Chapter 4

Advances and Trends in Voltammetric Analysis of Dyes

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Additional information is available at the end of the chapter

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Abstract

Since 1856 when W. H. Perkin synthesized the first synthetic dye (Mauveine), a wide variety of colors and shades are produced and used in several commercial products. The occurrence in water and wastewater has gained controversy regarding their toxicity and mutagenicity and it has been regulation by several regulatory agencies. Thus, analytical methods able to determine these colorings in several matrices with high sensitive and robust enough are relevant. Among several analytical methods, the use of electroanalytical methods, especially the voltammetric techniques, are of great interest due to the high selectivity, sensitivity, use of low quantity of sample, little or without sample treatment, and low waste generation, which contributes to reduced environmental impact. Over the past decades, the technical based on current-potential curves by using of static electrodes have gained considerable progress, as minimizing the effect of capacitive current and the possibility of pre-concentration of the analyte at the electrode surface, which has reflected in lower detection levels. The present work gives an overview about the analytical methods available in literature focusing on electroanalysis of dyes by using voltammetric techniques. The advances of the electroanalytical techniques and the use of different modifiers to increase sensitivity and selectivity are reviewed.

Keywords: voltammetry trends, dyes analysis, electroanalytical methods, dye determination

1. Introduction

Since 1856, when W.H. Perkin synthesized the first synthetic dye (mauveine), a wide variety of colors and shades has been produced and used in several commercial products, mainly in the industries of textiles, cosmetics, food, and others [1–4]. The dyes present complex organic structures with several chromophoric centers based on functional groups, such as azo, anthraquinone, polymethine, nitro, nitroso, aryl methyl, xanthine, coumarin, and others. They also have some particular physicochemical properties that are essential for their attachment in specific types of natural fibers, such as cotton, silk, leather, and hair and synthetic fibers, such as polyamide, polyester, and cellulose acetate. Thus, they can be commercially classified as due chromophoric group or due fixation to the fiber and can also be assigned as reactive, direct, acid, vat, sulfur, dispersed, premetalized, optical brighteners, and so on.

The use and release of dyes in the environment has received great attention since approximately 9% (40,000 tons) of the dyes produced worldwide (450,000 tons) are discharged in to textile wastewater [5, 6]. Their occurrence in water and wastewater has gained controversy regarding their toxicity and mutagenicity, and it has been regulated by several regulatory agencies [7]. Besides that, their addition in food has obeyed rigorous control, and a little amount of dye is allowed for this strict end. Thus, analytical methods able to determine these colorings in surface water, commercial formulation, industrial effluents, and food are of great interest. For monitoring in environmental samples, where the dye is much diluted, is required very sensitive and robust methods as well in food samples that usually are based on complexes matrices. In this context, several analytical methods are described in literature and are compiled here. The most popular method is the UV–visible (UV–vis) spectrophotometry, and it is based on the presence of chromophoric groups responsible for the color of the dye solution [8–10]. However, due to its medium sensitivity coupled with matrix interference and band overlapping in simultaneous measurements, this technique is losing space. The development of methods for the detection of dyes using chromatographic techniques has also been exploited, particularly due to low levels of detection and high types of available detectors [11–14]. Nevertheless, while chromatography-based methods are effective for the detection and quantification of the dyes in the wide range of matrices, such methods require the use of a large amount of organic solvents and a laborious sample preparation. In this context, electrochemical techniques, especially the voltammetric techniques, have been used as alternative methods due to the high selectivity, sensitivity, low cost, use of low-quantity sample, little or no sample treatment, and low waste generation, which contribute to reduced environmental impact.

The voltammetric techniques gained notoriety in the early 1920s, when Jaroslav Heyrovsky developed the polarography based on the use of dropping mercury electrode [15]. Over the past decades, the technical based on current-potential curves (polarography and voltammetry) by using static electrodes have gained considerable progress, as minimizing the effect of capacitive current (techniques of differential pulse voltammetry and square wave voltammetry) and the possibility of preconcentration of the analyte at the electrode surface, which has reflected in lower detection levels. Furthermore, the use of stationary solid electrodes (electrodes as gold, platinum, and carbon) has shown improvements, because there is the possibility of modifying

the surface of these electrodes with high diversities of materials, such as metal nanoparticles, polyaminoacids, carbon nanotubes, graphene, and imprinted molecular polymer, which improved considerably the sensitivity and/or selectivity of the electroanalytical method [16–18].

The present work gives an overview about the analytical methods available in literature, focusing on electroanalysis of dyes by using voltammetric techniques.

2. Electroanalysis of food dyes

Food additives are substances (or mixtures) that are added during the process of food manufacturing, processing, or packaging with the purpose to prevent changes and/or to confer, intensify, and maintain color, aroma, taste, or any other action required to improve the quality or aspect of the food [19–21]. Among the food additives used, we can highlight the color additives, usually added only to make them more attractive and tasty to the consumers [20, 22].

Until the middle of the nineteenth century, all the coloration used in dyes came from extracts of animals or vegetables [20, 23]. But currently, natural dyes have been replaced by synthetic dyes, because they present better stability, uniformity, and tinctorial power [6, 24, 25]. As a reflection of this progress, at the end of the nineteenth century, more than 90 dyes were used by the food industries. In 1906, started in the USA, a great concern and the first legislation was imposed to the control the use of food colorants, in which only seven dyes were authorized [26].

Color additives can be classified in different ways. In Brazil, a simple one is stipulated by the *Agência Nacional da Vigilância sanitária* (ANVISA) in the resolution of the *Nacional de Normas e Padrões para Alimentos* (CNNPA) n° 44, of 1977. These agencies establish that food colorings can be classified as natural organic dyes (derived from vegetables or animals), artificial dyes (synthetic organic dyes), synthetic organic dyes identical to natural dyes (synthetic organic dyes whose chemical structure is derived from natural organic dyes), inorganic dyes (obtained from mineral substances), and caramel dyes (natural dyes obtained by heating sugars) [23, 27]. **Figure 1** exemplifies the distribution of the dyes used in food (food and drink) products in the world, which shows the supreme use of synthetic additives by food industries.

Due to the inefficiency of resolutions, control, and monitoring, many illegal dyes were used in food products, which resulted in cases of allergic reactions and even deaths, as reported in 1860 after two people consumed a dessert that contained copper arsenate [23]. In India, studies indicated that 61.6% of the analyzed foods presented dyes not allowed in the country [28]. This occurs because the synthesis in most cases is complex and the purification requires time and money.

Food legislation is a very important factor in ensuring the quality of food. The first supervisory agency was created in the USA and became known as the 1906 FD&C Act [26]. Nowadays, there are several agencies that dictate and supervise the dye additives allowed, not only to maintain the good quality of food but also to preserve the health of the people, since research

indicates that certain substances with dyeing power have great mutagenic potential besides adverse reactions. In the USA, all color additives are regulated by the Federal Food, Drug, and Cosmetic Act (FD&C) [29, 30]. However, the use of additives must be approved by the USA Food and Drug Administration (FDA) by a color petition process and listed in Title 21 of the Code of Federal Regulations (CFR, 2014) [23, 30, 31]. In the European Union (EU), the first legislation was created in 1950 [26]. Currently, food additives are controlled by EU Regulation (EC) No1333/2008 and food additives are divided into 20 groups, according to their functionality [30]. Among them, 43 colorants are permitted as food additives, of which 17 are synthetic and 26 are natural [26].

Table 1 shows some types of synthetic color additives commonly used in food and whether they are recognized or not by the European Union (EU), US Food and Drug Administration (FDA), *Agência Nacional da Vigilância sanitária* (ANVISA), and World Health Organization (WHO).

The search for highly sensitive, efficient, and rapid methods of analysis of these additives has been growing. This is justified by a great demand for coloring additives to be used in food. Therefore, the inspection agencies need to specify the types of substances that can be used and chosen one that is not harmful for the human health. In addition, the presence of food dyes has also been reported in wastewater, and there is a demand for analytical methods applicable in environmental matrices.

The first works for the detection of food dyes using electroanalytical methods are dated to 1979, and they were based on the use of mercury electrodes [33, 34]. Fogg and Yoo [33] have used differential-pulse polarography (DPP) for the determination of mixtures of Tartrazine-Sunset Yellow FCF, Tartrazine-Green S, and Amaranth-Green S in soft drinks. In another work, FOGG et al. [35] used differential-pulse adsorptive stripping voltammograms (DPASV) for the determination of 13 food dyes assigned as Amaranth, Carmoisine, Ponceau 4R, Red 2G, Erythrosine, Sunset Yellow FCF, Tartrazine, Quinoline Yellow, Green S, Indigo carmine, Patent Blue V, Brilliant Blue FCF, and Chocolate Brown HT. For Amaranth, Carmoisine, Ponceau 4R, Red 2G, Sunset Yellow FCF, Tartrazine, and Chocolate Brown HT, the signals were attributed to the reduction of the azo to hydrazo group. After optimization for each analyte individually, the sensitivities for food dyes were in the range of 5.5–38 and 120–1500 mA L mol^{-1} by using dropping mercury electrode (DME) and hanging mercury drop electrode (HMDE), respectively.

Dominguez and collaborators [36] have demonstrated that Sunset Yellow FCF and Tartrazine can be determined in soft drinks sample by DME and DPP techniques. The sensitivities of the

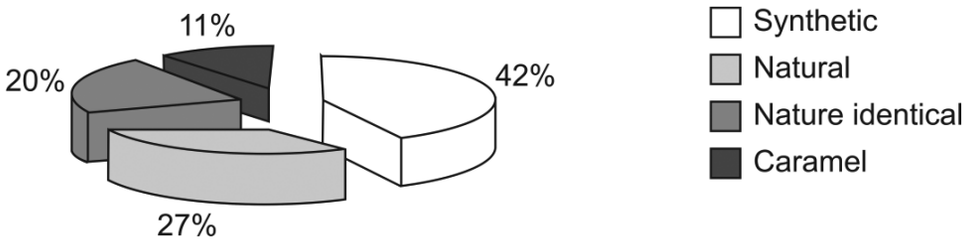
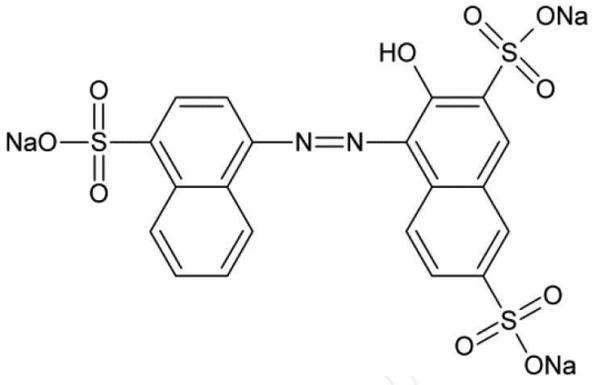
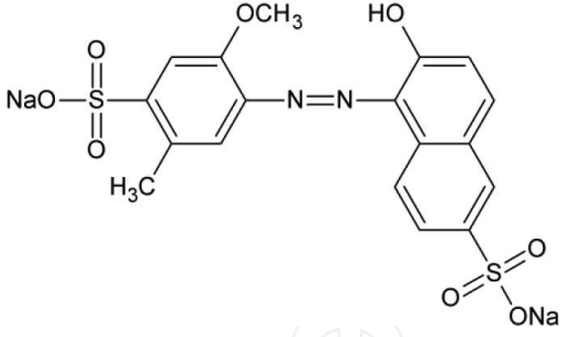


Figure 1. Distribution of the types of coloring additives used in food in the 1992 world market [23].

Color additives	Permission to use in food				
	Synonymous	EU	FDA	ANVISA	WHO
Amaranth 	Acid Red 27 Azorubin SFD&C Red Dye No. 2	No	No	Yes	Yes
Allura red 	Disodium 6-hydroxy-5-[(2-methoxy-5-methyl-4-sulfophenyl) azo]-2-naphthalenesulfonate FD&C red No. 40	No	Yes	Yes	Yes

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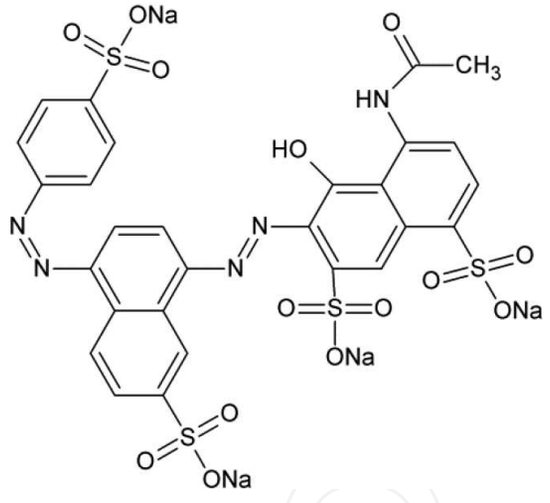
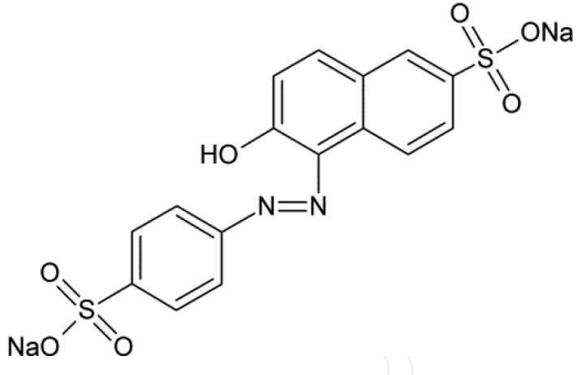
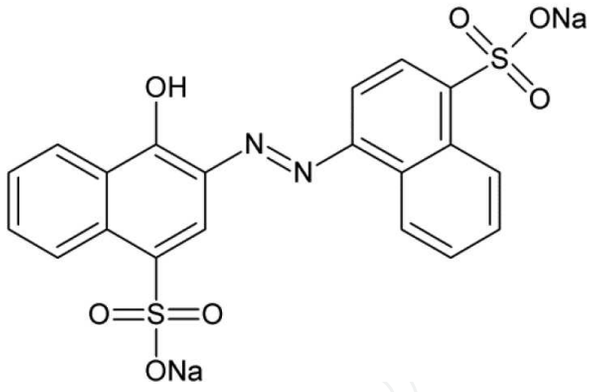
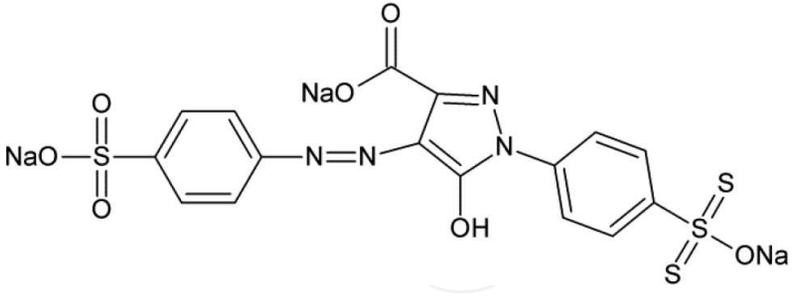
Color additives	Permission to use in food				
	Synonymous	EU	FDA	ANVISA	WHO
Brilliant black BN 	Food Black 1	No	No	No	Yes
Sunset yellow 	Food Yellow 3 Orange Yellow S FD&C Yellow No. 6	Yes	Yes	Yes	Yes

Color additives	Permission to use in food				
	Synonymous	EU	FDA	ANVISA	WHO
Carmoisine 	Acid Red 14 Chromotrope FB Disodium 4-hydroxy-3-[(4-sulfo-1-naphthalenyl)azo]-1-naphthalenesulfonate Mordant Blue 79	Yes	No	Yes	Yes
Tartrazine 	Acid Yellow 23 FD&C Yellow No. 5	Yes	Yes	Yes	Yes

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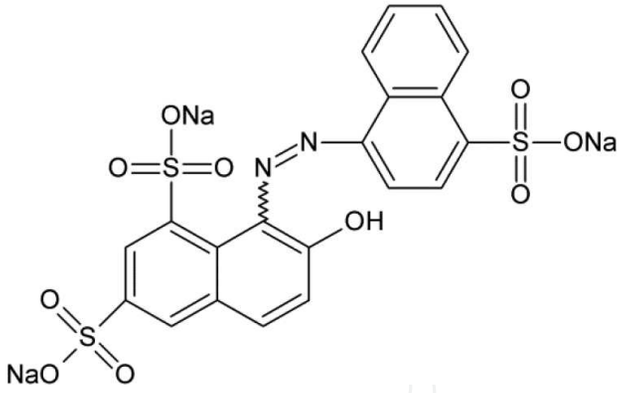
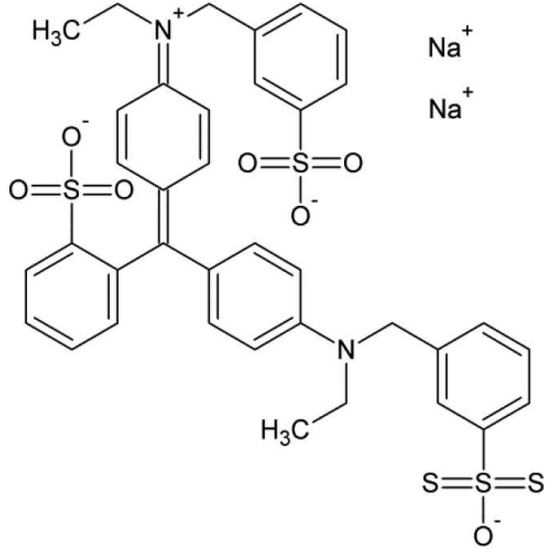
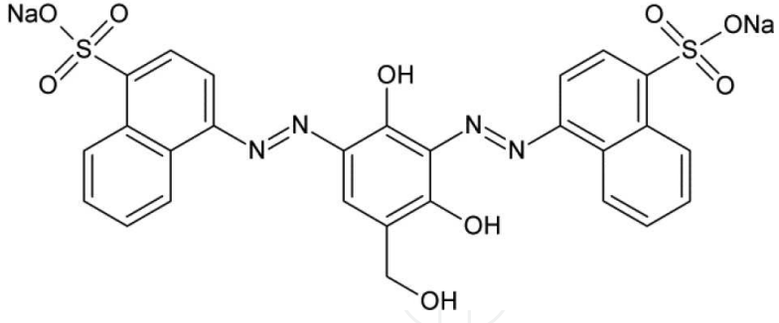
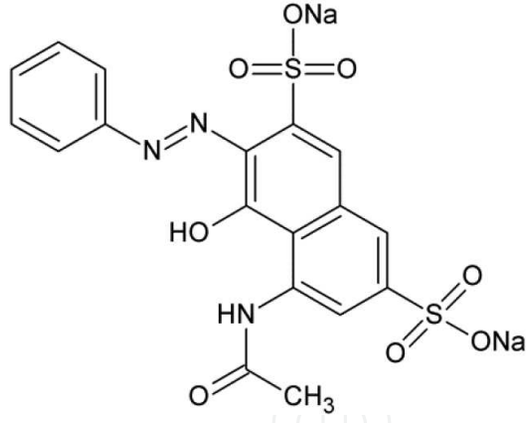
Color additives	Permission to use in food				
	Synonymous	EU	FDA	ANVISA	WHO
Ponceau 4R 	Acid Red 18 New Coccine Ponceau 4 R	Yes	No	Yes	Yes
Brilliant blue FCF 	Acid Blue 9 Alphazurine FG E133 Erioglaucine disodium salt FD&C BLUE No. 1	No	Yes	Yes	Yes

Color additives	Permission to use in food				
	Synonymous	EU	FDA	ANVISA	WHO
Brown HT 	Chocolate Brown HT Food Brown 3 C.I. 20285	No	No	No	Yes
Red 2G 	Acid Red 1, Amidonaphthol Red G, Azophloxine	Yes	No	No	

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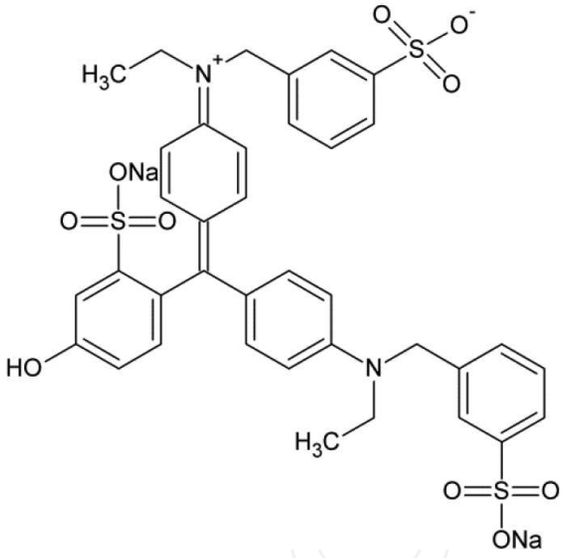
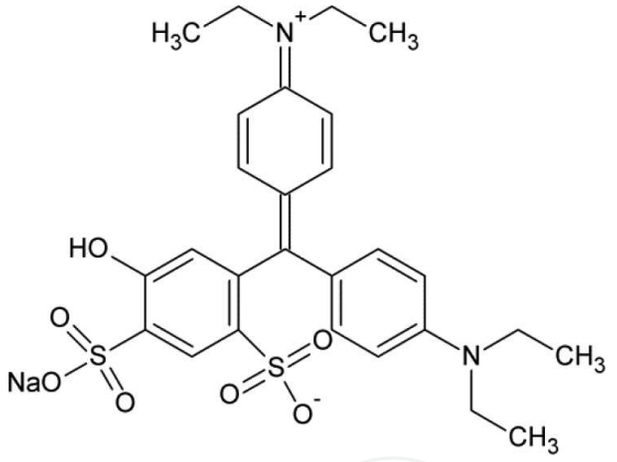
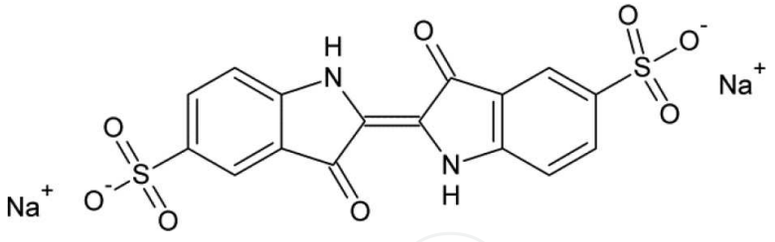
Color additives	Permission to use in food				
	Synonymous	EU	FDA	ANVISA	WHO
Fast green FCF 	Food green 3 FD&C Green No. 3	No	Yes	Yes	Yes

Color additives	Permission to use in food				
	Synonymous	EU	FDA	ANVISA	WHO
Patent blue V 	Acid blue 3 sodium salt Food Blue 5 sodium salt	Yes	No	Yes	Yes
Indigotine 	Indigo carmine, Acid Blue 74, Indigo-5,5′-disulfonic acid disodium salt Indigocarmine FD&C Blue No. 2	Yes	Yes	Yes	Yes

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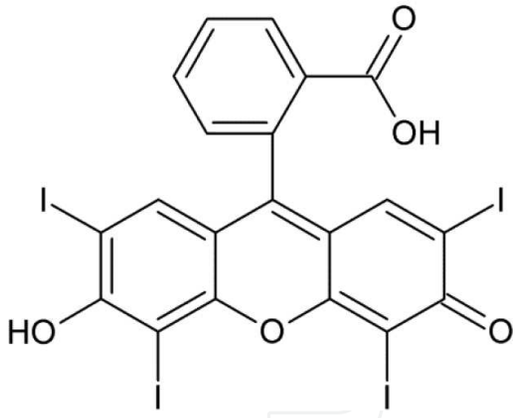
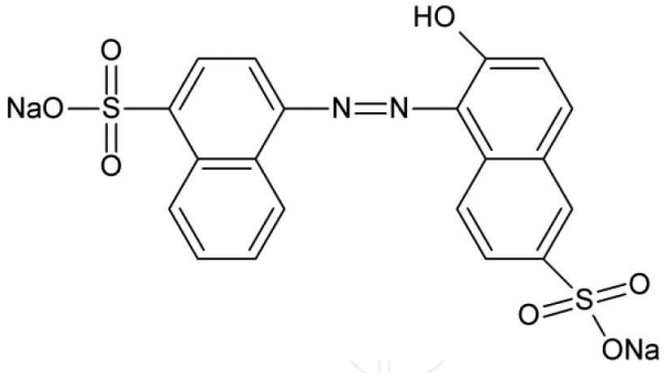
Color additives	Permission to use in food				
	Synonymous	EU	FDA	ANVISA	WHO
Erythrosine 	FD&C Red No. 3	Yes	Yes	Yes	Yes
Fast red E 	CI Food Red 4 CI (1975) No. 16045	No	No	No	Yes

Table 1. Synthetic color additives used in food in EU, FDA (USA), ANVISA, and WHO (adapted from Refs. [26, 32]).

proposed methods were 4.56×10^{4} (±0.03) and 1.98×10^{4} (±0.02) μA L mol^{-1} and the detection limits were 1.3×10^{-8} and 3.0×10^{-8} mol L^{-1} for Sunset Yellow FCF and Tartrazine, respectively. In the work of ALBA and co-authors [37], a method was developed for the determination of the synthetic food colorants Tartrazine, Allura Red, and Sunset Yellow by DPP. Using as a response, for the three analytes, the signal intensity related to the reduction of the azo to hydrazo group on the surface of a DME, linear relationships were obtained between 0.050 and 7.5, 0.050 and 7.5, and 0.050 and 10 μmol L^{-1}, and the detection limits 0.013, 0.020, and 0.011 μmol L^{-1} for Allura Red, Tartrazine, and Sunset Yellow, respectively. Combeau et al. [38] proposed a method for the determination of Azorubin, Allura Red, and Ponceau 4R in soft drinks by DPP. Reductions of the azo groups (for all dyes) were promoted under the surface of a DME. Using as electrolyte 0.1 mol L^{-1} KCl, the detection limits were 22, 50 and 44 μg L^{-1} for Azorubin, Allura Red, and Ponceau, respectively. Finally, the application in the food dye sample showed low values of standard deviation in relation to the amount added and found for all analytes.

Although most studies are based on the reduction of food dye molecule as a basis for its monitoring, some chapters describe the use of electrochemical oxidation process, as described by Fogg and Bhanot [39] in the 1980s, using stationary solid electrodes. In the work of Desimoni et al. [40], the authors used carbon glass electrode (GCE) modified with Nafion for the detection of Patent Blue (V) dye, by oxidation of the R–OH to R=O group. Under optimized conditions such as electrolyte (0.1 mol L^{-1} acetate buffer solution) and pH (5.0), an analytical curve was constructed in the interval from 9.5×10^{-8} to 9.9×10^{-7} mol L^{-1} using differential pulse voltammetry (DPV), found a detection limit of 7.6×10^{-8} mol L^{-1}. In another work, Nayak and Shetti [41] developed a glucose-modified carbon paste as sensor for erythrosine. The measurements were performed in phosphate buffer solution pH 11.2, since the sensor exhibited higher catalytic activity. The mechanism proposed by the authors is exemplified in **Figure 2**. Using square-wave voltammetry (SWV), an analytical curve was constructed between 1.0×10^{-7} and 1.0×10^{-4} mol L^{-1} with detection limit of 2.16×10^{-8} mol L^{-1}. The method was applied in human urine sample, with recoveries between 91.6 and 98.0% and relative standard deviation of 1.12%.

Zhang and collaborators [42] have proposed the determination of food dye Ponceau 4R and Allura Red using a multi-wall carbon nanotube-modified GCE. In this case, the dye signal occurred by the oxidation of the R−OH group for both analytes. By means of DPV measurements, linear relationships were found in pH 7.0 phosphate buffer 0.1 mol L^{-1} solution from 25 μg L^{-1} to 1.5 mg L^{-1} and 50 μg L^{-1} to 0.6 mg L^{-1} and detection limit of 15 and 25 μg L^{-1} for Ponceau 4R and Allura Red, respectively. The proposed method was applied in soft drinks samples with high accuraty and feasibly. In the work of Sierra-Rosales et al. [43], the authors used a GCE modified with multi-walled carbon nanotubes (MWCNTs) and 1,3-dioxolane as a dispersant agent for the determination of Tartrazine, Sunset Yellow, and Carmoisine. For the three dyes, the oxidation occurred by the loss of one $1e^{-}$ and one H^{+} from oxidation of the R−OH group. Analytical curves were constructed by DPV in 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) using 2 min of accumulation time. Linear regions were obtained in the interval from 1.0 to 7.0, 0.55 to 7.0, and 0.54 to 5.0 μmol L^{-1} and limits of detection of 0.22, 0.12, and 0.11 μmol L^{-1} for Tartrazine, Sunset Yellow and Carmoisine, respectively. Finally, the method was applied in soft drinks sample reaching recoveries from 87 to 109% for all the

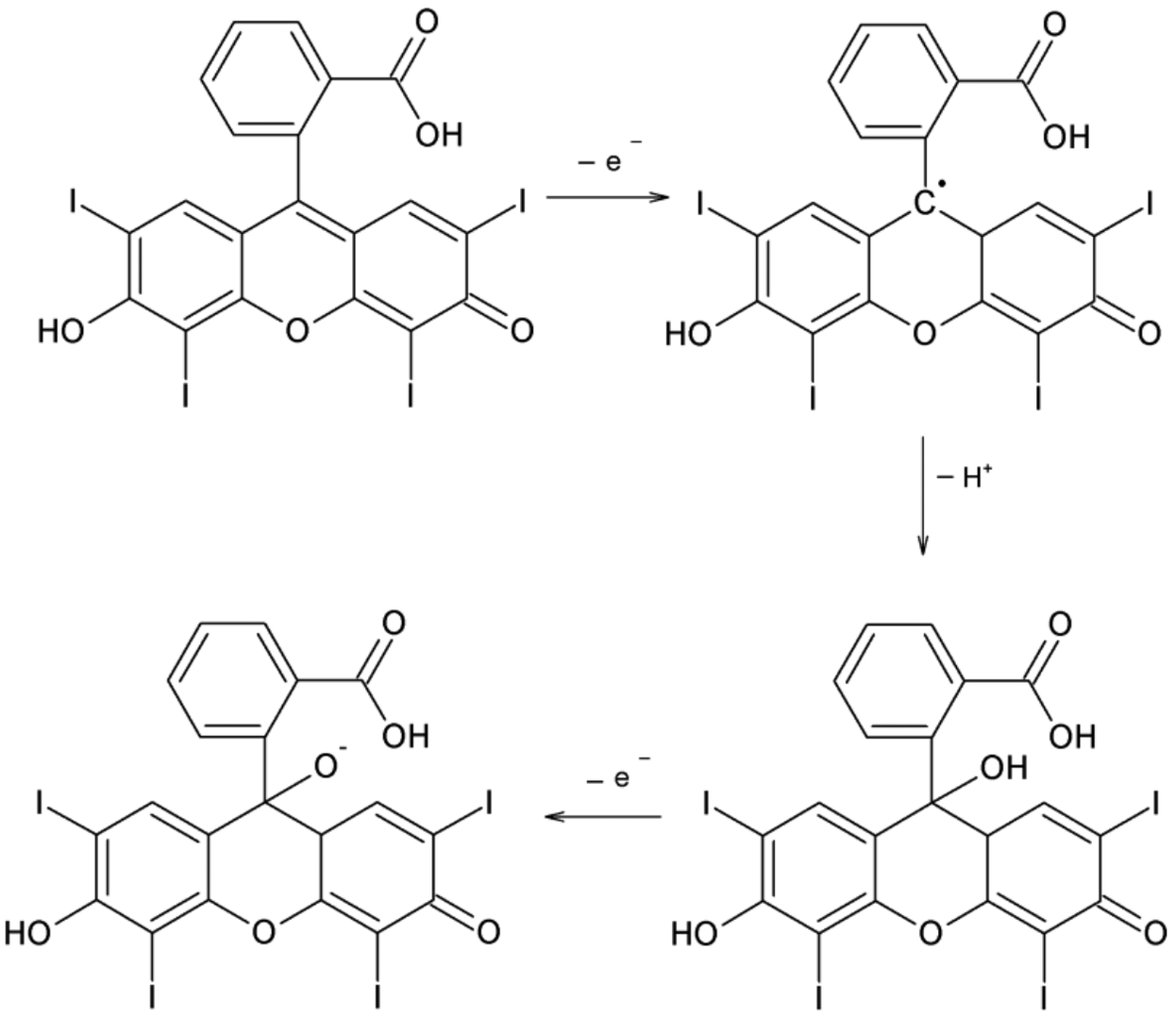


Figure 2. Oxidation mechanism of erythrosine on glucose-modified carbon paste sensor in basic phosphate buffer solution [41].

analyzed dyes. The method was compared with high-performance liquid chromatography (HPLC) method and showed great proximity between both methods.

3. Electroanalysis of hair dyes

The use of hair dyes with the purpose to change the look is a common practice for men and women. In the 1950s, only 7% of Americans usually had their hair colored. Nowadays, more than 75% of American women use hair dyes [44]. In the same way, in Japan, the hair dyeing process has grown from 14–41% in 1992–2001 to 60–85% in the last 20 years, mainly from high school women [45]. In Brazil, the IBOPE agency indicated that 26% of the population uses hair dyes, of which 85% are women and 15% are men [46].

The first records of hair dye were identified in Egypt, where the natural dye known as henna, extracted from the leaf of *Lawsonia inermis* plant, was found in the mummies' hair [47–49].

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Some other natural dyes were also used in the past, such as chamomile. In addition to these types, in some Asian countries, it was found that the extracts from nutgall, logwood, and brazilwood were used to cover gray hair [50]. However, due to short variety of colors, the natural hair dyes lost space after the first development of synthetic hair [7, 51]. Since then, the great demand and use of these products have made the technological development and growth of this market seek new products with high fixation and low price.

Hair dyes are usually classified according to the fixation on hair. They can be assigned as direct dyes (semipermanent and temporary dyes) and oxidative dyes (permanent dyes) [50, 52]. Direct dyes are separated into semipermanent or temporary dyes. The first of these (semipermanent dyes) are low molecular weight substances derived from nitroanilines, nitrophenylenediamines, and nitroaminophenols [53]. The semipermanent dyes are responsible for 10% of the economy of hair dyes and are marketed with a mixture of 10–12 different dyes to achieve the desired shade, which can remain in the hair for up to 6 weeks. Due to the low molecular weight, it allows the dye to diffuse into the cortex region, developing Van der Waals and weak polar interactions [50]. However, the temporary dyes, that present high molecular mass, cannot permeate to the region of the cortex [54]. Thus, these dyes are deposited only due to Van der Waals interactions or simple adsorption on the hair, which justifies their short durability. The products marketed as temporary dyes, such as shampoo, sprays, and lotions, have in their composition a mixture of two to five different types of temporary dyes to acquire the desired shade [55].

The second class of dyes is the permanent dyes (or oxidative dyes). They can promote permanent fixation into the hair. The process involves opening of the cortex and interaction of the components of the dye with inner regions of the hair strand [7, 55]. Oxidative dyes are the most representative among hair dyes due to their versatility, easy application, and mainly high fixation, which is reflected commercially; they represent 80% of the economy in this sector, in the USA and EU [56]. The products marketed as permanent dyes are available in kits containing two components: the first component is a mixture containing precursor agents, which are aromatic amines such as *p*-phenylenediamine (PPD) and *p*-aminophenol, and coupling agents, which are electron donor substances such as resorcinol (RSN) and naphthol [53]. The second component consists of an oxidizing agent in alkaline media, since the hair bleaching process is more effective in basic solutions [50, 53]. When the two components are mixed, the oxidizing agent (i.e., hydrogen peroxide) promotes the oxidation of the precursor agent (usually PPD), forming intermediates such as *p*-quinoneimine (PDQ) [18]. After this process, the dye itself will begin to form from the reaction of the intermediate formed, PQD, with the coupling agent (usually RSN) [7]. The reactions involved in the dye formation process (**Figure 3**) occur within the hair, that is, upon penetration of the coupling, precursor and oxidizing agents, into the cortex.

However, besides the motivation for the development of a wide variety of shades for hair dyes, the human health risks of these substances have also been the subject of research. The main worry is about the additives that may contain azo compounds and other amine, nitro, and other derivatives, which may be hazardous for the human health [49, 57–59]. As an example, in 1975, AMES et al. [60] evaluated for the first time the mutagenicity of hair dye ingredients. In a recent work, Hudari et al. [18] have shown that when PPD is used as a precursor agent, besides the formation of dyes, there is also the formation of the trimer called Bandrowski's Base (**Figure 3**), which is associated with several allergic reactions and possible carcinogenic properties [61–63].

For these reasons, several electroanalytical methods have been proposed for the identification and/or determination of hair dyes and their ingredients. In the early 1960s, Olson and co-authors [64] studied the electrochemical behavior of *p*-nitroaniline on the surface of a carbon paste electrode. They established that reduction of the $–NO_2$ groups involves $6e^-$ and can form amine products [64, 65]. In the work of Tong et al. [66], the authors used a rotating disk electrode to study the PPD reactions at the electrode. For quantitative purposes, Lawrence and coauthors [67] use a GCE for determination of PPD by cyclic voltammetry (CV) and SWV. PPD presented a reversible behavior regarding the oxidation of the $–NH_2$ groups and subsequent reduction of the groups =NH, with the participation of $2e^-$ and $2H^+$ in oxidation and reduction processes. Analytical curves were constructed using the CV and SWV, where linear relationships were found between 2–200 μmol L^{-1} and 2–20 μmol L^{-1} and limits of detection was 1.2 and 0.6 μmol L^{-1}.

Aiming for better levels of detection and selectivity, the search for new electrode materials and the modification of the surface of the electrodes became preponderant for the development of electroanalytical methods for the determination of hair dyes. As an example of new electrode materials, Oliveira and Zanoni [68] have used a self-organized Ti/TiO_2 nanotubular array electrode to monitor the reduction of azo group to hydrazo group in the hair dye basic brown 17 after a process involving $2H^+$ and $2e^-$. After optimization of SWV technique, an analytical curve was constructed in the interval from 1×10^{-7} to 7×10^{-6}mol L^{-1}. The method exhibited a limit detection of 2.7×10^{-9} mol L^{-1}. As an example of the use of modifiers, Hudari et al. [18] proposed a composite carbon nanotube/chitosan for the modification of the surface of a GCE

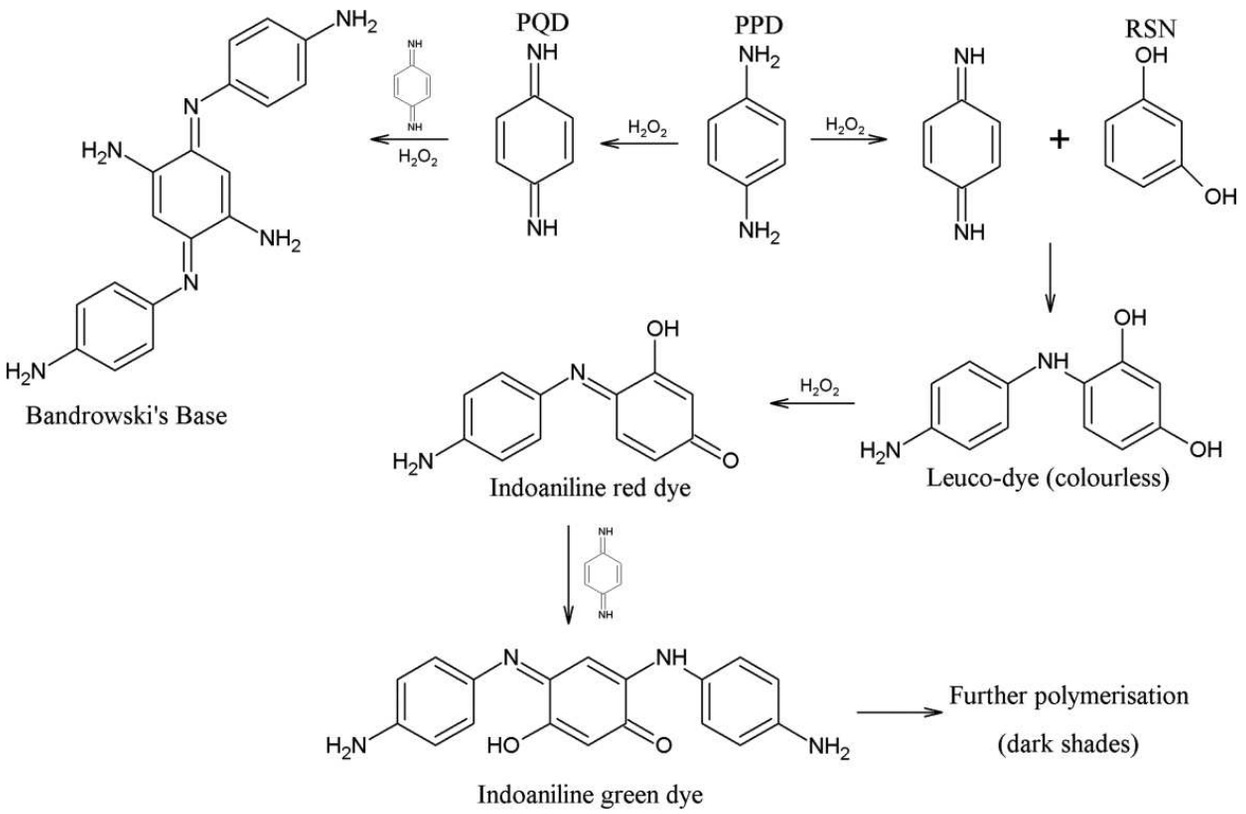


Figure 3. Reactions involved in the formation of permanent dyes using PPD, RSN, and H_2O_2 as the precursor, coupling, and oxidizing agents, respectively [49].

for the determination of the precursor and coupling agents *p*-phenylenediamine (PPD) and resorcinol (RSN), respectively, in commercial permanent dye sample. The determination and subsequent quantification of the analytes was done through the oxidation of the $–NH_2$ to =NH groups (involving $2H^+$ and $2e^-$) and the –OH to =O groups (involving $2H^+$ and $2e^-$) present in the PPD and RSN molecules, respectively. Using linear sweep voltammetry (LSV) and measurements in 0.1 mol L^{-1} ammonia buffer (pH 8.0) solution, a linear relationship was found in the range of 0.55–21.2 mg mL^{-1} for both analytes with detection limits of 0.79 and 0.58 mg mL^{-1} for PPD and RSN, respectively. Finally, the method was applied in a sample of commercial hair dye and compared with the UV–vis spectrophotometric method, which, with great agreement between the two methods. In the work of Zhao and Hao [69], the authors developed a molecular imprinting electrochemical sensor for the determination of 2,6-Diaminopyridine. Similar to PPD, the 2,6-Diaminopyridine exhibits a reversible behavior due to the oxidation of the $–NH_2$ group and subsequent reduction of the =NH group. A wide linear range was found between 0.0500 and 35.0 mg kg^{-1} with limit of detection of 0.0275 mg kg^{-1}. The method was applied in samples of commercial dyes with a recovery from 98.40 to 103.8% and relative standard deviation of less than 1.51%. Corrêa et al. [70] used a composite electrode to preconcentrate carboxyl-functionalized magnetic nanoparticles for the determination and quantification of the Basic Brown 16. In this case, the determination of dye was made by the signal referring to the oxidation of the –OH group, which allowed a linear relationship between 1.00×10^{-7} and 1.00×10^{-6} mol L^{-1} with limits of detection and quantification of 1.01×10^{-8} and 2.37×10^{-8} mol L^{-1}, respectively. Finally, the method was applied with great success for the determination of hair dye in wastewater and also in samples of dye removed from dyed hair strands.

In recent years, miniaturized systems, such as printed electrodes, have also deserved attention. Disposable electrodes have been widely used as a viable alternative for rapid measurements of dye in low concentrations [71–73]. As an example, Hudari and coauthors [16] proposed a method for the determination of hair dye Basic Blue 41 using screen-printed carbon electrodes modified with graphene. The well-defined peak is attributed to the reduction of the azo group. After multivariate optimization of SWV instrumental parameters, such as frequency (54.8 Hz), pulse amplitude (43.7 mV), and step potential (6 mV), an analytical curve was constructed in the range of 3.00×10^{-8} to 2.01×10^{-6} mol L^{-1} with limits of detection and quantification of 5.00×10^{-9} and 1.70×10^{-8} mol L^{-1}, respectively. The sensor was successfully applied in wastewater samples and validated by comparison with HPLC-DAD method with good accuracy.

4. Electroanalysis of textile dyes

Textile dyes are a class of colored substances used to impart permanent color to textile fibers. The most used class of dye is the azo dyes that present low cost and great diversity of colors and other promissory characteristics [74, 75]. The dye can be fixed to the fiber by several mechanisms, mainly due ionic Van der Waals and hydrogen interactions, but also due covalent bond [76].

The ionic bonds are frequently found in the dyeing of wool, silk, and polyamide. It came from the interactions between oppositely charged ions of the dye bearing charged groups and in the

protonated groups in the fibers [76]. The Van der Waals has been found in dyeing of wool and polyester. It results from an approach between the π orbitals of the fiber and dye molecule [76]. Hydrogen interactions have been found in the dyeing of wool, silk, and synthetic fibers, such as ethyl cellulose. It has resulted from the interaction between hydrogen atoms covalently bonded in the dye and free electron pairs of donor atoms in the center of the fiber [76]. Covalent bonds have been used in cotton fiber dye. They are formed between reactive groups (electrophilic groups) of the dye molecule and nucleophilic groups on the fiber [76, 77].

On the other hand, the textile dyes can also be classified based on the chemical structure (azo, antraquinone, etc.) or based on the method used to transfer the dye to the fiber. The main classes of textile dyes are reactive, direct, azoic, acid, vat dyestuffs, sulfur, disperse premetalized, and bleaching [76]. The main characteristics of this class are show below.

Reactive dyes bear in their structure an electrophilic group (reactive) that can form covalent bond with hydroxyl groups, amino groups, and thiol groups present in cellulose fibers, wool and polyamides for instance. In most cases, the reactive dyes bear an azo group or anthraquinone group, like chromophores, ethyl sulfonyl sulfate, and chlorotriazine, as reactive center. They are highly soluble in water and commonly used in dyeing of cellulose like cotton or flax, but also wool is dyeable with reactive dyes. Among the reactive dyes, the most used are the azo dyes because the azo group (−N=N−) confers to these dyes resistance to light, acids, bases, and oxygen. However, these desired proprieties makes them hazardous for the environment even at low concentration.

Direct dyes are anionic dyes soluble in water and can be used to dye cellulose fibers (rayon, silk, and wool) by Van der Waals interactions. They can be used for cellulosic fibers, normally applied from an aqueous dyebath containing an electrolyte, either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4). They mostly show chromophore azo groups (diazo, triazo).

Azoic dyes are products insoluble in water and cannot be applied directly on fibers as dyes. They are produced within the fibers itself. Acid dyes are the major class of anionic dyes that present sulfonic groups, for instance, to increase the solubility in water and to promote a dye bearing negative charge to the dye molecules. The textile acid dyes are effective for protein fibers such as silk, wool, nylon, and modified acrylics. These dyes are characterized by substances with a chemical structure with the presence of azo, anthraquinone, triarylmethane, azine, xanthine, ketonimine, nitro, and nitrous groups, which provide a wide color range and degree of fixation.

Vat dyestuffs are mainly based on indigos, toringoides, and anthraquinone dyes. They are slightly soluble in water; in the dying process, they are reduced with dithionite in alkaline solution, transforming into a soluble compound (leuco form), and they are subsequently oxidized by air or another reagent, such as hydrogen peroxide, regenerating the original form of the dye on the fiber. In this type of dye, the carbonyl group can be present in an ethylenic group or alicyclic subunits. The main application of this type of dye has been the cotton dye.

Sulfur dyes are characterized by macromolecular compounds with polysulfide bridges (−S_n–), which are highly insoluble in water. First, they are applied after prereduction in sodium

dithionite, which gives them the soluble form; these are subsequently reoxidized onto the fiber by contact with air. These compounds have been used mainly in dyeing of cellulosic fibers, imparting colors such as black, olive green, marine blue, and brown.

Disperse dyes are scarcely water-soluble dyes, originally used for dyeing synthetic fibers, and usually applied from fine aqueous suspensions and the presence of surfactants. They are used in hydrophobic fibers, such as cellulose acetate, nylon, polyester, and polyacrylonitrile.

Premetalized dyes are characterized by the presence of a hydroxyl or carboxyl group in the ortho position of azo chromophore, allowing the formation of complexes with metallic ions. They are useful mainly for dying protein fibers and polyamide.

Bleaching dyes are a class of compounds that have been used to decrease the color of natural textile fibers. The process involves the dyeing of fiber with chemical bleaches or white dyes, also known as optical brighteners or fluorescent brighteners. These dyes present carboxylic groups, azomethine (−N=CH–) or ethylenic (−CH=CH–) groups allied to benzene, naphthalene, pyrene and aromatic rings.

During the dyeing process, usually, there is a loss of around 10–50% of the dye to the environment [77, 78]. Considering that some dyes are highly toxic and mutagenic, and can also disturb the light penetration in surface water and therefore the photosynthetic process [79], their discharge deserves attention. The literature reports that azo dyes represent 60–70% of all organic dyes produced in the world [74], and they can be easily reduced to amine groups. So, the development of efficient and low-cost methods for the determination of this kind of dye is very important; electroanalytical method has been shown to be a successful alternative to this end.

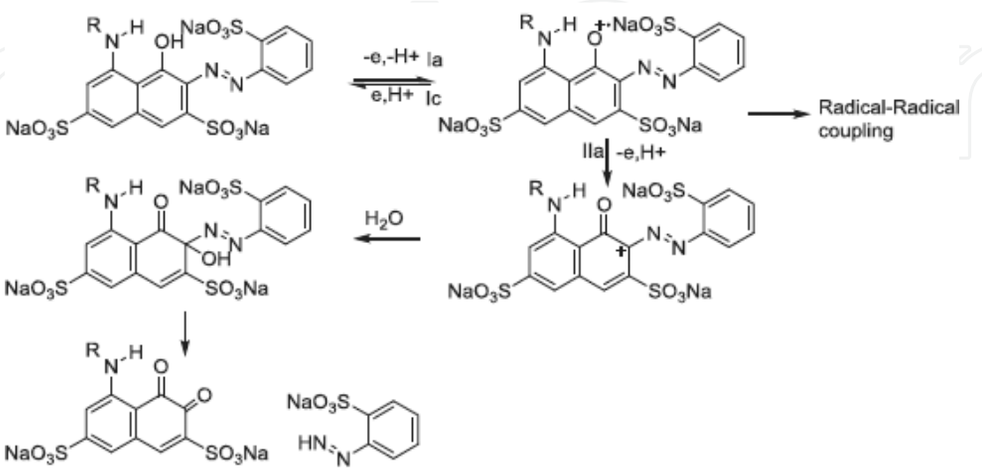
The electrochemical reduction of two reactive dyes, Procion Red HE-3B 9 (RR120) and Procion Green HE-4BD (RG19), has been reported by cyclic voltammetry, differential pulse and DC polarography, chronoamperometry, and controlled potential electrolysis at mercury electrodes [80]. These dyes can be present in dyebath and wastewaters, considering that in the dye-fiber reaction the efficiency varies from 50 to 90%. Procion Red HE-3B (RR120) and Procion Green HE-4BD (RG19) are dyes with bis-azo groups that are reduced to bis-hydrazo derivative after transfer of four electrons generating the hydrazo derivative. Linear correlations in the range 1.0×10^{-7} mol L^{-1} to 1.0×10^{-5} mol L^{-1} were obtained between peak current and dye concentration for the peaks due to the reduction of both bis-azo and bis-monochlorotriazine group from the. The method allowed a limit of detections of 0.1 μmol L^{-1} for both dyes [80].

The electrochemical oxidation of Reactive Black 5 (RB5), a vinyl sulphone azo dye, has been also proposed by Radi et al. [81] at glassy carbon electrode (GCE) in phosphate buffer solutions in the pH range 2.85–11.79, employing cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Under alkaline conditions, these dyes react with the hydroxyl groups of cellulose, by nucleophilic substitution or forming a covalent bond. RB5 presents a well-defined oxidation peak at 0.614 V *vs* Ag|AgCl using DPV in phosphate buffer at pH 4.20 that can be used for this determination from 6.0×10^{-7} to 15×10^{-6} mol L^{-1} in phosphate buffer (0.2 mol L^{-1}, pH 4.20). The limit of detection and quantification were 4.0×10^{-7} and 1.1×10^{-6} mol L^{-1}, respectively.

Reactive Red 231 has been also determined by glassy carbon electrode by cyclic and differential pulse voltammetry on a glassy carbon electrode in phosphate buffer [82]. The dye oxidation shows two peaks, attributed to the following process shown in **Scheme 1**. Using anodic differential pulse voltammetry in pH 3.77, analytical curves were constructed from 0.25 mmol L^{-1} to 200 mmol L^{-1}. The method offers a reproducibility of RSD 4.7% and a detection limit of 0.20 mmol L^{-1}. The method has been applied to determine the dye in environmental water samples, with recoveries from 85 to 97%.

Turquoise blue 15 (AT15) is a reactive dye widely used in the textile industry to color natural fibers and has been determined in aqueous solution at mercury and glassy carbon electrode [83]. Using linear cathodic stripping voltammetry in acidic medium, the copper phthalocyanine is reduced in only one step, but it exhibits two reduction waves in an alkaline medium at glassy carbon electrode. The reduction of AT15 at mercury electrode (HMDE) is similar to the reduction at glassy carbon electrode, shown three cathodic peaks. These peaks can be attributed to ligand reduction. In addition, an extra peak could be observed at less negative potential, with preaccumulation, attributed to the reduction of the metal center. So, the results suggest a adsorption of the dye on mercury electrode stabilized by coordination bond metal/phthalocyamine ring first, and next the reduction of Cu(II) and pyrrole ring. Using the best experimental conditions, linear analytical curves were obtained for the first reduction step from voltammograms recorded at accumulation time of 180 s from 1.00×10^{-8} mol L^{-1} to 1.00×10^{-7} mol L^{-1}. The repeatability of the method shows a relative standard deviation from 1.36 to 2.05%. Detection limits were estimated from 8.34×10^{-9} to 1.50×10^{-7} mol L^{-1}, and the method was applied with success in tap water and in textile plant effluent sample [83].

The determination of Black 5 and Red E was determined by quartz crystal resonator sensor coated with mesoporous carbon cryogel [84]. The determination of the dyes is based on the vibrational motion of the plate in a resonant frequency, where the frequency is sensitive to mass loading on the electrode. Analytical curves were obtained from 25 to 100 ppm. The



Scheme 1. Oxidation mechanism of Reactive Red 231 on a glassy carbon electrode in phosphate buffer [82].

method is selective since the method is based on the size of each reactive dye and the micropores of the activated carbon resonator.

The analysis of vat dyes Indanthrene Olive Green B dye (VG3), which present an anthraquinonoid group and a ketonic group, has been also reported by differential pulse voltammetry in alkaline solution using glassy carbon electrode [3]. A typical linear scan voltammogram obtained for VG3 dye presents three reduction cathodic processes at −0.57, −0.67, and −0.99 V. A good linear correlation from 1.0×10^{-4} to 7.0×10^{-4} mol L^{-1} was obtained in sodium hydroxide 0.1 mol L^{-1} preaccumulated during 30 s at 0 V on glassy carbon electrode. The detection limit was 5×10^{-5} mol L^{-1}.

Santos et al. [85] has also reported the analysis of the disperse dye Disperse Red 13 (DR13) at glassy carbon electrodes (GCEs) modified with polyglutamic acid (PGA). This dye bears reductive nitro and azo group and presented a well-defined peak at −0.66V when reduced in a mixture of DMF/BR (pH 4, 1:1 v/v) and Bu_4NBF_4/DMF. At glassy carbon electrode modified with polyglutamic acid, the cathodic peak of DR13 shifts at least 200 mV to a less negative potential, and the peak intensity is 2.5 times higher compared to bare electrode. A linear calibration curve was obtained in DMF/BR buffer (pH 4) from 2.5×10^{-7} to 3.0×10^{-6} mol L^{-1}. The limit of detection was 1.5×10^{-8} mol L^{-1} and the repeatability presented an RSD of 4.29%. The method was applied in river water sample and dyebath wastewater.

The poly-L-lysine-modified glassy carbon electrode was also applied in determination of Cibacron Blue F3GA [17]. The dye presents an anthraquinone group as chromophore and amine group that is oxidized at 0.75 V. A linear calibration curve was obtained from 1.0×10^{-6} to 1.0×10^{-5} mol L^{-1} in BR buffer pH 2.0 after a preconcentration off-line by 10 min. The method reached a limit of detection of 4.5×10^{-8} mol L^{-1}, and it was applied in tap water and raw water sample.

The simultaneous determination of Orange G (Or G) and Orange II (Or II) in industrial wastewater has been proposed by using carbon paste electrode containing Fe_2O_3 nanomaterials/oxygen functionalized multiwalled carbon nanotubes/triton X-100 modified (Fe_2O_3/MWCNTs-COOH/OP/CPE) [86]. The optimized conditions for dyes analyses were 10 μL of MWCNTs-COOH/OP dispersion on the MWCNTs-COOH/CPE surface, accumulation time of 4 minutes, pH 7 of supporting electrolyte 0.1 mol L^{-1}. A liner calibration curve was observed by DPV method from 0.1–20.0 μmol L^{-1} to 0.2–50.0 μmol L^{-1} and detection limits of 0.05 and 0.1 μmol L^{-1} for Or G and Or II, respectively. The developed sensor was applied to the simultaneous detection of Or G and Or II in different industrial wastewater samples. The RSD was lower than 5%, the recoveries for Or G and Or II in these samples ranged from 96.8 to 105.1% and from 97.4 to 103.8%, respectively.

The determination of direct orange 8 dye in a flow stream was developed by using a wall-jet electrode system and square-wave stripping method [87]. The DO8 shows an electrochemically oxidizable phenolic group at −0.65V. After optimized experimental conditions, and using stripping voltammetric method, a linear calibration curve was obtained from 1.0×10^{-4} to 1.5 mg mL^{-1}. The method shows a reproducibility of 2.0 % and recovery of 98%.

Abrasive stripping voltammetry (AbrSV), based on a mechanical transfer of material onto the surface of a solid electrode and the subsequent voltammetric measurement of the electrochemical stripping process, has been proposed by Chen et al. [88]. They analyzed six different solid

compounds of widely different natures in room temperature ionic liquids (RTILs), among them the Prussian blue (PB) and indigo dye. In PB analysis, a reversible oxidation and reduction peak centered at around 0.6 V were observed. The authors indicates that the reduction and oxidation reactions originated from a surface redox species: $Fe_4^{III}[Fe^{II}(CN)_6]_3 + M^+ + e^- \rightarrow MFe^{II}Fe_3^{III}[Fe^{II}(CN)_6]_3$, where M^+ could be a cation, such as K^+, Li^+, or H^+. In addition, indigo electroanalysis shows a large reduction peak at −1.19 V, corresponding to indigo reduction: $H_2IN \rightarrow H_2IN_2^-$.

Hydrodynamic electrode system based on a vibrating probe (250 Hz, 200 lm lateral amplitude) has been applied to determine indigo in a complex plant of indigo sample, with high levels of organic and inorganic impurities after the reduction by glucose in aqueous 0.2 mol L^{-1} NaOH [89]. The soluble leucoindigo is determined by oxidation response at the vibrating electrode. In alkaline media, indigo is reduced in the presence of glucose to give leucoindigo that does not interfere in the electrode process. The best analytical signal was obtained using high scan rate, low vibration amplitude (250 Hz), and high temperature (75°C). The method was applied in 25 different samples of plant-derived indigo.

Finally, the determination of alizarin red S (AR), an anthraquinone dyes used in textile industry, has been proposed by flow-through potentiometric sensor [90]. The sensor is based in the use of a sensitive poly (vinyl chloride) membrane and the use of aliquate 336, Mg^{II}phthalocyanine (MgPc), Cu^{II}phthalocyanine (CuPc), and Fe^{II}phthalocyanine (FePc) plasticized poly (vinyl chloride) membrane. The sensor allowed detection limits of 5.9×10^{-7}, 1.9×10^{-6}, 2.3×10^{-6}, and 1.9×10^{-6} mol L^{-1} for aliquate, MgPc, CuPc, and FePc membrane-based sensor, respectively, and accuracy higher than 99.4%. The method shows a linear calibration curve from 0.1–1.8 to 1.0−40 μg mL^{-1} and a detection limit of 0.08 and 0.5 μg mL^{-1} for 10^{-4} and 10^{-3} mol L^{-1} AR as a carrier, respectively.

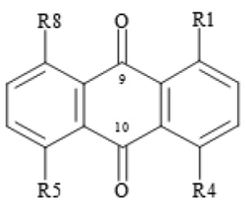
5. Electroanalysis of marker dyes

The marker dye are used mainly in the groundwater protection and in the prevention of tax frauds, such as identification of fuel with high sulfur concentration [91, 92]. These dyes are cataloged based on their characteristics and following a standard that depends on the type of dye and degree of coloring. An example of dyes commonly used as marker is the Solvent red 24 and Solvent blue 35, structures of which are shown in **Table 2**. The "Solvent red" and "Solvent orange" dyes usually bear azo group in their structure unlike the "solvent green" and "solvent blue" that bears anthraquinone groups. These dyes are used in fuel coloring due their higher solubility in organic solvents, nonpolar and slightly polar. They are commonly used as marker solvent in petroleum derivatives, such as waxes, lubricants, plastics, and other nonpolar materials. The marker dye usually has the chemical structure protected and only the manufacturer can detect it by specific methods. Neverthelees, some marker dyes are known in the literature and are commonly added to fuels with the purpose of control specific types of fuels, comprove the authentic, discourage robberies and adulterations, as well as control the distribution and use of some specifics fuels [93, 94]. In Brazil, the adulteration of fuel has been a common problem, and the marked dyes are applied to distinguish the hydrated ethanol from

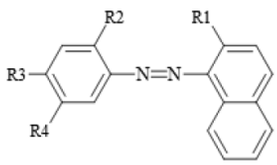
the dehydrated ethanol. In agreement with Brazilian laws, a solvent dye with orange coloration is prescribed to be added to dehydrated ethanol as a control. The aviation fuels are also marked as a guarantee to prevent fraud or other dilutions [95, 96].

In many countries, particularly those in the European Community, fuel distributors use marker dyes to diesel, "the red diesel," since it is significantly cheaper than heavier diesel fuels with a higher sulfur concentration that can promote damages to both the environment and the engine. In view of such problems, enforcement agencies have adopted the addition of marker dyes as a method of prevention as a way to curb the adulteration of these types of fuels. Among these dyes, red dyes, which are present in azo groups, such as Red Solvent 19, Red Solvent 24, and Red Solvent 26, are prominent. The aviation kerosene, as well as heating oils and so on, has also been marker with dyes, whose purpose is to prevent their mixing with poor-quality products. Nowadays, all the countries of the European Union are being obliged to adopt a marker dye; the most common is the "Solvent Yellow" 124. This dye can easily detect in adulterated fuels by dilution

Anthraquinone group



Azo group



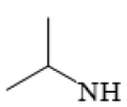
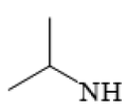
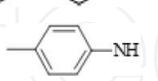
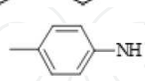
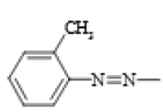
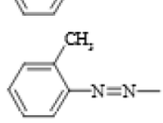
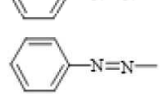
	Ring substituent					
Dye	**R_1**	**R_2**	**R_3**	**R_4**	**R_5**	**R_8**
Anthraquinone						
Solvent Blue 14		H	H		H	H
Solvent Blue 36		H	H		H	H
Solvent Blue 35		H	H		H	H
Solvent Green 3		H	H		H	H
Azo						
Solvent Red 24	OH	H		H	–	–
Solvent Red 26	OH	CH_3		CH_3	–	–
Solvent Red 164	OH	H		H	–	–
Solvent Yellow 14	OH	H	H	H	–	–

Table 2. Molecular structures of marker dyes.

with solvents or in poor-quality products at very low levels [97]. In the USA, the Environmental Protection Agency (EPA) designates the use of a red dye, the "Red Solvent 26," to identify and label high sulfur fuels [98]. In Brazil, in recent years, a fuel alcohol marking system has been adopted [99], whose purpose is to ensure its quality, as well as to free it from adulteration fraud by addition of water. The marker dyes, such as Quinizarine (QNZ), solvent blue 14 (S-14), Solvent Blue 14, Solvente Blue 35 (SB-35), Solvent Orange 7 (SO-7), and Red Solvent 24 (SR-24) can be legally added for the purpose of meeting the requirements of the ANP, or illegally, for circumventing inspection agencies.

Thus, analytical methods, able to determine these marker dyes and help the protection of quality of fuel, are highly demanded. Some electrochemical methods are proposed in the literature with this purpose and they are resumed below.

The determination of solvent blue 14 (SB−14), 1,4-bis(pentylamino)anthraquinone, in fuel samples has been studied by square-wave voltammetry (SWV) at glassy carbon electrode in a mixture of aqueous solution and N,N-dimethylformamide [100]. SB-14 dye presented a well-defined cathodic peak at around −0.41 V *vs* Ag|AgCl attributed to the reduction of the central quinone group in the dye molecule. The best conditions for SB-14 determination were obtained in a mixture DMF:BR buffer pH 2.0, using square-wave voltammetry operating at *f*: 60 Hz, ΔE_s: 6 mV and E_{sw}: 50 mV. Under optimized conditions, there is a linear response from 1.0×10^{-6} to 6.0×10^{-6} mol L^{-1} and a detection limit of 2.90×10^{-7} mol L^{-1}. The method was applied to dye SB-14 determination in kerosene, after cleanup with a self-packed SPE column (SiO_2) and alcohol samples with average recovery from 93.00 to 98.10%.

A similar method has been also developed for determining solvent Orange 7 (SO-7), an azo dye in fuel ethanol samples [4]. The optimal conditions adopted a mixture of N,N-dimethylformamide (DMF) and Britton–Robinson buffer pH 7.0 (1:1, v/v). In this medium, a well-defined anodic peak at +0.70 V *vs* Ag|AgCl was observed. Using optimized parameters based on the SWV technique, it was possible to construct a linear relationship from 4.0×10^{-6} to 18.0×10^{-6} mol L^{-1}. The proposed method was successfully applied to the direct quantification of the SO-7 dye in fuel ethanol samples, with recovery between 97.2 and 106%.

The screen-printed carbon electrode in Britton–Robinson buffer with N,N-dimethylformamide (7:3, v/v) in presence of 5.50×10^{-4}mol L^{-1} of dioctyl sulfosuccinate sodium (DSS) has been reported to analyze solvent blue 14 (SB-14), 1,4-bis(pentylamino)anthraquinone [101]. The SB-14 showed a cathodic peak at −0.40 V due to reduction of the central quinone group to hydroquinone derived after a two-electron process. Using the optimal conditions, $f = 60$Hz, $\Delta E_s = 4$mV and $E_{sw} = 50$mV, and pH 3.0, an improved interaction between the dye and the anionic surfactant by electrostatic interaction was obtained in a mixture of B–R buffer (pH 3.0)/DMF (7:3, v/v) + 1.40×10^{-3}mol L^{-1} DSS surfactant. A calibration curve was constructed from 2.00×10^{-7} to 2.00×10^{-6}mol L^{-1} with limit of detection and quantification of 9.30×10^{-8} and 3.0×10^{-7} mol L^{-1}, respectively. The developed method was applied for the quantification of SB-14 dye in alcohol samples without any pretreatment and in kerosene (after rapid cleanup procedure based in solid-phase extraction cartridge) with recoveries of 82.00–99.00%, respectively. The values are in good accordance with other reference methods based on spectrophotometric analysis.

The 1,10-dihydroxyanthraquinone, quinizarine (QNZ), has been determined by square-wave voltammetric technique in a mixture of Britton-Robinson buffer 0.08 mol L^{-1} with 30% of acetonitrile [102]. The QNZ was oxidized at glassy carbon electrode in and the well-defined peak at +0.45 V *vs* Ag|AgCl. This peak can be attributed to the oxidation of the phenolic hydroxyl group present in the dye marker to its quinone derivative after two electrons' transfer. An analytical curve was constructed for QNZ concentrations ranging from 2.0×10^{-6} to 1.4×10^{-5} mol L^{-1}. The method was successfully applied for determining QNZ in gasoline and diesel oil, the recoveries were 94.20 and 90.80%, respectively. For diesel oil sample, the QNZ was first extracted by liquid-liquid extraction using ACN: BR, 7:3 v/v and next was performed a solid-phase extraction cartridge of C18 adopting.

Quinizarine has been also determined by square-wave voltammetric technique using screen-printed carbon electrode (SPCE) in the presence of cetyltrimethylammonium bromide (CTAB) [103]. In the presence of 7.50×10^{-4} mol L^{-1} CTAB in a mixture of BR buffer (pH 7.0) and DMF (7:3, v/v), quinizarine (QNZ) shows a cathodic peak at −0.68 V, without CTAB the peak was observed at −0.78 V. The peak in the presence of CTAB was three times higher than the one obtained in its absence. These peaks are both attributed to the electron-transfer involving the reduction of central quinone group to form hydroquinone derived after a two-electron process. The electroanalytical method presented a linear response from 5.00×10^{-7} to 6.00×10^{-6} mol L^{-1} and a detection limit of 2.70×10^{-7} mol L^{-1}. The methodology was applied in the dye marker quantification in diesel oil and kerosene samples with recovery values ranging between 84.0 and 98.7%.

6. Conclusion

The voltammetric methods have shown to be a powerful tool for dye determination considering the great diversity of dye and different utilities. Different voltammetric techniques have been proposed, such as differential pulse, square-wave stripping, abrasive stripping hydrodynamic, polarography, chronoamperometry, and others. These techniques minimizing the effect of capacitive current (techniques of differential pulse voltammetry and square-wave voltammetry) and possibility of preconcentration of the analyte at the electrode surface promoted analysis applicable at lower detection levels. Furthermore, different electrodes have been proposed, such as dropping mercury electrode, glassy carbon, screen-printed electrode, Ti/TiO_2 nanotubular array electrodes, and others. The use of solid stationary electrodes improved the applicability of the method, since they can be easily modified and offer the possibility to increase the sensitivity and selectivity of the selected dye. The main modifiers found in literature are based on the use of metal nanoparticles, polyaminoacids, carbon nanotubes, graphene, molecularly imprinted polymers, and others that offers higher sensitivity and/or selectivity. So, the voltammetric methods allow the detection of dyes in different matrix in concentration level until 10^{-9} mol L^{-1}, similar to other instrumental techniques such as chromatography. The main advantages of voltammetric methods are that they are low cost, are environmental friendly and quick, and, in many cases, do not require long steps of cleanup sample.

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