Synthetic Dyes

Subjects: Materials Science, Textiles Contributor: Gururaj Kudur Jayaprakash

Synthetic dyes are commonly used in food products like soft drinks, vegetable sauces, jellies, etc. Most artificial dyes can cause cancer, therefore it is very important to develop sensors to detect them in food samples.

voltammetry dyes sensors electron transfer carbon paste modifications

1. Introduction

Dyes play an integral part in the present world. They are responsible for imparting colors due to chromophoric (azo, azoxy, nitro, carbonyl, thiocarbonyl) and auxochromic groups. They are different from pigments as the former are organic compounds and become attached chemically to the substrate while the latter do not form any chemical bonds and can be organic or inorganic compounds ^{[1][2]}.

2. Dye Classification

Broadly, dyes can be classified into natural and synthetic based on the source of origin. Natural dyes can be extracted from natural sources such as fruits, flowers, leaves, roots, barks, etc., whereas synthetic dyes are synthesized in laboratories by the use of chemicals. In addition, they can be classified based on general structure into anionic, cationic, and non-ionic, and categorized based on application characteristics into ten different types (acidic, basic, mordant, reactive, direct, disperse, sulfur dye, pigment, vat, azo insoluble) ^[2].

3. Synthetic Dyes (Advantages and Disadvantages)

Dyes influence every sphere of human life, be it food, leather, cosmetics, or the drug industry. By 1900, with an increase in demand, synthetic dyes gained immense attention and replaced natural dyes due to a variety of reasons such as low-cost production, easy availability, easy application, more color stability, resistance to light, pH changes, oxygen, etc. However, as every coin has two sides, dyes also have pros and cons. Therefore, considering their importance and large-scale industrial use, we cannot neglect their drawbacks. Some of these are described below ^[2].

- They are not environmentally friendly as their synthesis involves extreme conditions such as high pH, high temperature, strong acids, and heavy metal catalysts.
- The most common substrate for dye production is petroleum, which is a non-renewable source of energy.

• Synthesis generates a large amount of effluent which contains toxic chemicals generated as side products.

The increasing dependency of various industries on synthetic organic dyes, and their solubility in water, are a cause of great concern; due to inadequate environmental legislature, industrial effluent is discharged into water bodies without proper treatment. Although dyes constitute only a small proportion (less than or equal to 1 ppm) of the industrial effluent, they are quite stable and are resistant to light, various chemicals, and biological activities owing to their complex structure, remaining as such for a long period. Hence their accumulation causes an increase in biochemical oxygen demand (BOD), affecting the pH and chemical oxygen demand (COD) ^[3].

In addition, their increase affects the color of water bodies and affects absorption properties of planktonic life (decrease in photosynthetic activity). It is also seen that some of the dyes sequester metal ions and cause toxicity in marine animals ^[4].

These dyes also react with various other organic byproducts of the effluent, forming harmful aromatic complexes that result in mutations and cancers in aquatic animals. Recent studies have shown that dyes have genotoxic, cytotoxic, and mutagenic properties when exposed in greater concentrations to living organisms. They can also cause DNA fragmentations, allergies, skin irritations, and malfunctioning of various organs when acted upon by different biotic and abiotic factors due to the formation of toxic breakdown products ^{[5][6]}.

4. Industrial Applications

In the food industry ^{[Z][8]}, dyes act as color additives that impart appealing bright colors to the food products without giving any nutritional value. The first artificial food coloring was prepared from coal tar in 1856 and since then hundreds of dyes have been prepared, out of which only a few are permitted by food regulatory bodies (FDA, FSSAI, EEC) owing to health concerns. They have been reported as creating various health issues such as toxicity, cancers, allergies, hypersensitivities, etc., but still, research is ongoing to elucidate the harmful effects of food dyes on health.

The list of commonly used permitted dyes along with color imparted is given in <u>Table 1</u>.

Table 1. List of food permitted dyes along with wavelength and color they impart.

Color	Wavelength Å	Dyes
Red	6400–7000	Carmoisine, Erythrosine, Allura Red
Yellow	55005900	Tartrazine, Sunset Yellow

Color	Wavelength Å	Dyes	
Blue	4500–5100	Brilliant Blue, Indigo Carmine	
Green	5100–5500	Fast Green	[–] ast Red, ssary.

Textile industry: It has been observed that 7×10^5 tons of synthetic dyes are produced every year around the globe, out of which about 2×10^5 tons are lost after various processing processes as waste effluent into water bodies. This waste effluent disturbs various water parameters such as pH, salinity, COD, BOD, etc., as most of the dyes contain aromatic rings causing toxicity and mutagenicity, ultimately affecting aquatic life adversely ^{[9][10][11]}.

The two important classes of dyes that are employed in the textile industry include azo and anthraquinone.

Azo dyes are characterized by the presence of -N=N- bonds mainly imparting yellow, orange, and red colors. Anthraquinone is used for violet-blue or green colors.

Pharmaceutical industry: This industry ^[12] also employs various food dyes in processing pharmaceutical products such as tablets, capsules, syrups, etc. Dyes provide appealing appearance and easy identification for similar drugs. However, considering various ill effects of dyes, certain permissible amounts are fixed for using dyes. Dyes often used in the manufacturing process are tartrazine, quinoline, Sunset Yellow, amaranth, Allura Red, erythrosine, and Brilliant Blue.

On similar grounds, dyes are used in other industries for their color attracting properties and to appeal to the customers as per their requirements.

Dye degradation methods are categorized into three types: chemical, physical, and biological. The physical method includes adsorption (using activated carbon, silica, fly ash, bio adsorbent, polymeric adsorbent), irradiation, and filtration; the chemical methods include oxidation (using UV, H_2O_2 , O_3), coagulation, and precipitation; while biological methods include aerobic and anaerobic methods ^{[6][13]}.

5. Methods for Dye Detection

Various chemical methods have been reported for the detection of dyes, such as chromatography (HPLC, TLC, RPLC), capillary electrophoresis, mass spectrometry, spectrophotometry, immunoassay techniques (ELISA), etc. Among these the most employed technique is HPLC. However, these techniques are time-consuming and are expensive using highly skilled labor. Moreover, capillary electrophoresis, ELISA, and mass spectrometry do not work on neutral molecules and require charged molecules to work ^{[14][15]}.

Besides the above-mentioned techniques, electrochemical methods, especially voltammetric techniques such as cyclic voltammetry (CV), differential pulse voltammetry (DPV), square-wave voltammetry (SWV), polarography, etc., have gained immense attention. The voltammetric studies employ the use of a three-electrode system: working electrode, counter electrode (non-reactive), and a reference electrode (helps to monitor the potential of the working electrode). The working electrodes can be solid (mainly graphite, carbon, diamond, bismuth, platinum, and gold) or liquid (mercury) and can be easily modified using organic and inorganic ions, molecules, polymers, or nanoparticles (NPs) for enhancing the electron transport rate ^[16].

Compared with other detection methods, voltammetric methods offer many advantages [17]:

(i) they decrease the capacitive current; Apart from the above-mentioned properties, they are fast, cost-effective,
(ii) they are best for organic and inorganic molecules, which are electroactive; user-friendly, and show high
(iii) they give lower detection limits as the preconcentration of the analyte is prevented; specificity and sensitivity
(iv) an easily renewable surface of the working electrodes is possible; with low-quantity sample usage ^{[18][19]}.

- (v) lightweight and small instruments are employed;
- (vi) they not only determine the concentration but also give the composition of different species;
- (vii) they can also be applied to solid analytes.

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