Development of Electrochemical Sensors for the Detection of Different Dyes Used as Artificial Food Colorants

Synopsis submitted

by

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1. Introduction

In the realm of culinary aesthetics, food colour plays a pivotal role far beyond mere visual appeal. It serves as a potent tool in influencing human perception and expectations, rendering a food product more marketable. Achieving consistency in colour is paramount in meeting these consumer expectations. To this end, different natural and artificial food colourants are employed. Initially, natural colourants derived from plants and microbes held sway in the industry but were gradually supplanted by synthetic alternatives. Synthetic food colourants, primarily derived from coal tar compounds, mostly belong to the azo group of dyes, with some being natural identical man-made colours like riboflavin. While natural food colours are often perceived as healthier and more consumer-friendly, they come with certain shortcomings, like, being costlier, less durable, and more susceptible to degradation from heat, light, and pH changes [1]. In contrast, synthetic colourants are more stable across various environmental factors, ensuring consistent colour uniformity, water solubility, and less susceptibility to pathogenic contamination [2].

In light of these considerations, the usage of artificial food dyes is on the rise in Indian marketplaces. Key examples of artificial food dyes currently in use include Amaranth (AMR), Indigo carmine (ICN), Malachite green (MG), Erythrosine, Ponceau 4R, Allura red, Sunset yellow, Tartrazine, Brilliant blue, and Azorubine. As consumer preferences and market dynamics continue to evolve, the role of food colourants in shaping the sensory experience and marketability of food products remains indispensable.

The excessive consumption of artificial colours in food poses significant health risks to the human body. The widespread use of both authorized and unauthorized food colourants, coupled with their associated toxicities and potential adulterations, presents global concerns of varying severity across different countries. Diseases like irritations, diarrhea, vomiting, tumors, and permanent damage to the cornea and conjunctiva may arise from unlimited intake of these artificial food dyes. To address these concerns, the Joint Food and agriculture organization of the United Nations (FAO) and the World health organization (WHO) expert committee on food additives (JECFA) have fixed the highest allowable daily intake limits for these colours, with some dyes even being banned. Regrettably, in many regions of India, sellers and vendors still use these artificial colours beyond the permitted limits in numerous commercial food products. Consequently, it is much required to monitor the levels of daily dye intake in foods,

underscoring the urgent need for a rapid and efficient method of detection across various samples. In this context, conventional approaches such as High-performance liquid chromatography (HPLC) [3], [4], spectrophotometry [5], and capillary electrophoresis [6] are available. While these methods are highly accurate, they are plagued by significant drawbacks including lengthy sample preparation times, the requirement for skilled operators, and complex instrumentation [7]. Naturally, these strategies are not easily adaptable for routine and extensive use in detecting artificial food colourants in foods. Efforts to develop more user-friendly and efficient detection methods are essential to ensure compliance with safety standards and safeguard public health.

The present thesis titled "Development of electrochemical sensors for the detection of different dyes used as artificial food colorants" describes the development of some electrodes, specific for an individual synthetic food colour. Among various artificial food colourants, three colours namely Malachite green (MG), Amaranth (AMR), and Indigo carmine (ICN) have been selected whose detection schemes are studied in this thesis.

2. Motivation and research objectives

The enhancement of carbon paste electrodes (CPEs) through nanoparticle modification is a vastly researched domain in electrochemical studies. It provides superior characteristics and heightened functionality for diverse sensing and analytical uses. Nanoparticles are ingrained into the carbon paste structure boosting its conductivity, expanding its surface area, as well as delivering a catalytic capability. The present work throws light on the usage of the nanoparticles modified CPE for the measurement of a few synthetic food colours viz., MG, Amaranth and ICN, separately. With the advancement of the sensors, different exploratory parameters like, effect of pH, effect of buffer, effect of scan rate, and effect of concentration variation have been examined in thoroughly. The goals of this thesis work can be outlined as follows:

- Selection and synthesis of nanoparticles
- Characterization of the nanomaterials in terms of their dimensions, structural and morphological variations.
- Investigating different electrocatalytic properties of the electrodes (high conductivity, wide potential range, renewable surface, etc.) as well as optimizing the experimental conditions like buffer, pH, scan rate, concentration, etc.

- Studying various electro-analytical characteristics (selectivity, sensitivity, repeatability, reproducibility, etc.) of the developed electrodes.
- Application of the developed electrodes to the real samples.

Considering the stated objectives, the entire study has been segmented into five chapters. A succinct breakdown of the thesis organization by chapter is provided below.

3. Organization of the thesis

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Chapter 1 explains the basis of the issue and illustrates the objectives of this thesis work. The chapter then portrays the distinctive transduction systems. Further, it concentrates on the various electrochemical procedures utilized as of recently for determination of artificial food colourants alongside their advantages and disadvantages. Followed by it, the nanoparticles based modified carbon paste electrode (CPE) systems have been described as a way to alleviate the impediments brought about by ordinary electrochemical identification procedures. A presentation of this modification is followed by a short literature review on nanoparticles modified CPE based sensing. The chapter ends with the summarized objectives and scope of the work.

Chapter 2 discusses the basic CPE and then the nanoparticles embedded graphite paste electrode (GPE) synthesized for the determination of green coloured dye named Malachite green (MG) in pond water and fish fillets. Also, the comparative study of MG determination with other research reports is presented in this chapter. The electrochemical characteristics of the developed electrode and the experimental parameters for the detection of MG are discussed here in detail followed by analysis of real samples.

Chapter 3 discusses the CPE and then the nanoparticles ingrained GPE for the determination of red coloured Amaranth (AMR) dye in different children's consumable candies. Also, the comparative study of AMR determination with other research reports is presented in this chapter. The electrochemical characteristics of the developed electrode and the experimental parameters for the detection of AMR are discussed here in detail followed by analysis of real samples.

Chapter 4 discusses the CPE and then the modified GPE to determine blue coloured Indigo carmine (ICN) in different candies. A comparative study of ICN determination with earlier research reports is presented. The electrochemical characteristics of the developed electrode and the experimental parameters for the detection of ICN are discussed here in detail followed by analysis of real samples.

Chapter 5 shows a general overview of the work done and highlights the concluding comments. The strengths as well as weaknesses of the proposed framework have been investigated here with certain suggestions and a few proposals are presented as future scopes of work.

4. Contribution of the thesis

The research objectives were formulated following a thorough literature review by former researchers who had worked with modified CPEs. The contribution of this thesis is outlined chapter by chapter in alignment with these research objectives.

- In **chapter 2**, CPE is modified with copper oxide (CuO) nanoparticles for the detection of MG molecule. Sol-gel method is applied for this synthesis of nanoparticles. The electrochemical characteristics of this electrode with the results in real samples have been presented here. A LOD of 0.18 µM and a wide linear range of 1-1000 µM are obtained.
- In **chapter 3**, the sensitive and selective determination of AMR in children's consumable candies has been performed using yttrium oxide (Y_2O_3) nanoparticles ingrained CPE. Y_2O_3 nanoparticles also have been synthesised in-house using sol-gel method. Overall analytical performance of this electrode has been presented with a LOD of 3.6nM and a wide linear range of 0.05-100µM.
- In **chapter 4**, ICN detection has been narrated using a Y_2O_3 embedded graphite paste electrode. The materials synthesis, characterization and electrochemical responses are discussed. Besides, the reasons behind the individual detection of AMR and ICN using the same nanoparticles modified graphite paste electrode (Y_2O_3@GPE) are also discussed. A linear range of 5-300µM and a LOD of 0.11 µM is achieved here.

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5. List of publications

Paper published in International Journals

1. Samhita Dasgupta, Shreya Nag, Runu Banerjee Roy, Rajib Bandyopadhyay, Panchanan Pramanik, Deepak Kumar Das, Bipan Tudu, "Development and detailed performance study of a carbon paste electrode for the electrochemical detection of malachite green," ***Nano LIFE,*** vol. 13, no.2, 2350006, pp. 1-9 , 2023. [DOI: 10.1142/S179398442350006X].
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3. Samhita Dasgupta, A.H.M. Toufique Ahmed, Ipshita Bhattacharjee, Shreya Firdoushi, Don Biswas, Sumani Mukherjee, Rajib Bandyopadhyay, Bipan Tudu, "Crafting a graphite electrode with embedded Y_2O_3 nanoparticles for the electrochemical detection of amaranth in candies," ***IEEE Sensors Journal,*** vol. xx, no.xx, pp.xx-xx, September xx, 20xx. [DOI: 10.1109/JSEN.2024.3400317]. **[Article in Press].**
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