradhan Mantri Matsya Sampada Yojana (PMMSY), and Kisan Credit Card with an investment of Rs. 27,500 crores have been coined to the fish industry for boosting this industry. By seeing the huge potential of this sector GOI has sanctioned INR 6000 crore under PMMSY for the fish market leading to the increase in income of fishermen, fish vendors, and MSME requirements of appropriate fish quality management system for establishing a proper supply chain (Freitas et al., 2021). This scheme envisages performing many changes like digitalization, value-chain efficiency, creation, and maintenance of women jobs in the fish-processing sector. GOI is promoting aquaculture export by 10 % and 15 % reduction in basic customs duty on fish meal, krill meal, and fish lipid oil, respectively.

During spoilage, fish undergo various physiological and chemical changes, such as rigor mortis, enzyme activity, and microbial growth. These processes contribute to the deterioration of fish quality, primarily through the breakdown of proteins and non-protein nitrogenous substances. This degradation is largely driven by microbial activity, resulting in the formation of volatile amines. One significant transformation during spoilage involves the conversion of TMAO (Trimethylamine Oxide) into TMA (Trimethylamine), DMA (Dimethylamine), and ammonia, which together are referred to as TVB-N (Total Volatile Basic Nitrogen). TVB-N compounds significantly impact the fish by altering its texture, color, and odor, and are commonly used as fish freshness indicators (Cai et al., 2015; Chen et al., 2017; Hao et al., 2021; Tonezzer 2021). Assessing fish freshness during storage involves various indicators such as pH, TVB-N levels, and microbial counts. The pH level changes as spoilage progresses, often becoming more alkaline due to the production of basic amines. TVB-N levels provide a quantitative measure of

spoilage, with higher values indicating more degradation. Microbial counts provide the extent of microbial growth and activity, which further indicates how fresh the fish is. These indicators collectively help in monitoring and ensuring the quality of fish during storage (Tilami et al., 2018; Mustafa et al., 2020; Hao et al., 2021).

Polyaniline (PANI) is a versatile conducting polymer that shows potential as a sensor material due to its leach-free nature, accurate in detection abilities, and cost-effectiveness. It stands out for its ecological and thermal stability and possesses unique properties that can be altered by different chemical treatments, resulting in structural changes. The addition of electrons and reduction of the nitrogen (N) atom, along with the removal of the polaron-stabilizing acid, can modify its structure (Silversteinet al., 2005; Sambasevam et al., 2015). Its sensitivity to nitrogen-containing groups makes it particularly suitable for analyzing the volatile bases generated by fish during spoilage. Additionally, its ability to respond to pH changes makes it ideal for detecting amines that contribute to spoilage (Huang et al., 2006; Kushwandi et at al., 2012; Jarad et al., 2016). Previous studies have demonstrated PANI's effectiveness as a cost-effective, highly stable, and reproducible material for detecting ammonia vapor (Matindoust et al., 2017; Kumar et al., 2017; Wang et al., 2018). Similarly, synthetic dyes such as bromophenol blue and bromocresol purple act as pH indicators and have been utilized as detecting materials for amines, showing high sensitivity to acid-base reactions within the pH range of 5.61 to 6.23 (Koxmak et al., 2019). These synthetic indicator dyes can exhibit different colors under acidic and alkaline conditions, making them valuable for determining pH levels. Various studies have employed different sensing dyes to develop rapid, easy-to-use sensors for monitoring food freshness (Zaragozá et al., 2015; Majdinasab et al., 2018; Wells et al., 2019)

Currently, all the detection platforms are partially or completely dependent on the high-end equipment of the laboratory (fluorescence microscope, high-performance liquid chromatography, gas chromatography-mass spectrometer, etc.). Various conventional methods (total plate count, total volatile basic nitrogen (trimethyl amine, thiobarbituric acid, free fatty acid, peroxide value, etc.) utilized for monitoring the quality of fish are lengthy, tedious, time-consuming, costly, and full of human error. These methods are not based on real-time or infield usage. Biosensors are suitable substitutes to create user-friendly, economical, and portable systems for analyzing the quality of perishable items.

Colorimetric, enzyme, gas sensors, and electrochemical sensors have already been developed for monitoring fish quality (Duarte et al., 2020). China has determined 25 mg/100 g as an acceptable standard for TVB-N content in fish. In this concern, a colorimetric sensor based on total volatile basic nitrogen has already been developed to observe fish spoilage (Zhang et al., 2021). A few wires with sensors connected to a cloud platform can analyze data in real-time, control various processes, and broadcast information seamlessly to multiple devices or users. Fish quality and supply management require big data storage with transmission in a portable analyzing system. For the development of these compact portable smartphone systems, the cost of production and operation is high to monitor the quality of fish. There is a strong requirement for an efficient, sensitive, novel, less time-consuming, and accurate system for better fish supply chain management. Artificial intelligence is an emerging tool to generate an onsite, flexible sensitive system for fish quality prediction. A combination of e-tongue/e-nose with a biosensor-based smartphone can increase the detection ability of the system. The integration of smartphones with specialized sensors and software has become a powerful tool for detecting spoilage in real-time. Advancements in both hardware and software have transformed them into versatile devices, enabling them to process data, initiate signals, and conduct analyses within the food sector (Meng et al., 2017; Xu et. al., 2017; Doğan et al., 2024). Evaluating fish freshness is challenging due to its perishable nature, and current advanced techniques are expensive, bulky, and time-consuming, limiting their use by the fishermen/ retailer/ buyer.

Citrus essential oils like pomelo peel oil have shown potential as preservatives for maintaining fish quality. Essential oils are naturally derived metabolites known for their antimicrobial and antioxidant properties. These oils serve as a natural alternative to synthetic additives (Bordoloi et al., 1999; Gonz´alez-Mas et al., 2011). Active components in citrus essential oils, such as limonene, pinene, and terpinolene, exhibit a broad spectrum of antimicrobial, antifungal, anti-inflammatory, and antioxidant activities (Haute et al., 2016; Huang et al., 2018). Citrus essential oil is classified as Generally Recognized as Safe (GRAS) due to its nutraceutical benefits and economic significance (Huang et al., 2018). Techniques such as chitosan coating and oregano oil have already been utilized to extend the shelf life of fish by inhibiting spoilage organisms (Zhang et al., 2015; Haute et al., 2016; Yu et al., 2017). However, the use of pomelo peel oil has not been explored yet; hence this study aims to investigate its benefits.

To the best of our knowledge limited studies have explored using smartphone-based optical sensors to detect fish spoilage. The advanced techniques face limited use in the fish industry due to their high cost and need for technical expertise and such methods were not suitable for field analysis and were beyond the reach of common people and small producers. Additionally, the characteristics and functional properties of essential oil from pomelo peel remain inadequately addressed. The potential antibacterial effects of pomelo peel are not fully utilized to enhance the storage stability of fish fillets. Further, the effect of essential oil on the storage stability of fish fillets was not investigated using the PANI smartphone-based optical sensor.

The entire work is organized into the following objectives to achieve the aim of the present research/ thesis:

1. To develop and characterize the polyaniline-based sensor for monitoring the freshness of fish during storage
2. To develop the dye-based sensor for monitoring the freshness of fish during storage
3. To design and develop a cradle (smartphone sensing system) for determination of spoilage
4. To calibrate and validate the developed cradle for development of a mobile application for monitoring of chemical spoilage of fish during storage
5. To study the effect of extracted essential oil from pomelo peel on storage stability using developed sensor