*j*ESE

Review

Some progress in voltammetric methods to detect malachite green in real samples using carbon electrodes

Madhusudan Dasnur Nanjappa[1] and Gururaj Kudur Jayaprakash[2,✉]

[1]Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi 221 005, Uttar Pradesh, India
[2]Department of Chemistry, Nitte Meenakshi Institute of Technology, Bangalore, Karnataka, 560064, India

Corresponding author: ✉rajguru97@gmail.com; Tel.: +91-953-876-2343

Abstract

Carbon electrode materials have generated considerable research interest in recent years due to their ease of use, higher charge transfer kinetics, and cost-effectiveness. Malachite green (MG) is an organic compound with metallic-looking powdered green crystals, which got its name from the color of malachite. MG can be easily converted to leuco-malachite green, a colorless form (LMG). Because both MG forms are dangerous for human health, detecting them in the environment is important. Many researchers across the globe worked on MG detection using various techniques, and this article provides brief information on their results. In this review article, some specific information about electrochemical detection techniques, which are frequently employed for MG determination, is discussed. This review highlights some advances in voltammetric methods using carbon-based electrodes such as glassy carbon, carbon paste, pencil graphite, and their chemically modified forms in various configurations that can be used for the electrochemical detection of MG. Some of the future scopes in using these advanced, carbon-based electrodes in MG determination are also discussed.

Keywords

Toxic organic dye; electrochemical sensors; modified carbon electrodes; voltammetry techniques, real samples

Introduction

Malachite green (MG) is a well-known organic dye that is a derivative of triphenyl-methane, with the chemical formula $C_{23}H_{25}N_2Cl$, color index of 42000, and the IUPAC denomination as 4-[(4-di-methylaminophenyl)-phenyl-methyl]-N, N-dimethylaniline (Figure 1) [1].

MG is highly soluble in water and ethanol and develops a blue-green color solution. The three phenyl rings in the MG structure provide significant hydrophobic properties, making it a fascinating

probe for electrochemical research [2]. It is a common fabric dye and fades slowly by the action of strong acids and bases. The base causes the color to fade because it converts the dye back to the alcoholic color base, which is colorless, but in the presence of an acid, the H^+ ions coordinate with the lone pairs of electrons of the amino groups. This reduces resonance in the molecule and leads to fading [3].
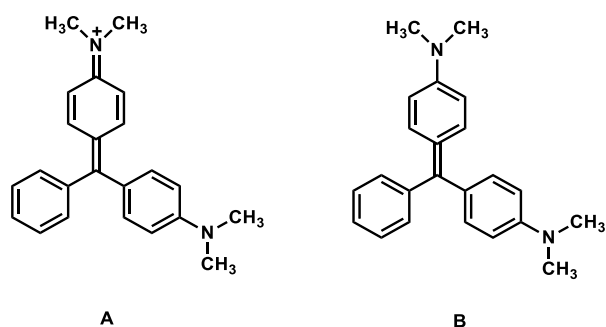

Figure 1. Chemical structures of (A) malachite green and (B) leuco-malachite green

Since MG is cheap and efficient against major protozoal and fungal species, it is widely employed as a biocide in aquaculture [4]. MG is used as an antiseptic in African aquaculture against fungal and parasitic infections. It is also used in dying jute, leather, paper, polymers, and as a food ingredient. Due to its water solubility, the untreated discharge of industrial effluents into water resources results in the contamination of water bodies and subsequent absorption of the contaminant by various fish species. In the dyeing process, around 10-15 % of all colors are lost to wastewater [5]. Among the synthetic dye pollution, MG has been classified as one of the most harmful since long-term exposures to its high concentrations can result in carcinogenesis, chromosomal fractures, mutagenesis, teratogenicity, and pulmonary toxicity, among others. Researchers discovered that MG, and particularly LMG, may stay in edible fish tissues for long periods. Eating contaminated fish can cause major difficulties for human health, such as a detrimental influence on the reproductive and immunological systems. MG is even designated as a class II health hazard [6].

Since leftover MG in aquaculture water can severely pollute water resources, several nations and regions have enacted legislation and regulations limiting or outright prohibiting the use of MG in aquaculture. Because of the restricted light penetration, MG may substantially influence the photo-synthetic job in aquatic life [7]. It may also be harmful to species due to aromatics and metals, chlorides, and other chemicals. Therefore, it is preferable to break down the dye into a non-toxic form before releasing it into the water supply to reduce contamination. These pollutants cause high biochemical oxygen demand (BOD), high chemical oxygen demand (COD), toxicity, foul odor, and, most importantly, wastewater color. Because dyes in water are extremely visible, even in very low quantities, the color of these pollutants may be identified [8]. This impact is undesirable because the color inhibits photosynthetic activity within the environment by blocking sunlight access to aquatic vegetation and wildlife. A chemical like this has lately been linked to an increased risk of cancer. Malachite green is a cytotoxic chemical for mammalian cells that also works as a liver tumor promoter. Because of all these detrimental effects of MG, the proper way of its detection, determination, and degradation must undoubtedly be figured out.

MG may be determined using a variety of analytical techniques, including liquid chromatography-tandem mass spectrometry (LC-MS/MS), surface-enhanced Raman spectroscopy (SERS), immune-logy, spectrophotometric methods, and fluorescent approaches. However, these procedures are troublesome, time-consuming, and expensive apparatus is required. Additionally, these techniques

offer lesser sensitivity with a higher limit of detection levels and are less suitable for the standard analysis of MG.

Electrochemical techniques, on the other hand, are more practical approaches that reveal some significant applications for the evaluation of biologically active substances, pharmaceuticals, food, water, soil, and some other biological samples. This is because of their quick rate analysis, straightforward working procedures, high sensibility, flexibility, and selectivity, as well as their low cost, exceptional response, and ease of handling in the available laboratory settings [9,10]. In the context of electrochemical techniques, the effectiveness of chemically changed electrodes looks to be a useful tool for enhancing low-level analysis through successfully transformed materials. Due to their high reproducibility, propensity for modification by numerous modifiers, ability to execute steady and well-resolved voltammograms, and low cost and simple preparation processes, carbon-based materials have been widely used in the voltammetric analysis for sensitive and selective identification of bioactive molecules [11].

The primary objective of this review paper is to provide a comprehensive overview of the requirements for detecting malachite green (MG) and to highlight recent advancements in voltammetric technology utilizing modified electrodes. By considering crucial factors and simulating the performance of each approach, this article intends to showcase the research trends in MG detection using different types of carbon electrode materials.

Detection techniques for MG in standard and real samples

Malachite green (MG) has garnered significant attention among researchers due to numerous issues associated with its use. Various analytical methods have been developed to detect and quantify MG in response. These methods include high-performance liquid chromatography (HPLC), mass spectrometry (MS), immunological approaches such as enzyme-linked immunosorbent assays (ELISA), Raman spectroscopy (particularly surface-enhanced Raman spectroscopy or SERS), and spectrophotometry.

HPLC is a widely employed chromatographic technique that utilizes a high-pressure infusion system to separate components in the mobile phase. It offers high accuracy and can analyze samples with different polarities or variable volumes of mixed buffer [12]. HPLC techniques such as HPLC-UV and HPLC-DAD exhibit detection limits ranging from 0.1 μg kg^{-1} to 1.7 μg kg^{-1}.

Mass spectrometry plays a significant role in MG detection, with atmospheric pressure chemical ionization (APCI) and extractive electrospray ionization (ESI) being commonly used interfaces for MS analysis. Mild ionization methods in APCI and ESI generate low-energy ions for analysis [13]. Mass spectrometry methods have demonstrated detection limits of 0.005 μg kg^{-1} to 2.5 μg kg^{-1}.

Immunological approaches, such as ELISA, rely on the specific antigen-antibody response for MG detection. ELISA methods utilize a color response between an enzyme and a substrate to quantify MG levels in a sample. ELISA offers high sensitivity, specificity, throughput, and cost-effectiveness, with detection limits ranging from 0.06 ng mL^{-1} to 4.8 ng mL^{-1}.

Raman spectroscopy, a technique that monitors molecule vibrations to reflect molecular structure, has gained popularity. SERS, a variant of Raman spectroscopy, amplifies the Raman signal of molecules adsorbed on a metal substrate by 10^6-10^{14} times. SERS has been successfully employed for MG detection, often combined with other approaches such as cloud point extraction [14]. The detection limits of SERS range from 0.5 μg L^{-1} to 40.0 μg L^{-1}.

Spectrophotometric methods, particularly UV/visible spectrophotometry, offer simplicity and cost-effectiveness. MG can be directly measured by the absorbance at 610-630 nm using a UV/visible spectrophotometer. However, direct absorbance methods are susceptible to interferences from

chemicals in complex mixtures. To overcome this, rigorous clean-up processes like solid phase extraction (SPE) and cloud point extraction are often required. Additionally, fluorescent probes, sensors, and quantum dots (QDs) in fluorescence resonance energy transfer (FRET) devices have gained popularity for MG detection, with detection limits ranging from 0.28 ng mL^{-1} to 2.9 ng mL^{-1}.

While these methods have shown promise, they also have some drawbacks. One challenge is the inability to reuse active substrates, leading to increased production costs. Specific methods may encounter difficulties with pre- or post-column transformations, interferences, expensive equipment, low mass resolution, or interference from structural mimics. Researchers are actively working to address these limitations and enhance MG detection and determination methods' accuracy, sensitivity, and efficiency [15-17].

Electrochemical detection of MG in standard and real samples

The electrochemical detection method is based on the electrochemical properties of a substance in solution [18]. It is a typical green analytical approach since the instrumental setup is simple and cost-effective, and the application requires minimal energy. MG is generally electroactive on carbon paste, gold, and glassy carbon electrodes (GCE). The use of naked (bare) electrodes, however, is unsuitable because other chemicals quickly poison electrode surfaces, lowering their specificity and sensitivity. The approach based on chemically-altered electrodes is preferred because of their enhanced selectivity and sensitivity. Modified electrodes containing suitable catalysts, however, improve the dynamic range in the quantitative analysis and speed up the response for MG detection [19].

Detection of MG using glassy carbon electrode (GCE)

Zhu *et al.* [20] investigated the electrochemical behavior of MG and leucomalachite green (LMG) using cyclic voltammetry with a glassy carbon electrode. They found that MG could be detected at pH 7.4 without interference from LMG. The authors also employed differential pulse voltammetry (DPV) for calibration, with a linear calibration plot ranging from 0.2 µM to 1.2 µM of MG. Additionally, adsorptive stripping voltammetry (ADSV) was used for MG detection in aquaculture water. Interference studies showed that various metal and acidic ions did not affect the measurement of MG. This electrochemical method proved effective for detecting MG in ambient water samples, utilizing an unmodified glassy carbon electrode [20].

Muresan *et al.* [21] modified glassy carbon electrode (GC/CeO$_2$/Nafion) for electrochemical detection of MG. The electrode was modified by drop-casting CeO$_2$ nanoparticles (NPs) and Nafion. CeO$_2$ NPs improved catalytic activity, surface area, and electron transport, while Nafion enhanced electrode stability. Square wave anodic stripping voltammetry (SWASW) showed high sensitivity, resolving power, and increased oxidation current with the GC/CeO$_2$/Nafion electrode. Analytical characteristics included sensitivity (0.28±0.01 A/M), detection limit (1.025 µM), and linear range (1 to 10 µM). The electrode exhibited strong selectivity against MG and high short-term stability after 50 scans [21]. A rapid, accurate, and easy electrochemical method for the detection of MG was developed by Yi *et al.* [22]. They created a glassy carbon electrode (GCE) coated with a multi-wall carbon nanotube-hexadecyl hydrogen phosphate (MWNT-DHP) film. The MWNT-DHP film demonstrated remarkable facilitation of electron transfer, resulting in a significant shift in potential and enhanced MG oxidation peak current in cyclic voltammograms. The catalytic effects of the MWNT film on MG oxidation were also observed. The MWNT-DHP film-modified GCE exhibited a substantial increase in the oxidation peak current of MG due to the large surface area, adsorptive characteristics, and moderate electric properties of MWNT. The method demonstrated excellent performance with a wide

linear range, high sensitivity, low detection limit (6.0 nmol L^{-1}), outstanding repeatability, and long-term stability. It showed high selectivity for MG detection, as demonstrated by minimal interference from various foreign species. The method was successfully applied to the analysis of MG in fish samples, highlighting its potential for real-time sample analysis [22].

Using three various types of ordered mesoporous silica, including SBA-15, MCM-41, and MCM-41-NH$_2$, Sacara *et al.* [23] developed innovative glassy carbon electrodes modified with silica for the electrochemical detection of MG. To attain good stability, more Nafion coating was put on the electrode. Following previous findings, the anodic oxidation of MG involves the ejection of an integral unit of the central carbon attached to a phenyl group, followed by the intramolecular coupling of two phenyl fragments, which results in the formation of the oxidized form of N,N,N',N'-tetramethylbenzidine, which is 1,1'-biphenyl-4.4'-diamine. For the examination of the effectiveness of innovative silica-modified glassy carbon electrodes towards the MG (10^{-6}-10^{-4} M) in 0.1 M phosphate buffer of pH 3, the scientists utilized the SWASW technique. According to the SWASV measurements, the oxidation peak of MG at the GC/SBA-15/Nafion electrode is shown at 0.85 V *vs.* Ag/AgCl/KCl (Figure 2A), where peak height varies with MG concentration. The authors looked at how the electrochemical reaction of MG at modified electrodes was affected by the concentration of silica suspension, quantity of Nafion solution, and pH of the electrolyte. According to the results of the investigation, the presence of any form of silica at the GC electrode surface enhanced the electrochemical response compared to the GCE, which had not been changed. This was attributable to the adsorption of MG on the silica surface.

Due to the affinity between MG and the functional group -NH$_2$, MCM-41-NH$_2$ performed better than the other two types of silica. The authors observed two oxidation peaks, one at 0.4 V and the other at 0.85 V *vs* Ag/AgCl/KCl$_{sat}$, corresponding to the GC/MCM-41-NH$_2$/Nafion modified electrode. This shows that there are two one-electron stages in the oxidation process.
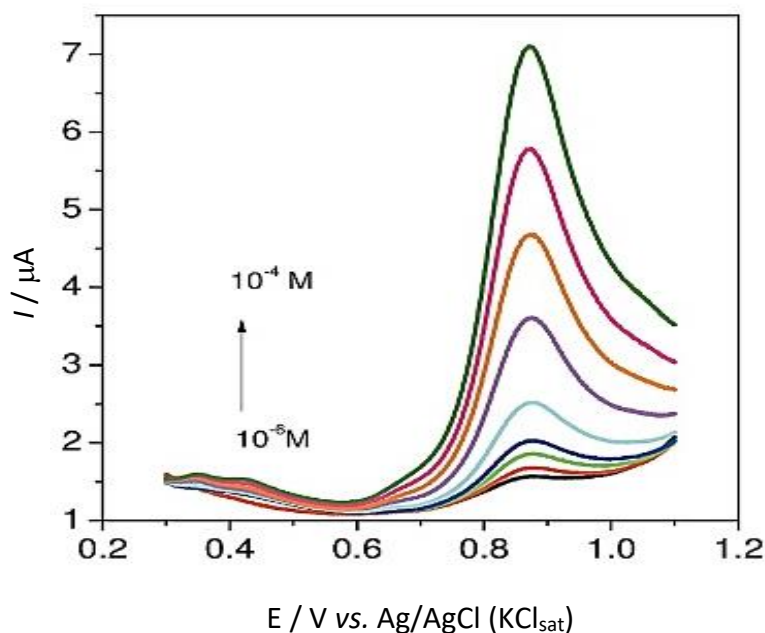

Figure 2. *SWASV curves at GC/SBA-15/Nafion electrode. Reproduced under terms of the CC-BY license [23] Copyright [2017], Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim*

During the electrochemical detection of MG, the GC/MCM-41-NH$_2$/Nafion modified electrode demonstrated an outstanding detection limit of 0.36 µM with a sensitivity of 0.164±0.003 A/M and linear range of 1-6 µM.

The unique silica-modified glassy carbon electrodes demonstrated high stability for up to five days, less time than previous electrodes, and great repeatability with five consecutive experiments using the same electrode. New glassy carbon electrodes with silica modifications were discovered to have good MG detection selectivity. However, the impact of potential foreign species, such as salts and contaminants, was not considered. The authors employed a commercial product (Promedivet, Romania) often used as a biocide in aquaria for ornamental fish to examine the implementation of the novel GC/MCM-41-NH$_2$/Nafion electrode in practical sample analysis. It was discovered that a new electrode effectively found the MG [23].

Glassy carbon electrodes were modified using multi-walled carbon nanotubes and cetylpyridinium bromide (GC/MWCNTs/CPB), according to Zhao *et al*. [24]. It was discovered that adsorption of the CPB surfactant caused a substantial rise in the anodic peak current of MG. Utilizing cyclic voltammetry, the electrochemical behavior of MG (2×10^{-6} M) at a modified GC electrode making GC/MWCNTs/CPB was observed in 0.1 M phosphate buffer solution of pH 7.0. It was shown in Figure 3 (curve-b) that MG in PBS solution showed a minor anodic peak at 0.42 V *vs*. saturated calomel electrode (SCE). The peak at 0.42 V emerged with the addition of CPB, and a considerable anodic peak appeared at 0.62 V *vs*. SCE as a result of the oxidation of MG (curve-c). It was hypothesized that the capacity of CPB to adsorb on the electrode surface would impair MG accumulation by impeding MG ability to transmit electrons. It brought about the gradual oxidation process and raised the concentration of MG used in the electrochemical reaction. Curve-d revealed that CPB does not generate any peak in the predicted potential range. It was determined that increasing the concentration of CPB surfactant up to a certain point enhanced the peak current of MG, but additional increases in the concentration of CPB might result in a drop in the peak current.
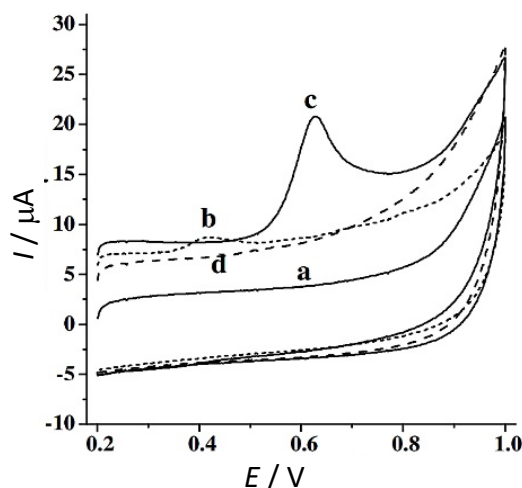

Figure 3. *Cyclic voltammograms of MWCNTs/GCE electrode in solution containing (a) phosphate buffer solution, (b) phosphate buffer solution+MG, (c) phosphate buffer solution+cetylpyridinium bromide (surfactant)+MG, (d) phosphate buffer solution+cetylpyridinium bromide. Potential is referred to the SCE reference. Reproduced under terms of the CC-BY license [24] Copyright [2009], Electrochemical Science Group*

The GC/MWCNTs/CPB modified electrode showed an outstanding detection limit of 9×10^{-10} M with good repeatability and stability, and the measured anodic peak current was proportional to the concentration of MG. The usefulness of GC/MWCNTs/CPB-modified electrodes for the detection of MG in the experimental sample analysis was examined by the authors. The modified electrode demonstrated excellent sensing capabilities toward MG in the sample of pond water. In addition, researchers have looked at how insoluble cationic Gemini surfactant affected the surface of glassy

M. D. Nanjappa and G. K. Jayaprakash

J. Electrochem. Sci. Eng. **13(3)** (2023) 437-449

carbon electrodes modified with multi-walled carbon nanotubes in the absence of CPB surfactant. In this case, enhanced electrode sensitivity toward the MG was demonstrated, although not as with CPB. It is still difficult to create electrodes for sensing applications with insoluble surfactants [24].

A novel multilayer-modified glassy carbon electrode with graphene quantum dots and gold nanoparticles was created by Hou *et al.* [25]. Gold nanoparticles and graphene quantum dots (GQDs) have typical diameters of 10 nm and 200 nm, respectively. According to the report, certain GQDs were aggregated, whereas the Au nanoparticles were evenly dispersed. Utilizing cyclic voltammetry, the authors examined the electrochemical behavior of multilayer modified electrodes made of GCE/(GQDs/Au). It was noted that both monolayer and multilayer modified electrodes for GCE/(GQDs/Au) showed a rise in peak current. This is attributed to the strong catalytic activity of the modified electrode. Additionally, the peak current augmentation was greater at the multilayer-modified GCE/(GQDs/Au) electrodes.

Using cyclic voltammetry, the authors calculated the electrochemical behavior of MG. In the presence of MG, GCE/(GQDs/Au) multilayer-modified electrodes showed high oxidation and reduction peaks. However, no redox peak was seen at the GCE/(GQDs/Au) multilayer modified electrodes in the absence of MG, indicating that GQDs and Au nanoparticles were naturally electro-inactive.

The use of GCE/GQDs/Au multilayer modified electrodes for the detection of MG in the fish samples was estimated by the authors. For the real sample analysis, it displayed good detection capability. With a linear range of 4.0×10^{-7} to 1.0×10^{-5} mol L^{-1} and a detection limit of 1.0×10^{-7} mol L^{-1}, the GCE/GQDs/Au multilayers modified electrode demonstrated high sensitivity. The obtained LOD, however, was higher than the detection limit of 1×10^{-7} nM from graphene oxide-modified GCE [26]. Additionally, this electrode showed excellent repeatability and stability for up to 10 days. Furthermore, it showed excellent selectivity for the MG by ignoring the effects of other foreign species such as ascorbic acid, uric acid, dopamine, caffeine, vitamin E, xanthine, hypoxanthine, leucomalachite green, and Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^- [25].

Table 1 displays literature data on the performance of the unmodified and modified glassy carbon electrode and some important parameters resulting from the electrochemical analysis.

Table 1. *Analytical results for electrochemical detection of malachite green in real samples using glassy carbon electrode (GCE)*

Electrode materials	LOD, nM	Linear range	Real samples	Ref.
GCE	4.379×10^4	43.79 - 437.9 µg/L	Aquaculture water	[20]
CeO$_2$ and Nafion-modified GCE	1025	1×10^{-6} - 1.0×10^{-5} mol/L	Fish	[21]
MWNT/DHP-modified GCE	6	5.0×10^{-8} - 8.0×10^{-6} mol/L	Carp	[22]
Silica/Nafion-modified GCE	360	1×10^{-6} - 6.0×10^{-6} mol/L	Water	[23]
MWNT-coated GCE	0.9	1×10^{-9} - 5×10^{-6} M	Pond water	[24]
GQDs/Au NPs-modified GCE	100	4.0×10^{-7} - 1.0×10^{-5} mol/L	Salmon	[25]
Graphene oxide (GO)-modified GCE	10^{-7}	1.0×10^{-16} - 1.0×10^{-12} mol/L	Water	[26]

Detection of MG using carbon paste electrode (CPE)

Huang and colleagues developed a sodium dodecyl benzene sulfonate-modified carbon paste electrode (CPE/SDBS), which was then used to establish a novel, sensitive, and uncomplicated voltammetric method for measurements of MG, which was based on the enhancement effect of surfactant [27]. The ability of the surfactant SDBS to bind to the hydrophobic C-H chains on the surface of the carbon paste electrode (CPE) served as the foundation for this electrode development. Positively charged MG will interact with the negatively charged head group of SDBS *via* electrostatic interactions during the adsorption process, causing MG to adsorb at the CPE surface

and significantly increase its electrode surface concentration. It was discovered that SDBS effectively boosts the oxidation peak current and thus the sensitivity of MG measurements too. Cyclic voltammetry was used to analyze the electrochemical response of MG at the CPE/SDBS modified electrode, and the results showed that the surfactant SDBS had an enhancing impact on the electrochemical determination of MG.

With a detection limit of 4.0×10^{-9} mol L^{-1} and a linear concentration range between 8.0×10^{-9} to 5.0×10^{-7} mol l^{-1}, the CPE/SDBS modified electrode demonstrated excellent sensitivity for the detection of MG. Additional interference analysis revealed that the presence of interfering substances including Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, ascorbic acid, uric acid, dopamine, caffeine, vitamin E, xanthine, hypoxanthine, and leucomalachite green did not affect the detection process. To test the sample analysis feasibility, this novel electrode was used to detect MG. It was highlighted that the proposed approach has tremendous promise for real sample analysis with good accuracy [27].

The voltammetric reaction of MG at the conductive carbon black paste electrode (CCBPE) was examined by Zhang *et al.* [28]. Their study revealed that paste electrodes constructed of conductive carbon black have good signal-to-noise ratios and more appealing voltammetric analytical capabilities. In addition, the surface topography of CCBPE was recorded using the SEM method. The authors concluded that the surface structure of the carbon paste is very important for sensing applications.

With a linear range of 10-510 nM, the CCBPE demonstrated a good detection limit of 6 nM. The selectivity of CCBPE for MG analysis was found impressive. Studies on interference have shown that non-native species such as inorganic ions (Na^+, K^+, NO_3^-, and PO_4^-) do not affect the method used to determine MG. Ascorbic acid, dopamine, methylene blue, and sodium dodecyl sulfate are a few examples of organic compounds that showed some competition to the MG during adsorption. By using the fishing water samples, it was calculated how much MG might be detected in practical samples. The aforementioned findings demonstrated that due to their simplicity, cost-effectiveness, and quick reaction in the measurement of MG, conductive carbon black paste electrodes are promising agents [28].

A very sensitive electrochemical approach for MG detection was developed by Ye *et al.* [29]. The innovative self-assembly modified carbon paste electrode based on ethylenediamine and graphene oxide made the electrochemical sensor. The improved covalent connection between the carboxyl group of the carbon paste electrode and the amino group of ethylenediamine served as the design concept for the CPE/En/GO modified electrode. The electrode showed exceptional stability and a long lifespan because of the graphene oxide covering. Additionally, graphene oxide efficiently promotes the redox reaction of MG at the electrode surface, which increases in current intensity.

Using cyclic voltammetry, the electrochemical sensing capabilities of CPE/En/GO modified electrodes were proven. A redesigned CPE/En/GO electrode showed a higher peak current. Because GO has strong electrical conductivity, this work showed that attaching these two layers (En/GO) to the surface of the CPE might improve the sensing capability for the detection of MG. With the use of electrochemical impedance spectroscopy, the authors utilized $[Fe(CN)_6]^{4-/3-}$ as a probe to examine the characteristics of the electron transfer resistance at modified electrode. The outstanding interface quality of the CPE/En/GO modified electrodes was demonstrated by the EIS research. The electrochemical behavior of MG at CPE/En/GO modified electrode was investigated using cyclic voltammetry in a pH 7.5 Britton-Robinson buffer solution. From the standpoint of conductivity and accumulation, this investigation aided in estimating the cooperative impact of GO and En on the CPE surface.

With a detection limit of 5×10^{-9} mol L^{-1} and a good linear concentration range of 8.0×10^{-9} mol L^{-1} to 8.0×10^{-7} mol L^{-1}, the CPE/En/GO modified electrode demonstrated outstanding sensitivity.

Furthermore, it demonstrated outstanding consistency and stability for up to 7 days. However, the modified electrode showed extremely strong selectivity for the MG, although the interference investigation was performed with common interfering agents such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+}, Cu^{2+}, uric acid, xanthine, and hypoxanthine. The use of CPE/En/GO modified electrodes in MG determination in lake water used for the cultivation of ornamental fishes was studied. The sensitivity of the modified electrode demonstrated in the study of lake water pointed to its use in practical sample analysis [29].

CPE/Cu-BTC modified electrode was created by Li *et al.* for the accurate detection of MG [30]. Copper nitrate and 1,3,5-benzenetricarboxylic acid were used as starting materials to produce copper-based metal-organic frameworks. Cu-BTC materials provide several benefits, including a larger active surface, increased adsorption capacity, increased catalytic MG oxidation activity, and decreased charge-transfer resistance. Cu-BTC compounds were found to have a surface made up of uniform and porous nanoparticles.

$K_3[Fe(CN)_6]$ was used as a probe in cyclic voltammetry to determine the electrochemical sensing capabilities of the CPE/Cu-BTC modified electrode. The peak current on the surface of the CPE/Cu-BTC modified electrode increased significantly. It was also found that the reduction peak potential moved positively while the oxidation peak potential shifted negatively on the CPE/Cu-BTC modified electrode. By using linear sweep voltammetry (LSV) at various pH levels, it was possible to demonstrate the electrochemical oxidation capability of MG at CPE/Cu-BTC. According to obtained results, the oxidation peak potential changed negatively with rising pH levels, indicating that the ratio of protons to electrons transferred during MG oxidation is the same. Additionally, the oxidation peak currents on CPE/Cu-BTC modified electrodes were progressively raised with a rise of pH value in the range of 5.7-7.0, and then gradually lowered in the range of 7.0-8.0. These findings demonstrated the capacity of the CPE/Cu-BTC modified electrode to improve the oxidation signals of MG.

With a detection limit of 0.67 nM, the CPE/Cu-BTC modified electrode showed remarkable linearity throughout the potential range of 2-500 nM. The selectivity of the modified electrode was examined concerning potential interferences such as glucose, oxalic acid, ascorbic acid, citrate, thiourea, histidine, dopamine, uric acid, or hypoxanthine. Aquaculture drugs (furazolidone, nitro-furazone, oxytetracycline, and chloramphenicol) were also considered. For the MG, the electrode demonstrated excellent detection accuracy. To detect MG, a modified CPE/Cu-BTC electrode was tested in a water sample taken from fishing pools. In the real sample analysis, the electrode performed satisfactorily [30].

A very affordable and straightforward carbon paste electrode for the detection of malachite green was described by Dasgupta *et al*. [31]. Carbon paste electrodes provide excellent electro-analytical performance, are simple to manufacture, and are extremely sensitive.

In three distinct pH 6 buffer solutions of acetate buffer, phosphate buffer, and citrate buffer in the presence of MG, the researchers looked at how CPE responded. According to the findings, CPE responded most strongly to the phosphate buffer solution. Furthermore, cyclic voltammetry was used in pH 6 phosphate buffer solution to quantify the performance of CPE toward the detection of MG. No oxidation peak was observed in the absence of MG, but when MG was added, a distinct oxidation peak was observed. This proved that the CPE sensor was quite efficient in picking up MG. For up to 21 days, the carbon paste electrode showed excellent repeatability, sensitivity, and stability. It demonstrated two distinct linearity ranges for the detection of malachite green, namely 10-75 µM and 75-300 µM [31].

Table 2 represents collected literature data on the results obtained from the electrochemical analysis of MG using a carbon paste electrode.

Table 2. Analytical results for electrochemical detection of malachite green in real samples by carbon paste electrode (CPE)

Electrode material	LOD, nM	Linear range, mol/L	Real samples	Ref.
CPE	4	8.0×10^{-9} - 5.0×10^{-7}	Fish samples	[27]
Conductive carbon black paste electrode (CCBPE)	6	10^{-8} - 5.1×10^{-7}	Lake water	[28]
Ethylenediamine and GO-modified CPE	5	8.0×10^{-9} - 8.0×10^{-7}	Fish samples	[29]
Cu-BTC/ CPE	0.67	2.0×10^{-9} - 5.0×10^{-7}	Water and fish samples	[30]
CPE		10^{-5} - 7.5×10^{-5} & 7.5×10^{-5} - 3×10^{-4}	-	[31]
Hexadecyl pyridinium bromide modified CPE (HDPB/ABPE)	-	2.0×10^{-8} - 4.0×10^{-5}	-	[32]
Butyrylcholinesterase (BuChE) & polypyrrole (PPy)-modified CPE	250	0.00025 -0.01*	Fish samples	[33]

*ppm

Detection of MG using pencil graphite electrode (PGE)

An electrochemical sensor was created by Sanjay and colleagues as a tool for malachite green analysis [34]. The electrochemical sensor was created by altering pencil graphite electrodes with a two-dimensional graphene nanoribbons-CoB composite (GNR-CoB). The key benefit of adopting 2D GNR-CoB composite as an electrode material was the improvement of electron mobility which supports quick and accurate detection of MG. According to the authors, graphene nanoribbons (GNR) have a greater diffraction peak at $2\theta = 25.2°$ and 2D CoB has a wide diffraction pattern at $2\theta = 42.99°$. CoB produces a two-dimensional sheet-like structure that wrinkles around ribbons. These two values confirm the formation of the GNR-CoB nanocomposite.

The electrochemical behavior of the PGE/GNR-CoB modified electrode was also investigated using electrochemical impedance spectroscopy. The strong conducting nature of the GNR and the increased surface area of the electrode were demonstrated by a reduction in charge transfer resistance for PGE/GNR-CoB modified electrodes.

It was discovered that the PGE/GNR-CoB modified electrode showed higher sensitivity of 1.714 µA µM^{-1}cm^{-2}, a lower detection limit of 1.92 nM, and a linear range of 25-350 nM. The PGE/GNR-CoB modified electrode can detect the MG in the presence of many interferents with excellent repeatability and long-term stability for up to 25 days.

Conclusions

Electrochemical analytical procedures can be used as quantitative methods in practical applications for malachite green detection. Furthermore, it was discovered that GC electrode materials are the most widely utilized materials for electrochemical detection of MG and take part in the essential task of constructing high-performance electrodes. However, a few flaws should not be neglected. Many documented electrochemical methods, for example, are unsuitable for the examination of biological materials because they are consistently prone to influence from the matrix with many variables.

Future perspectives concerning electrochemistry

Several analytical methodologies have been found as quantitative instruments in practical applications, with largely positive outcomes. Developing analytical equipment with low cost, easy

operation, mobility, good resolution, and low LOD remains difficult. However, electrochemical analytical methods may be utilized to identify MG quantitatively. In recent years, electrochemical analysis has been presented as an alternative to standard approaches. In the detection of the degradation of organic dyes, electrochemical analytical technologies have revolutionized the field. In the future, changes to electrochemical methods will allow for more effective examination and elimination of previously identified flaws.

References

[1] S. Sarmah, A. Kumar, Photocatalytic activity of polyaniline-TiO_2 nanocomposites, *Indian Journal of Physics* **85** (2011) 713-726. https://doi.org/10.1007/s12648-011-0071-1

[2] M. M. Rahman, M. Y. A. Mollah, M. M. Rahman, M. A. B. H. Susan, Electrochemical Behavior of Malachite Green in Aqueous Solutions of Ionic Surfactants, *International Scholarly Research Notices* (2013) 839498. http://dx.doi.org/10.1155/2013/839498

[3] F. J. Foster, L. Woodbury, The Use of Malachite Green as a Fish Fungicide and Antiseptic, *The Progressive Fish-Culturist* **3(18)** (1936) 7-9. https://doi.org/10.1577/1548-8640(1936)318[7:TUOMGA]2.0.CO;2

[4] E. Sudova, J. Machova, Z. Svobodova, T. Vesely, Negative effects of malachite green and possibilities of its replacement in the treatment of fish eggs and fish: a review, *Veterinárni Medicína* **52** (2007) 527-539. https://doi.org/10.17221/2027-VETMED

[5] J. P. Jadhav, S. P. Govindwar, Biotransformation of malachite green by *Saccharomyces cerevisiae* MTCC 463, *Yeast* **23(4)** (2006) 315-323. https://doi.org/10.1002/yea.1356

[6] Z. Lin, D. Wang, H. Zhang, L. Li, Z. Huang, J. Shen, Y. Lin, Extraction and determination of malachite green from aquatic products based on molecularly imprinted polymers, *Separation Science and Technology* **51(10)** (2016) 1684-1689. https://doi.org/10.1080/01496395.2016.1175478

[7] S.M. Plakas, K.R. El Said, G.R. Stehly, W.H. Gingerich, J.L. Allen, Uptake, tissue distribution, and metabolism of malachite green in the channel catfish (*Ictalurus punctatus*), *Canadian Journal of Fisheries and Aquatic Science* **53** (1996) 1427-1433. https://doi.org/10.1139/f96-061

[8] D. J. Alderman, Malachite green: a review, *Journal of Fish Diseases* **8(3)** (1985) 289-298. https://doi.org/10.1111/j.1365-2761.1985.tb00945.x

[9] V. Sharma, G. K. Jayaprakash, Fabrications of electrochemical sensors based on carbon paste electrode for vitamin detection in real samples, *Journal of Electrochemical Science and Engineering* **12** (3) (2022) 421-130. https://doi.org/10.5599/jese.1313

[10] N. Hareesha, J. G. Manjunatha, Poly (maleic acid) modified carbon paste electrode for simultaneous detection of dopamine in the presence of uric acid: a cyclic voltammetric study, *Journal of Science: Advanced Materials and Devices* **5(4)** (2020) 502-511. https://doi.org/10.1016/j.jsamd.2020.08.005

[11] N. Hareesha, J. G. Manjunatha, C. Raril, G. Tigari, Sensitive and Selective Electrochemical Resolution of Tyrosine with Ascorbic Acid through the Development of Electropolymerized Alizarin Sodium Sulfonate Modified Carbon Nanotube Paste Electrodes, *Chemistry Select* **4(15)** (2019) 4559-4567. https://doi.org/10.1002/slct.201900794

[12] Y. -H. Li, T. Yang, X.-L. Qi, Y.-W. Qiao, A.-P. Deng, Development of a group selective molecularly imprinted polymers based solid phase extraction of malachite green from fish water and fish feed samples, *Analytica Chimica Acta* **624(2)** (2008) 317-325. https://doi.org/10.1016/j.aca.2008.07.004

[13] F. Wang, H. Wang, Y.-D. Shen, Y.-J. Li, J.-X. Dong, Z.-L. Xu, J.-Y. Yang, Y.-M. Sun, Z.-L. Xiao, Bispecific Monoclonal Antibody-Based Multianalyte ELISA for Furaltadone Metabolite,

Malachite Green, and Leucomalachite Green in Aquatic Products, *Journal of Agricultural and Food Chemistry* **64(42)** (2016) 8054-8061. https://doi.org/10.1021/acs.jafc.6b03233

[14]　N.-N. Xu, Q. Zhang, W. Guo, Q.-T. Li, J. Xu, Au@PVP Core-Shell Nanoparticles Used as Surface-Enhanced Raman Spectroscopic Substrate to Detect Malachite Green, *Chinese Journal of Analytical Chemistry* **44(9)** (2016) 1378-1384. https://doi.org/10.1016/S1872-2040(16)60956-8

[15]　J. G. Manjunatha, A surfactant enhanced graphene paste electrode as an effective electrochemical sensor for the sensitive and simultaneous determination of catechol and resorcinol, *Chemical Data Collections* **25** (2020) 100331. https://doi.org/10.1016/j.cdc.2019.100331

[16]　J. G. Manjunatha, B. E. Kumara Swamy, G. P. Mamatha, S. S. Shankar, O. Gilbert, B. N. Chandrashekar, B. S. Sherigara, Electrochemical Response of Dopamine at Phthalic acid and Triton X-100 Modified Carbon Paste Electrode: A cyclic voltammetry study, *International Journal of Electrochemical Science* **4** (2009) 1469-1478. http://electrochemsci.org/papers/vol4/4101469.pdf

[17]　N. Hareesha, J. G. Manjunatha, Surfactant and polymer layered carbon composite electrochemical sensor for the analysis of estriol with ciprofloxacin, *Materials Research Innovations* **24(6)** (2020) 349-362. https://doi.org/10.1080/14328917.2019.1684657

[18]　C. Raril, J. G. Manjunatha, Fabrication of novel polymer-modified graphene-based electrochemical sensor for the determination of mercury and lead ions in water and biological samples, *Journal of Analytical Science and Technology* **11** (2020) 3. https://doi.org/10.1186/s40543-019-0194-0

[19]　J. G. Manjunatha, B. E. Kumara Swamy, M. Deraman, G. P. Mamatha, Simultaneous voltammetric measurement of ascorbic acid and dopamine at poly (vanillin) modified carbon paste electrode: A cyclic voltammetric study, *Der Pharma Chemica* **4(6)** (2012) 2489-2497. https://www.derpharmachemica.com/pharma-chemica/simultaneous-voltammetric-measurement-of-ascorbic-acid-and-dopamine-at-poly-vanillin-modified-carbon-paste-electrode-a-c.pdf

[20]　D. Zhu, Q. Li, K.C. Honeychurch, M. Piano, G. Chen, Determination of Malachite Green in Aquaculture Water by Adsorptive Stripping Voltammetry, *Analytical Letters* **49(9)** (2016) 1436-1451. https://doi.org/10.1080/00032719.2015.1104321

[21]　A. M. Sacara, C. Cristea, L. M. Muresan, Electrochemical detection of Malachite Green using glassy carbon electrodes modified with CeO_2 nanoparticles and Nafion, *Journal of Electroanalytical Chemistry* **792** (2017) 23-30. https://doi.org/10.1016/j.jelechem.2017.03.030

[22]　H. Yi, W. Qu, W. Huang, Electrochemical determination of malachite green using a multi-wall carbon nanotube modified glassy carbon electrode, *Microchimica Acta* **160** (2008) 291-296. https://doi.org/10.1007/s00604-007-0814-z

[23]　A. M. Sacara, V. Nairi, A. Salis, G. L. Turdean, L. M. Muresan, Silica-modified Electrodes for Electrochemical Detection of Malachite Green, *Electroanalysis* **29(11)** (2017) 2602-2609. https://doi.org/10.1002/elan.201700400

[24]　L. Liu, F. Zhao, F. Xiao, B. Zeng, Improved Voltammetric Response of Malachite Green at a Multi-Walled Carbon Nanotubes Coated Glassy Carbon Electrode in the Presence of Surfactant, *International Journal of Electrochemical Science* **4** (2009) 525-534. http://www.electrochemsci.org/papers/vol4/4040525.pdf

[25]　J. Hou, F. Bei, M. Wang, S. Ai, Electrochemical determination of malachite green at graphene quantum dots–gold nanoparticles multilayers-modified glassy carbon electrode, *Journal of Applied Electrochemistry* **43** (2013) 689-696. https://doi.org/10.1007/s10800-013-0554-1

[26] J. Shao, Y. Zhao, F. Liu, W. Li, Y. Gao, Determination of malachite green and leucomalachite green based on electrochemiluminescence of Ru(bpy)$_3$$^{2+}$ at graphene oxide modified glassy carbon electrodes, *RSC Advances* **5(19)** (2015) 14547-14552. https://doi.org/10.1039/C4RA09915J

[27] W. Huang, C. Yang, W. Qu, S. Zhang, Voltammetric determination of malachite green in fish samples based on the enhancement effect of anionic surfactant, *Russian Journal of Electrochemistry* **44** (2008) 946-951. https://doi.org/10.1134/S1023193508080107

[28] X. Zhang, Y. Cui, Z. Lv, M. Li, S. Ma, Z. Cui, Q. Kong, Carbon nanotubes, Conductive Carbon Black and Graphite Powder Based Paste Electrodes, *International Journal of Electrochemical Science* **6** (2011) 6063-6073. http://electrochemsci.org/papers/vol6/6126063.pdf

[29] K. Zhang, G. Song, L. Yang, J. Zhou, B. Ye, A novel self-assembly voltammetric sensor for malachite green based on ethylenediamine and graphene oxide, *Analytical Methods* **4(12)** (2012) 4257-4263. https://doi.org/10.1039/C2AY26039E

[30] C. Li, K. Wu, Cu-BTC frameworks based electrochemical sensor for hazardous malachite green in aquaculture, *Analytica Chimica Acta* **1162** (2021) 338473. https://doi.org/10.1016/j.aca.2021.338473

[31] S. Dasgupta, S. Nag, R. B. Roy, R. Bandyopadhyay, B. Tudu, Malachite Green Detection Using Carbon Paste Electrode Based on Voltammetry, *2nd International Conference on Emerging Frontiers in Electrical and Electronic Technologies (ICEFEET)* (2022) 21974966. https://doi.org/10.1109/ICEFEET51821.2022.9847835

[32] P. Deng, J. Feng, Y. Wei, J. Xiao, J. Li, Q. He, Fast and ultrasensitive trace malachite green detection in aquaculture and fisheries by using hexadecylpyridinium bromide modified electrochemical sensor, *Journal of Food Composition and Analysis* **102** (2021) 104003. https://doi.org/10.1016/j.jfca.2021.104003

[33] A. N. Hidayah, S. Faridah, M. N. Azura, A. R. Gayah, M. Othman, A. B. Fatimah, Malachite Green and Leuco-Malachite Green Detection in Fish Using Modified Enzyme Biosensor, *Procedia Chemistry* **20** (2016) 85-89. https://doi.org/10.1016/j.proche.2016.07.014

[34] B. P. Sanjay, S. Sandeep, A. S. Santhosh, C. S. Karthik, D. N. Varun, N. K. Swamy, P. Mallu, K. S. Nithin, J. R. Rajabathar, Unprecedented 2D GNR-CoB nanocomposite for detection and degradation of malachite green - A computational prediction of degradation pathway and toxicity, *Chemosphere* **287** (2022) 132153. https://doi.org/10.1016/j.chemosphere.2021.132153