



Advancement in electrochemical strategies for quantification of Brown HT and Carmoisine (Acid Red 14) From Azo Dyestuff class

Fatemeh Karimi^{a,*}, Ersin Demir^{b,**}, Nida Aydogdu^b, Moein Shojaei^c, Mohammad A. Taher^c, Padideh Naderi Asrami^d, Marzieh Alizadeh^e, Younes Ghasemi^e, Somaye Cheraghi^{c,***}

^a Department of Chemical Engineering, Quchan University of Technology, Quchan, Iran

^b Afyonkarahisar Health Sciences University, Faculty of Pharmacy, Department of Analytical Chemistry, 03030, Afyonkarahisar, Turkey

^c Department of Chemistry, Shahid Behonar University of Kerman, Iran

^d Massoud Clinical Laboratory, Tehran, Iran

^e Department of Pharmaceutical Biotechnology and Pharmaceutical Sciences Research Center, Faculty of Pharmacy, Shiraz University of Medical Sciences, Shiraz, Iran



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ABSTRACT

Brown HT and carmoisine, which are the most used dyestuffs in pharmaceuticals, textiles, cosmetics and foods, are important components of the Azo family. Although the Azo group is not toxic or carcinogenic under normal conditions, these dyestuffs require great care due to the reduction of the Azo functional group to amines. In particular, fast, reliable, easy, on-site and precise determinations of these substances are extremely necessary and important. In this review, the properties, applications, and electrochemical determinations of brown HT and carmoisine, which are used as synthetic food colorants, are discussed in detail. Up to now, sensor types, detection limits (LOD and LOQ), and analytical applications in the developed electrochemical strategies for both substances were compared. In addition, the validation parameters such as the variety of the sensors, sensitivity, selectivity and electrochemical technique in these studies were clarified one by one. While the electrochemical techniques recommended for brown HT were mostly used for the removal of dyestuff, for carmoisine they included fully quantitative centered studies. The percentiles of voltammetric techniques, which are the most widely used among these electroanalytical methods, were determined. The benefits of a robust electrochemical strategy for the determination of both food colors are summed up in this review. Finally, the brown HT and carmoisine suggestions for future perspectives in electrochemical strategy are given according to all their applications.

1. Introduction

Dyestuffs contain at least one chromophore in their structure and an important place in human life and date back many years, can be briefly defined as follows (Karaman et al., 2022; Ghalkhani et al., 2022; Karimi-Maleh et al., 2022a; Mehdmandoust et al., 2021; Tajik et al., 2021a). They are organic-based substances that can absorb part or all of the wavelengths of light in the visible spectrum (400–700 nm) (Ghalkhani et al., 2022) (see Fig. 1). The first of the dyestuffs are natural resources obtained from plants and insects (Alsantali et al., 2021; Sequin-Frey, 1981). These dyes were preferred until the middle of the nineteenth century (Alsantali et al., 2021; Orna, 1980; Khan et al., 2022; Shen et al.,

2022). There has been a trend towards the use of synthetic dyestuffs due to production cost, increasing demand, and natural resource problems. Moreover, synthetic dyes have been the focus of attention of industrialists because they are cheaper, more stable to light and temperature (Ghalkhani et al., 2022; Alizadeh et al., 2022). Mauveine, known as the first synthetic dyestuff, was produced by Chemist William Henry Perkin in 1856 (Alsantali et al., 2021). However, after the natural dyes lost their appeal after the 1950s, synthetic dyes took place very quickly, especially in the industrial (Alsantali et al., 2021; Gurr, 2012). Moreover, synthetic dyes are widely used in many different industries such as pharmaceuticals, cosmetics, detergents, textiles, leather, and plastic nowadays. Apart from this, they are also preferred to increase the

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: fkm024@gmail.com (F. Karimi), dr.ersindemir@yahoo.com (E. Demir), somayecheraghi64@gmail.com (S. Cheraghi).

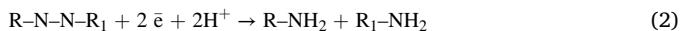
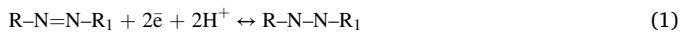


Fig. 1. Classification of Azo dyes.

organoleptic properties of foodstuffs (Chebotarev et al., 2020).

The most important family of synthetic dyes, azo dyes, was first obtained by Griess in 1865 (Alsantali et al., 2021; Griess, 1865). The general chemical skeleton of azo dyes, which are highly soluble in water, consists of aromatic groups and azo chromophore. The active functional group of this dye is that it contains a double bond between two nitrogen atoms (-N=N-). They are classified as monoazo, diazo, or poly azo dyes according to the number of azo functional groups they have (Alsantali et al., 2021; El Harfi and El Harfi, 2017). Among these, monoazo dyes make up the majority of commercial dyes (Alsantali et al., 2021). Azo dyes are present in half of all dyestuffs that can be commercialized (Alsantali et al., 2021). In other words, azo dyes, the largest family of synthetic dyes, are organic substances with the highest production and consumption worldwide (Berradi et al., 2019; Shah, 2014; Shi et al., 2021).

Due to its unique physical and chemical properties, azo dyes are widely used in the pharmaceutical, cosmetic, and leather industries, especially in the textile field (Alsantali et al., 2021). Over and above, they are not only used for industrial purposes, but also play an active role in drug carriers, biomedical applications, and coloring foodstuffs (Alsantali et al., 2021). Although azo dyes have biological effects such as antibacterial, antiviral, and cytotoxic, the chromophore azo groups in their structure are converted into highly toxic aromatic amines (Alsantali et al., 2021). Therefore, azo dyes and their metabolites hurt human health. Moreover, these substances should not be consumed excessively in terms of food safety and human health (Lipskikh et al., 2018; Mahale et al., 2021; Manjunatha, 2018; Arancibia Moya et al., 2017; Pliuta et al., 2021; Raril et al., 2018; Shah, 2020; Tvorynska et al., 2019). Adverse effects of some azo colors are known, including asthma and contact hypersensitivity. It can cause food bigotry, hypersensitivity, and hyperactivity among the young generation (Lipskikh et al., 2018; Mahale et al., 2021; Manjunatha, 2018; Arancibia Moya et al., 2017; Pliuta et al., 2021; Raril et al., 2018; Shah, 2020; Tvorynska et al., 2019). Therefore, the serious danger to the environment and human health, the use of some azo dyes is prohibited by the European Union Regulation (EC) 1907/2006 (Vineis and Pirastu, 1997). Finally, the determination of such important substances is of great importance and must be controlled by reliable analytical methods (Lipskikh et al., 2017).

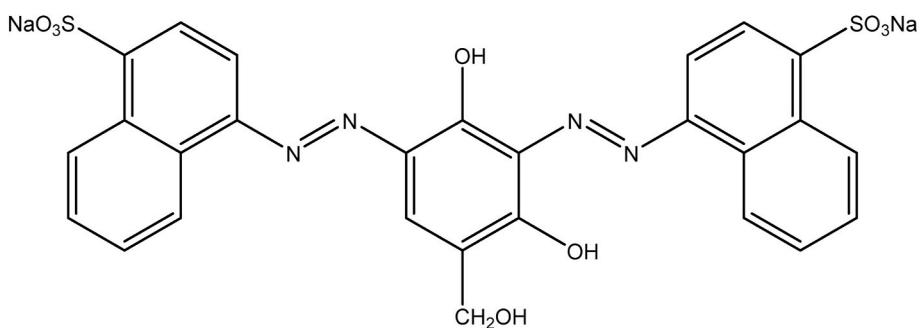
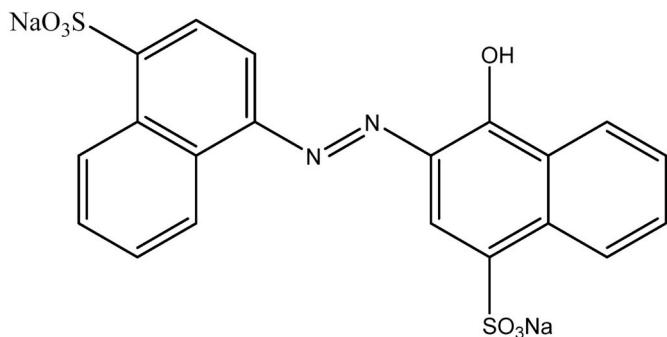


In this review, recent developments in the electrochemical determination of brown HT and carmasonine substances ([Scheme 1](#) and [2](#)), which are important members of azo dyes, are summarized. For this purpose, parameters such as the electrochemical methods used for both substances, the type of working electrodes, the working environment, and the applied samples were examined in detail. In addition, the developed electroanalytical methods were compared and their importance was examined. Also, validation parameters such as detection limits and working range in the proposed methods for brown HT and carmoisine were criticized. In addition, in this review, regression data were compared with classical analytical methods available in the literature for both substance determinations. In the upshot, recommendations on time, cost, and detection limits for electrochemical strategies in brown HT and carmoisine determinations were suggested.

2. Brown HT dye: Properties and applications

Brown HT dyestuff, whose IUPAC name is disodium 4,40-(2,4-dihydroxy-5-hydroxymethyl-1,3-phenylene bis-azo) di-(naphthalene-1-sulfonate), is mentioned such as “food brown 3”, “chocolate brown HT”, “E 155” and CI 20285 names in the literature (Hong et al., 2014; Moanta, 2009; Shokrollahi and Ahmadi, 2017). Brown HT, whose molecular formula is $\text{C}_{27}\text{H}_{18}\text{N}_4\text{Na}_2\text{O}_9\text{S}_2$, is a synthetic substance from the azo dye family and consists of brown powder (Leulescu et al., 2019). Brown HT is a crystalline substance with a triclinic structure (space group P1) between 1 and 50 μm as a powder at room temperature. In addition, brown HT is known to show antioxidant activity and is a very stable dyestuff against light and heat (Shokrollahi and Ahmadi, 2017; Nollet and Toldrá, 2012). It is generally used as a dye additive in foodstuffs such as flour and confectionery, cakes, canned meat, puddings, ice cream, sauces, and soft drinks (Grant and Gaunt, 1987; Hendy et al., 1978; Mangham et al., 1987; Phillips et al., 1987; Soylak et al., 2021) (Grant and Gaunt, 1987; Hendy et al., 1978; Mangham et al., 1987; Phillips et al., 1987; “Scientific Opinion on the re-evaluation of Brown HT (E 155) as a food additive,” 2010; Shokrollahi and Ahmadi, 2017; Soylak et al., 2021). Additionally, brown HT is authorized for use as a Food Coloring Agent in the UK (Leulescu et al., 2019) (Leulescu et al., 2019; “Refined exposure assessment of Brown HT (E 155),” 2014). An acceptable daily intake (ADI) dosage of brown HT is 0–1.5 mg per kg of body weight per day (Bellés, 2019; European Parliament and the Council of the European Union, 2008; “Scientific Opinion on the re-evaluation of Brown HT (E 155) as a food additive,” 2010). However, due to the reduction of azo dyes to toxic aromatic amines metabolites, such substances should be used and controlled carefully. High concentrations of brown HT exhibited toxic effects, including low levels of norepinephrine, dopamine, and gamma-aminobutyric acid (Shokrollahi and Ahmadi, 2017; Bawazir, 2012).

Until now, studies on Brown HT determination are few in the literature. It is very surprising that few studies have been done for the quantification of such an important dyestuff. Considering the studies, cloud point extraction-scanometry (CPE-scanometry) (Shokrollahi and Ahmadi, 2017), UV-Vis spectrophotometer (Soylak et al., 2021) and high-performance liquid chromatography/diode array detection (HPLC/DAD) (Hong et al., 2014) methods have been applied for the analysis of Brown HT. Although these methods provide high accuracy determination in routine analysis, they have some shortcomings such as long pre-processing, expensive instrument equipment, long analysis time, and expertise requirement. Therefore, scientists have turned to alternative methods for the analysis of dyestuffs. In this case, it would be a major source of neglect for Brown HT because of the many advantages of electrochemical methods. Moreover, electrochemical methods attract great attention in the last quarter due to their fast, cheap, simple, portable, selective, accurate, and reliable for the analysis of dyestuffs

**Scheme 1.** Chemical structure of Brown HT dyestuff.**Scheme 2.** Chemical structure of carmoisine dyestuff.

(Alizadeh et al., 2022).

2.1. Electrochemical strategies of Brown HT

Electrochemical methods are high performance strategy for analysis of electroactive materials (Karimi-Maleh et al., 2022b, 2022c; Khand et al., 2021; Hussain et al., 2022; Montazarolmahi et al., 2020; Sadeghi et al., 2020; Prasad and Sreedhar, 2018). Many of researchers focused to application of electrochemical sensors to monitoring of pharmaceutical and food additive in real samples (Karimi-Maleh et al., 2020, 2021; Mohanraj et al., 2020; Babu et al., 2021; Saghiri et al., 1999; Alidakhoh et al., 2021; Plotnikova et al., 2022; Fu et al., 2021). Studies on the electrochemical behavior, kinetic model, and analysis in natural samples of brown HT substance, which is one of the azo dyestuffs, are quite limited. The first study was carried out by Fogg and Yoo in 1979 and the direct differential pulse polarography (DPP) method was used (Fogg and Yoo, 1979a). In another study, the cyclic voltammetry (CV) method was preferred to define the Brown HT peaks (Tutunaru et al., 2019). The main purpose here is to study the removal of Brown HT by an electrochemical process. In the other study, removal of Brown HT substance was performed using electro-oxidation (EO), electro-Fenton (EF), and photoelectron-Fenton (PEF) methods (Pacheco- Álvarez et al., 2019). In the last study using the electrochemical method, Brown HT removal

process was performed using boron doped diamond electrode (BDDE) (Corona-Bautista et al., 2021) (see Table 1, Schemes 1 and 2).

As a result, no comprehensive study has been found for the full investigation of Brown HT electrochemical behavior, the elucidation of the electrode mechanism, and its quantitative determination in natural samples. Among the studies carried out, there is mostly electrochemical removal (electrochemical decomposition), which is a new application of the electrochemical strategy. Academicians have a great responsibility for the on-site, fast, reliable, and sensitive determination of Brown HT, which is important for human health and environmental pollution and is widely used in the industry.

3. Carmoisine dye: Properties and applications

Synonyms of carmoisine dyestuff, whose IUPAC name is disodium 4-hydroxy-3-[(4-sulfo-1-naphthalenyl)azo]-1-naphthalenesulfonate, are azorubine, E122, and Food Red 3. The chemical structure of carmoisine consists of azo, sulfo and hydroxyl functional groups and aromatic ring structures (Ai-Mashhedy and Fijer, 2016; Amin et al., 2010; Soylak et al., 2011). Carmoisine is a red colored synthetic azo group obtained from coal tar (Lipskikh et al., 2017). Due to its high stability feature, it does not deteriorate when exposed to oxygen and light and is highly soluble in water (Tajik et al., 2022). It is used as an additive, which provides red color to increase interest and make products such as food, beverage, medicine, and cosmetics more attractive (Lipskikh et al., 2017; Karatepe et al., 2017). The acceptable daily intake (ADI) dosage of carmoisine allowed by the World Health Organization and the United Nations Food and Agriculture Organizations has been determined as 4 mg/kg ("Scientific Opinion on the re-evaluation of Azorubine/Carmoisine (E 122) as a food additive," 2009). In addition, this amount is legal as 50 µg/kg in soft drinks and 500 µg/kg in sauces and spices in Russia (SanPiN 2.3.2.1293-03: Hygienic Requirements for Application of Food Supplements, 2003). Aromatic amines, which are metabolites of the functional groups contained in carmoisine, are potentially toxic substances (Micheletti et al., 2020). The main side effects of carmoisine are allergic reactions, hematuria, anemia, hyperactivity, reticulocytosis, oxidative stress, kidney, and liver diseases (Chebotarev et al., 2020; Lipskikh et al., 2017; Karatepe et al., 2017; Arvin et al., 2013). Moreover, if carmoisine is consumed in high concentrations, its mutagenic, toxic, and carcinogenic

Table 1
Reported CV techniques for determination of Brown HT.

Analyte	Method	Electrode	Linear range (µM)	LOD (µM)	LOQ (µM)	Sample	Medium	Ep (V)	Interference	Ref
Chocolate Brown HT	DPP	SCE	0–45.5	–	–	Orange, lime, blackcurrant drinks	pH 4.0	–0.18	–	Fogg and Yoo (1979b)
Chocolate Brown HT	CV	PtE	–	–	–	–	–	–	NaF, NaCl, NaBr, NaI	Tutunaru et al. (2019)
Chocolate Brown HT	EF, PEF, EO	BDDE	–	–	–	–	pH 3.0	–	–	Pacheco- Álvarez et al. (2019)
Brown HT	EF, PEF, EO, O ₃	BDDE	–	–	–	–	pH 3.0	–	–	Corona-Bautista et al. (2021)

effects can be met in individuals (Micheletti et al., 2020; Salama et al., 2016). Since it dissolves easily in water, carmoisine is included as an organic pollutant in terms of environmental contamination. Hereby, careful use and control of such substances is of great importance for human health.

Quantitative analyzes of carmoisine have been performed by various methods such as chromatography (Aksu D ö nmez et al., 2020; Yang et al., 2014; Zahedi et al., 2020), spectrophotometry (Lipskikh et al., 2017; Amraei et al., 2019), and capillary electrophoresis (Del Giovine and Bocca, 2003). However, these methods often have deficits such as difficult complex processing, long analysis time, needing an expert operator, and not being environmentally friendly because too many organic solvents are used. In contrast, the cost, speed, and ease of analytical methods are becoming more and more dominant for the assessment of substances in natural samples. Electrochemical methods have been preferred to identify a large number of substances including azo dyes due to their easy applicability, low cost, high sensitivity, and superior selectivity (Alizadeh et al., 2022; Arefi-Oskouei et al., 2022).

3.1. Electrochemical strategies of Carmoisine

In contrast to Brown HT, many studies have been conducted on the electrochemical behavior of carmoisine and its analysis in natural samples. According to the electrochemical strategies suggested in the carmoisine determination, it is reduced at about -0.2 V and oxidized at approximately $+0.8$ V depending on the pH of the medium and the indicator electrode type. Therefore, the carmoisine exhibited a well-defined, smooth and sharp peak not only in anodic studies but also in cathodic studies. Illumination studies of the carmoisine electrode mechanism have been carried out and reduction reaction has been proposed by two via. The first of these is the saturation of the azo ($-N=N-$) group with hydronium ions (Fig. 1). The second way is the decomposition (separation) reaction over the azo group (Fig. 2) (Sarvestani and Doroudi, 2022). For the oxidation reaction, the $-OH$ group in carmoisine is converted to oxygen radicals (Fig. 3) (Sarvestani and Doroudi, 2022).

Due to the superior properties of electrochemical methods, it has attracted great attention not only by scientists but also in industrial research and development (R&D) studies in recent years. Besides the use of electrochemical techniques as an analyzer, it can also be applied to the removal of dyestuffs. The differential pulse voltammetry (DPV) (41%) and square wave voltammetry (SWV) (29%) have been extensively used in the electrochemical studies carried out so far for carmoisine, an important red colorant. In addition, differential pulse polarography (DPP) (12%), linear sweep voltammetry (LSV) (12%) and cyclic voltammetry (CV) (6%) electrochemical techniques were applied

to determine carmoisine, respectively. When looking at the materials used as sensors, carbonaceous working electrodes such as graphite (GPE), carbon paste (CPE), multi-walled carbon nanotube (MWCNT), and glassy carbon electrode (GCE) were preferred to identify carmoisine dyestuff. In cathodic studies, mercury electrode, known as polarography and forming the basis of voltammetry, has been mostly preferred. Moreover, composite sensors have been built with materials such as molecular imprinted polymer (MIP), chitosan, metal oxide-nanoparticles (MO-NPs), carbon nanotubes (CNTs) and multi-walled carbon nanotubes (MWCNTs).

Differential pulse voltammetry (DPV), which is one of the most sensitive techniques among voltammetric methods, and its stripping technique (DPSV), is the most preferred electrochemical method for the determination of carmoisine (see Table 2). Both anodic and cathodic studies were carried out on different working electrodes with DPV and DPSV. In these studies, DPV strategies generally discussed the development of modified electrodes for the analysis of carmoisine in the food samples. In line with this goal, modified electrodes have been constructed by using some materials such as glassy carbon electrode (GCE), hanging mercury drop electrode (HMDE), and carbon paste electrodes (CPE), treating with multi-walled carbon nanotube (MWCNT), bismuth film, chitosan, and Mo_3/WO_3 nanocomposite. According to the electrochemical strategies for the assignment of carmoisine, the lowest detection limit (LOD) is 0.1 nM. In addition, the LOD value of other DPV studies is approximately μM and lower. This shows that the DPV technique can compete with other classical analytical methods to detect carmoisine.

Square wave voltammetry (SWV) is an important component of electrochemical method because it provides sensitive, accurate and reliable results in a few seconds (Acer et al., 2020; Demir, 2019; Demir et al., 2018). The SWV and its stripping technique (SWSV) have been the most widely used after DPV in the determination of carmoisine. In these studies, carbon paste electrode (CPE) and boron doped diamond electrode (BDDE) were applied as main working electrode. The anodic peak of carmoisine on cathodically pretreated (CPT)-BDDE was found $+0.86$ V, while its cathodic signal was obtained at -0.11 V. Also, the cathodic peak of carmoisine is more sensitive than the anodic peak and according to the limit of detection (LOD) value in this study. The other main electrode, CPE, modified with metal oxide nanoparticles (MO-NPs), carbon nanotubes (CNTs) and silica impregnated with cetylpyridinium chloride (SG/CPCI), was applied in the carmoisine determination. Considering all studies with SWS, the most sensitive voltammetric technique was developed using CPT/BDDE. According to these SWS strategies, the limit of detection (LOD) value of carmoisine is at the level of 2 nM. In other SWS studies, the LOD value is calculated between 7 nM

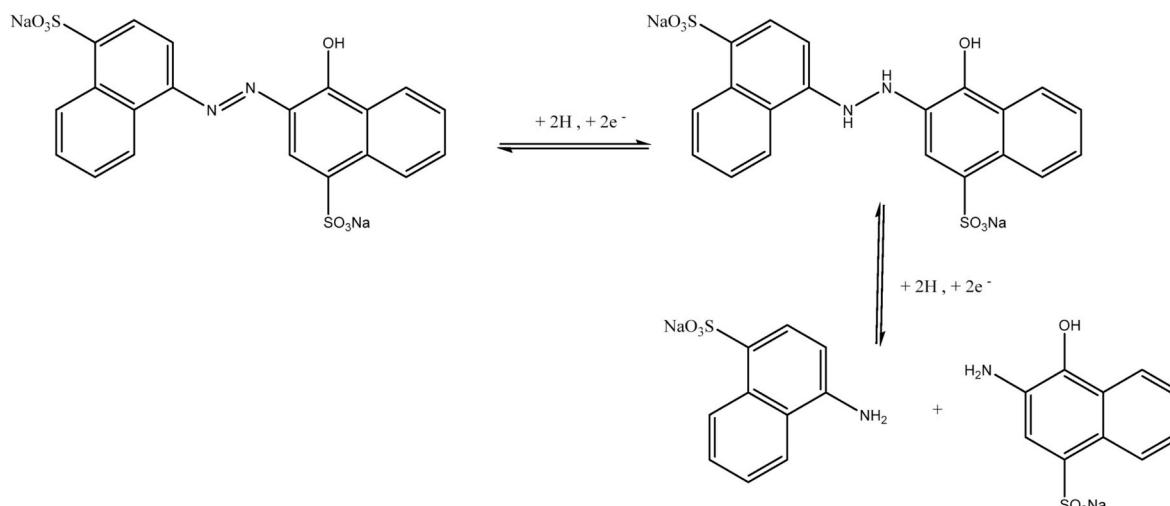
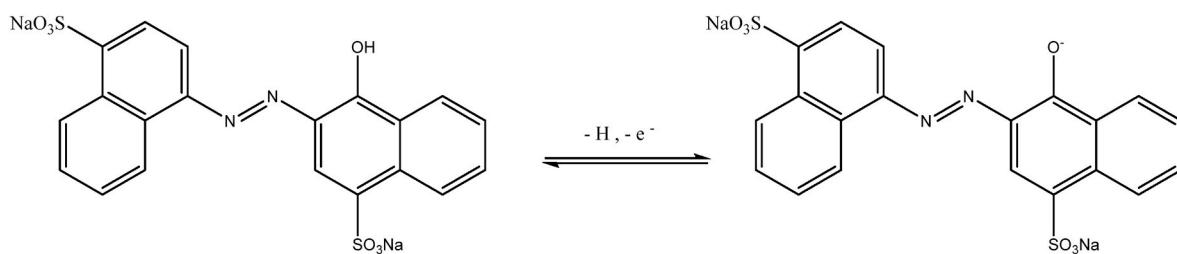


Fig. 2. The proposed mechanism for the electro-reduction of CMS (Sarvestani and Doroudi, 2022).

**Fig. 3.** The proposed mechanism for the electro-oxidation of CMS (Sarvestani and Doroudi, 2022).**Table 2**
Reported DPV techniques for determination of CMS.

Analyte	Method	Electrode	Linear range (μM)	LOD (μM)	LOQ (μM)	Sample	Medium	Ep (V)	Interference	Ref
CMS	DP-AdSV	MWCNT/GCE	0.55–70	0.12	–	Various soft drinks	pH 7	0.60	–	Sierra-Rosales et al. (2017)
CMS	DP-AdSV	GCE	0.099–0.99	0.039	–	Various soft drinks	pH 1.65	–0.15	–	Lipskikh et al. (2017)
CMS	DPV	MoO ₃ /WO ₃ /IL-CPE	0.5–100	0.15	–	Lemon juice Powdered juice	pH 7	0.80	Li ⁺ , F ⁻ , Br ⁻ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , K ⁺ , Cl ⁻ , Zn ²⁺ , NO ₃ ⁻ , SO ₄ ²⁻ , Ca ²⁺ , Mn ²⁺ , Fe ²⁺ , glucose, citric acid, thiamine, tryptophan, pantothenic acid, brilliant blue, indigo carmine	Tajik et al. (2022)
CMS	DPV	CPT-BDDE	0.0079–0.01	0.003	0.010	Candy	pH 2	–0.04	Indigo carmine, brilliant blue, tartrazine	Micheletti et al. (2020)
CMS	DPV	CPT/BDDE	0.058–1.3	0.007	0.021	Candy	pH 2	0.82	Indigo carmine, brilliant blue, tartrazine	Micheletti et al. (2020)
CMS	DPV	Bismuth film/GCE	0–120	5.9	17.9	Cherry flavor beverage	–	–0.45	–	Claux and Vittori (2007)
CMS	DPV	Bi-CHIT/GCE	1.0–41	1.0	–	Chocolate orange, Chocolate sour cherry	pH 7	–0.60	–	Asadpour-Zeynali and Mollarasouli (2014)

Table 3
Reported SWV techniques for determination of CMS.

Analyte	Method	Electrode	Linear range (μM)	LOD (μM)	LOQ (μM)	Sample	Medium	Ep (V)	Interference	Ref
CMS	SW-AdSV	SG/CPCI/CPE	0.08–1.0	0.01	0.02	Various soft drinks	pH 2	0.95	Na ⁺ , K ⁺ , CO ₂ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HPO ₄ ²⁻ , sucrose, glucose, ascorbic acid, fructose, sodium benzoate	Chebotarev et al. (2020)
CMS	SWV	CPT/BDDE	0.01–0.157	0.002	0.006	Candy	pH 2	–0.11	Indigo carmine, brilliant blue, tartrazine	Micheletti et al. (2020)
CMS	SWV	CPT/BDDE	0.2–1.6	0.007	0.020	Candy	pH 2	0.86	Indigo carmine, brilliant blue, tartrazine	Micheletti et al. (2020)
CMS	SWV	CdO/CNTs/1-E-3-MITFBr/CPE	0.1–700	0.04	–	Orange juice, lemon juice	pH 7	0.68	Li ⁺ , F ⁻ , Br ⁻ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , K ⁺ , Cl ⁻ , starch, glucose, tryptophan, isolucin, thiamine, pantothenic acid	Nezhad et al. (2018)
CMS	SWV	NiO/CNTs/1-M-3BIBr/CPE	70–650	0.02	–	Lemon juice, fruit juice	pH 7	0.70	Li ⁺ , Br ⁻ , Ca ²⁺ , NO ₃ ⁻ , K ⁺ , Na ⁺ , Cl ⁻ , starch, glucose, sucrose, alanine, isolucin, ascorbic acid	Bijad et al. (2018)

Table 4
Less used electrochemical techniques (CV, DPP and LSV) for determination of CMS.

Analyte	Method	Electrode	Linear range (μM)	LOD (μM)	LOQ (μM)	Sample	Medium	Ep (V)	Interference	Ref
CMS	CV	MIP (1-polynaphthylamine)/Dispersed MnO ₂ nanorods graphite nanopowders	1.9–24	1.1	3.82	Well water sample	pH 1	–0.20	Rhodamine B6	Piri et al. (2018)
CMS	DPP	TPPC/DME	–	–	–	Lipstick	pH 9.2	–	–	Barros (1987)
CMS	DPP	–	0.04–80	0.083	–	Soft drinks and sweets	pH 9	–0.47	–	Chanlon et al. (2005)
CMS	LS-AdSV	HMDE	0.0125–0.25	0.061	–	–	–	–0.48	–	Castrillejo et al. (1990)
CMS	LSV	GCE	3.9–190	–	–	–	pH 2	0.84	–	Fogg and Bhanot (1980)

and 40 nM. Exhibiting excellent detection capability, the SWV technique is able to compete with other available conventional analytical methods. Likewise, carmoisine was procured quickly, precisely, reliably, and without preprocessing in real examples like candy, some juices, and various soft drinks. They have satisfactorily analyzed carmoisine in the presence of both some organics and various ions with high recovery and low relative error. Consequently, the determination of carmoisine by SWV strategies with high reliability, high sensitivity, high accuracy, and very fast speed, even in natural samples or in complex martial environments has been performed amazingly (Table 3).

Rarely used electrochemical techniques for the electrochemical determination of carmoisine, an important member of the azo dye family, are: differential pulse polarography (DPP) (12%), linear sweep voltammetry (LSV) (12%) and cyclic voltammetry (CV) (6%) (see Fig. 4). The CV method provides major information in the study of qualitative properties such as the electrochemical behavior of the substance, the kinetic model and the elucidation of the mechanism. It is also possible to use it in quantitative analysis, but its sensitivity is very poor compared to other voltammetric methods. Considering the LOD value of the CV technique used for the determination of carmoisine, it is around 1.1 μ M. This value is approximately 100 times lower than the LOD value in DPV and SWV techniques recommended for the analysis of carmoisine. The same situation is observed in differential pulse polarography (DPP). However, the LOD value obtained in linear sweep adsorptive stripping voltammetry (LS-AdSV) using a hanging mercury drop electrode (HMDE) is almost close to both DPV and SWV techniques. Considering all these conditions, DPP, LSV, and CV voltammetric techniques have shown superior successful, even they were used sparingly for the determination of carmoisine in samples such as cosmetics, beverages, and water (see Table 4).

4. Advancement of nanomaterial sensors

In respect of nanomaterials with unique properties and wide range application (Badmus et al., 2021; Zhang et al., 2020; Karimi-Maleh et al., 2022d; Miao et al., 2020; Yorseng et al., 2020; Ashok et al., 2020; Atarod et al., 2021; Lu et al., 2021; Dehhaghi et al., 2021), bare SCE, PtE, and BDDE electrodes have been used for brown HT in electrochemical investigations so far (Tutunaru et al., 2019; Pacheco-Álvarez et al., 2019; Fogg and Yoo, 1979b). These studies are mostly electrochemical dyestuff removal studies. But for carmoisine, the situation is just the opposite like direct quantitative analyzes in natural samples. The determination of carmoisine by using voltammetric methods such as The DPV and SWV and polarography is predominant. Various nanomaterials have been used for electrochemical analysis of carmoisine dyestuff

(Lipskikh et al., 2017; Bijad et al., 2018; Piri et al., 2018; Chanlon et al., 2005; Castrillejo et al., 1990; Fogg and Bhanot, 1980). Among them, are most preferred carbonaceous nanomaterials. Carbon nanomaterials such as graphite (GPE), carbon paste (CPE), multi-walled carbon nanotube (MWCNT), and glassy carbon electrode (GCE) have been most used in the determination of carmoisine due to their unique properties such as excellent conductivity, stability, and high surface area. In addition, composite nanosensors have been developed to increase sensor efficiency. Many materials have been used for this, such as polymers, nanoparticles, and carbon nanotubes. With these composite electrodes, both more sensitive detection limits were reached and better catalytic performance was demonstrated. This new generation of nanosensors has enabled the determination of dyestuffs at nanomolar (nM) levels (Nasehi et al., 2022; Arabali et al., 2020; Keyvanfar et al., 2014; Tajik et al., 2021b). In addition, BDDE and mercury (HMDE) indicator electrodes have taken their place in the literature as nanosensors in the determination of carmoisine. As a result, sensors for brown HT and carmoisine determinations will be made in the coming years due to environmentally friendly and portable analysis possibilities. However, it should focus more on the production of new materials for the determination of such dyes in natural samples.

5. Perceptive of electrochemical strategies and future outlooks for Brown HT and carmoisine

Electrochemical strategies enable not only the determination of dyestuffs but also the analysis of numerous organic or inorganic substances, from drugs to many heavy metals (Demir et al., 2021; Isildak et al., 2018; Lu et al., 2018; Miraki et al., 2019; Karimi-Maleh et al., 2016, 2019; Taherkhani et al., 2014). In addition, these methods have numerous advantages such as precise measurements, low cost, ease, and cost (Alavi-Tabari et al., 2018; Eren et al., 2015). Electrochemical strategies provide important information about not only electron transfer processes from the reactions of dyestuffs such as brown HT and carmoisine, but also important chemical processes such as adsorption, chemical chemistry, and catalysis. In addition, it will be able to provide on-site and online analysis with the miniaturized sensors to be developed in the future (Gupta et al., 2015; Baghizadeh et al., 2015). Moreover, with the commercialization of these sensors, it will be possible to obtain simple, easy, reliable, and sensitive results about the analytes in a very short time (Jamali et al., 2014). Thus, it will take its place among the routine analyzes of electrochemical dyes such as brown HT and carmoisine, which is a very environmentally friendly analytical method in terms of green chemistry. In particular, both qualitative and quantitative analyzes of banned food dyestuffs, even at trace levels, will be performed in seconds with the nanosensors to be produced.

These methods, which have come a long way in the determination of numerous substances in recent years, have not yet reached the desired level. In front of this, although the electrochemical methods have many superior features, some aspects need to be developed (John et al., 2021; Asrami et al., 2017; Shamsadin-Azad et al., 2019; Akhgar et al., 2012). In particular, multiple analysis systems are the most important deficiency that needs to be developed for the analysis of multi-analyte systems (Baghayeri et al., 2014; Ensafi et al., 2010; Karimi-Maleh et al., 2012; Alizadeh et al., 2020). Although multi-channel electrochemical measurement systems have been developed for this, they are not at the desired level. Therefore, there is a need to develop more selective, sensitive, and sensitive sensors for the simultaneous determination of dyestuffs. Moreover, although intra-day and inter-day electrochemical measurements are reproducible, the shelf life of the electrodes is an area open to improvement.

6. Conclusion

Brown HT and carmoisine are important members of the azo dyestuff class. These dyestuffs are agents that directly act on human health and

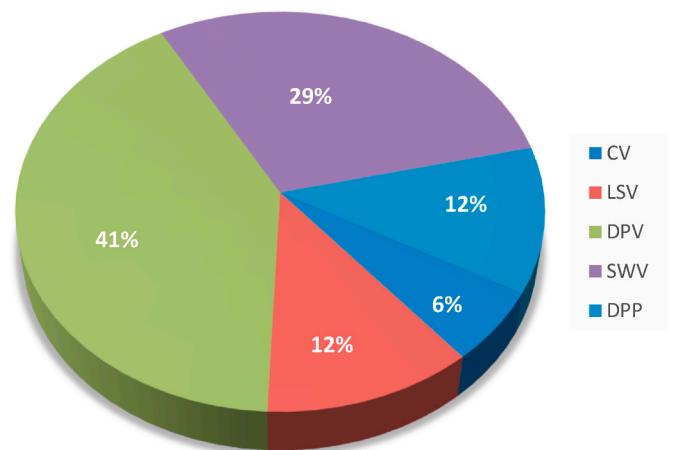


Fig. 4. Percentiles of current electrochemical methods for determination of carmoisine.

food safety at an extremely high level. Although these substances do not have a direct carcinogenic effect, they have permanent effects on human health by reducing the azo group to amines. There is a need for a fast, accurate, and reliable analytical method for the determination of such important dyestuffs in textiles, foods, pharmaceuticals, and cosmetic samples. Electrochemical methods, which are easy, portable, inexpensive, and sensitive, are the ideal candidates for the search for new methods. For this reason, these methods have been extensively preferred in the examination, determination, and application of numerous substances in recent years. Until now, voltammetric modules have been extensively used for Brown HT and Carmoisine diagnostics. Among these electroanalytical strategies in carmoisine determination, differential pulse voltammetry (DPV), square wave voltammetry (SWV), differential pulse polarography (DPP), linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were 41%, 29%, 12%, 12%, and 6%, respectively. Electrochemical methods used for the Brown HT were mostly preferred for removal studies, but only one study was performed for determination. In these studies, a glassy carbon electrode (GCE) was used in addition to the mercury electrode (HMDE or DME) in cathodic studies, while carbon-based sensors were preferred in anodic studies. Moreover, a more sensitive and selective sensor was constructed by treating the surfaces of bare electrodes with polymers, metal oxide nanoparticles (MO NPs), ionic liquid (IL), and carbon nanotubes (CNTs and MWCNTs). These two azo dyes, which are indispensable dyestuffs in foods, provide the detection limits (LOD) at the nanomolar (nM) level with the developed nanosensors and the proposed electrochemical strategy. In addition, the brown HT and carmoisine were determined with high recovery selectively on composite nanosensors in the presence of some anions, cations, and various organic substances by the proposed electrochemical strategy. These methods, which are green chemists, have played an important role in the *in situ*, sensitive, inexpensive and selective analysis of these dyestuffs. As a result, electrochemical techniques enable to compete with traditional analytical methods for the analysis of widely used agencies such as brown HT and carmoisine selectively, sensitively, and accurately.

CRediT authorship contribution statement

Fatemeh Karimi: Writing – original draft, preparation and revise of paper. **Ersin Demir:** Writing – original draft, preparation and revise of paper. **Nida Aydogdu:** Writing – original draft, preparation and revise of paper. **Moein Shojaei:** Writing – original draft, preparation and revise of paper. **Mohammad A. Taher:** Writing – original draft, preparation and revise of paper. **Padideh Naderi Asrami:** Writing – original draft, preparation and revise of paper. **Marzieh Alizadeh:** Writing – original draft, preparation and revise of paper. **Younes Ghasemi:** Writing – original draft, preparation and revise of paper. **Somaye Cheraghi:** Writing – original draft, preparation and revise of paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

1-E-3-MITFB	1-ethyl-3-methylimidazolium tetrafluoroborate
1-M-3BIBr/NiO/CNTs	1-methyl-3-butylimidazolium bromide
ADI	Acceptable daily intake
Bi	Bismuth
CHIT	Chitosan
CMS	Carmoisine
CNTs	Carbon nanotubes
CPCl	Cetylpyridinium chloride
CPE	Carbon paste electrode

CPE-scanometry	Cloud point extraction-scanometry
CPT-BDDE	Cathodically pretreated boron-doped diamond electrode
CV	Cyclic voltammetry
DME	Dropping mercury electrode
DPP	Differential pulse polarography
DPSV	Differential pulse stripping voltammetry
DPV	Differential pulse voltammetry
DSC	Differential scanning calorimetry
EC	European Union Regulation
EF	Electro-Fenton
EO	Electro-oxidation
GCE	Glassy carbon electrode
GPE	Graphite carbon paste
HMDE	Hanging mercury drop electrode
HPLC/DAD	High-performance liquid chromatography - diode array detection
HPLC-DAD	High-performance liquid chromatography diode array detector
IL:	Ionic liquid
LOD	Limit of detection
LOQ	Limit of quantification
LS-AdSV	Linear sweep adsorptive stripping voltammetry
LSV	Linear sweep voltammetry
MIP	Molecularly imprinted polymer
MWCNT	Multi-walled carbon nanotubes
O ₃	Ozone
PEF	Photoelectron-Fenton
Pt E	Platinum electrode
R&D	Research and development
SCE	Saturated calomel electrode
SG	Silica impregnated
SIC	Sequential injection chromatography
SW-AdSV	Square wave adsorptive stripping voltammetry
SWV	Square wave voltammetry
TG	Thermogravimetry
TPPC	Tetraphenylphosphonium chloride
UPLC	Ultra performance liquid chromatography
UV-Vis spectrophotometer	Ultraviolet-visible spectrophotometer

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