

Electrochemical Sensing of Textile Dyes Using Graphene Oxide: A Comprehensive Review

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ABSTRACT

The widespread use of synthetic textile dyes has raised grave environmental and public health concerns owing to their persistence, toxicity, and prevalence in industrial effluents. Electrochemical sensing offers a sensitive, rapid, and cost-effective method for detecting toxic dyes at trace levels. Graphene oxide (GO) — with its large surface area, abundant oxygenated functional groups, excellent electrical conductivity after reduction, and facile chemical tunability — has emerged as a versatile material for constructing high-performance dye sensors. This review highlights the successes in real-sample analysis (wastewater, industrial effluents, and textile rinse waters). It identifies persistent challenges, such as fouling, matrix interferences, long-term stability, and scale-up for field deployment. This comprehensive overview aims to guide researchers and practitioners towards robust, field-ready GO-based electrochemical sensors for sustainable dye monitoring and remediation.

Keywords- Graphene oxide; Electrochemical sensor; Textile dyes; Water pollution; Azo dyes; Differential pulse voltammetry; Nanocomposites; Environmental monitoring; Wastewater analysis; Sustainable remediation

I. INTRODUCTION

Because dyes are intricate, aromatic molecular structures that are meant to remain stable, they are challenging to break down. Owing to the ineffectiveness of the dyeing process, over 2 million tons of dyes are produced annually throughout the dyeing and finishing processes, of which 50% are textile dyes. Currently, over 100,000 dyes are commercially available, with azo dyes accounting for over 70% by weight. (Arora, 2014). Unfortunately, due to their high resilience to temperature, water, light, chemicals, soap, detergents, and other factors like bleach and perspiration, most of these colours evade traditional wastewater treatment procedures and persist in the environment. These compounds are more resistant to biodegradation because of their complex aromatic

structure and synthetic origin. (Drumond Chequer et al., 2013)

Textile wastewaters are characterized by extreme variations in several parameters, including pH, color, salinity, chemical oxygen demand (COD), and biochemical oxygen demand (BOD). The many organic-based compounds, chemicals, and colors employed in the dry and wet processing stages determine the composition of the wastewater. Textile effluents are primarily contaminated by resistant organic, colored, hazardous, surfactant, chlorinated, and salt contaminants. (Dos Santos et al., 2007)(Drumond Chequer et al., 2013)(Ben Mansour et al., 2012). However, these textile effluents also contain heavy metals, metalliferous substances, and phthalocyanine dyes, such as chromium (Cr), arsenic (As), copper (Cu), and zinc (Zn). This is

because these effluents have high values for a number of physicochemical and biological parameters that indicate the degree of pollution, such as color, temperature, salinity, pH, biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total nitrogen (TN), total phosphorus (TP), and non-biodegradable organic compounds. (Berradi et al., 2019) Additionally, the presence of minute quantities of dyes (less than 1 mg/L for some dyes) in water, which are highly visible, along with the effects of additional contaminants in textile wastewater, negatively impacts the visual appeal and cleanliness of water bodies such as lakes and rivers, damaging the aquatic environment. (Drumond Chequer et al., 2013) (Banat et al., 1996)

Dyes exist in a wide range of chemical forms, primarily relying on substituted aromatic and heterocyclic groups, such as naphthyl, phenyl, and aromatic amines, which are considered carcinogenic. Many dyes consist of azo compounds ($-N=N-$) connected by azo bridges. The intricate chemical makeup of synthetic organic pigments in dyes makes them resistant to deterioration and durable for the life of the fabric. They are challenging to handle in wastewater and do not decompose when exposed to sunlight, water, or soap. Wastewater color is a clear indicator of water contamination. (Talarposhti et al., 2001) (Anliker and Clarke, 1982)

Textile dyes can be detected using a variety of traditional methods, including colorimeters, which measure the light absorbance of dyes; chromatography techniques such as High-Performance Liquid Chromatography (HPLC), which separates dye components based on their interactions with stationary and mobile phases; spectroscopic techniques such as UV-Visible spectroscopy, which measures the absorbance of particular wavelengths to identify and quantify dyes; Raman Spectroscopy, which provides molecular fingerprinting of dyes; and capillary electrophoresis (CE), which separates dye ions under an electric field to enable their detection. Although highly sensitive, conventional dye detection techniques such as ultraviolet-visible spectroscopy, mass spectrometry (MS), and chromatography are frequently costly, time-consuming, and require specialized laboratory equipment and trained personnel, making them unsuitable for quick on-site monitoring. Rapid detection is crucial for early warning, regulatory compliance, and real-time dye discharge monitoring. For broad acceptance, a low cost is necessary. In this regard, electrochemical sensors are promising.

Voltammetry, which measures the current as a function of the applied voltage to identify dyes, and amperometry, which measures the current at a fixed potential and is ideal for continuous monitoring, are two electrochemical detection methods used for the selective detection of textile dyes. Electrochemiluminescence (ECL) combines luminescence and electrochemical reactions to produce highly sensitive results. There are

unquestionably more advantages to using electrochemical sensors than traditional detection techniques, such as improved sensitivity and selectivity, quick analysis with timely findings, affordable equipment, portability, and a simpler sample preparation procedure. Redox changes in the dye molecules reacting with a sensor nanomaterial were measured using electrochemical sensing. (Adane et al., 2021) (Kolatoğlu et al., 2020) (Ulina and Yamanaka, 2020)

Graphene is an extraordinarily versatile two-dimensional nanomaterial composed of a single sheet of carbon atoms organized in a hexagonal lattice. Some of its special qualities include a large surface-to-volume ratio, outstanding electrical conductivity, increased mobility of electrons at room temperature, and remarkable mechanical strength and flexibility. Owing to these properties, graphene plays an important role in various technologies, influencing everything from large-scale membrane and mechanical applications to nanoscale electrical and optical devices. (Ramirez et al., 2024) (Thangamuthu et al., 2019)

GO represents graphene in a single-layered oxidized state. Oxygen-containing groups on the surface significantly decrease π - π stacking, which lowers the conductivity and introduces defects in the GO lattice in graphene oxide. Due to the hydrogen bonds that develop between the hydroxyl groups of the solvent and those on the surface, it can dissolve in water and some organic solvents. It is stable at ambient temperatures and is simple to produce. This characteristic makes it easy to create thin sheets of GO and its derivatives on various substrates. Due to its abundant oxygen-containing functional groups, GO is easily functionalized and is extremely receptive to complexing with various chemicals and metal ions. GO's electrical conductivity can be improved by lowering. The material obtained after reduction is called reduced graphene oxide (rGO). Although rGO is a close relative of graphene, its distinct characteristics give it a unique position within the graphene family. (Yadav et al., 2022)

II. TEXTILE DYES AND ENVIRONMENTAL IMPACT

Complex unsaturated chemical compounds, called dyes, absorb light and produce visible-spectrum colors. Furthermore, a dye is a material that can absorb a portion of the visible spectrum (chromophore). The portion of light that is reflected rather than absorbed by the dye gives it its colour. Conjugated double bonds form a chemical structure that facilitates light absorption. Therefore, aromatic amines are frequently used as colorants. The chemical structure and application of dyes determine their classification. Numerous functional groups, including azo, nitro, anthraquinone, carbonyl, methine, arylmethane, and others, serve as the foundation for chromophore-containing centers. Furthermore, auxochromes are electrons that donate or withdraw electrons from substituents to create or enhance the colour

of chromophores. The most prevalent auxochromes are hydroxyl, carboxyl, amine, and sulfonate groups. (Benkhaya et al., 2020) (Drumond Chequer et al., 2013)

Owing to the ineffectiveness of the dyeing process, up to 200,000 tons of these colors are lost to effluents annually throughout the processes of dyeing and finishing in the textile sector. Unfortunately, due to their high resilience to light, temperature, water, detergents, chemicals, soap, and other factors like bleach and perspiration, most of these colours evade traditional wastewater treatment procedures and persist in the environment. These compounds are more resistant to biodegradation because of their complex, stable aromatic structure and synthetic origin. Therefore, in terms of both volume and effluent composition, wastewater from textile factories is the most harmful among all industrial sectors. (Drumond Chequer et al., 2013) (Department of Textile Engineering, Mawlana Bhashani Science and Technology University, Tangail, Bangladesh et al., 2022) Bleaching and dyeing produce enormous amounts of effluent during the chemical process, which is full of important pollutants such as a higher concentration of biological and chemical oxygen demand (BOD and COD), suspended solids (SS), nitrogen (organic), residual heavy metals, dispersants, acids, salts, alkali, and different dyes. Therefore, the discharge of the aforementioned contaminants deteriorates water quality, spreading toxicity and having a major impact on plant photosynthesis, resulting in oxygen deficiency. Its limited light penetration and inadequate oxygen consumption also significantly affect the aquatic environment. As a result, effluents must be sufficiently treated before being released, which places greater emphasis on water reuse options. (Velusamy et al., 2021a) (Drumond Chequer et al., 2013) (Department of Textile Engineering, Mawlana Bhashani Science and Technology University, Tangail, Bangladesh et al., 2022) (Adane et al., 2021)

The two primary parts of dye molecules are auxochromes, which not only contribute to the chromophore but also decrease the molecule's solubility in water and increase its affinity for the fibre. Chromophores are responsible for producing the colour. Azo ($-\text{N}=\text{N}-$), carbonyl ($-\text{C}=\text{O}$), nitroso ($-\text{N}=\text{O}$), thiocarbonyl ($-\text{C}=\text{S}$), nitro ($-\text{NO}_2$), and alkenes ($-\text{C}=\text{C}-$) are the most prevalent atom groups that make up the chromophore. These auxochromic groups can be basic (NH_2 , NHR , and NR_2) or acidic (COOH , SO_3 , and OH groups). Functional groups, such as carboxylic, amine, and azo groups, are present in textile dyes and are difficult to remove using traditional techniques. Dyes are often composed of conjugated aromatic structures (such as perylene, anthracene, and benzene rings) with chromophoric and auxochromic groups. (Benkhaya et al., 2020) (Islam and Mostafa, 2019) (Adane et al., 2021) The solubility of dyes can also be used to classify them as either soluble (such as acid, metal complex, basic, mordant, direct, and reactive dyes) or insoluble (such as azoic, sulfur, vat, and disperse dyes). (Velusamy et al., 2021b) (Islam and Mostafa, 2019).

III. BASICS OF ELECTROCHEMICAL SENSING

An electrochemical sensor is an independent integrated device that converts data from electrochemical processes into signals suitable for analysis. The IUPAC defines a chemical sensor as "a device that converts chemical data into an analytically usable signal, ranging from the concentration of a single sample component to complete composition analysis." The two primary functional components of a chemical sensor are a physicochemical transducer and a receptor. (Baranwal et al., 2022)

The purpose of a chemical sensor is to provide precise, real-time information about the chemical composition of its environment. Such a gadget should ideally be able to react continuously and reversibly without affecting the samples. The electrical signal generated by the interaction between the target analyte and the recognition layer is where the analytical data are extracted from electrochemical sensors. (Baranwal et al., 2022)

Chemical sensors are becoming increasingly popular for a wide range of applications due to their many advantages, such as small size, low detection limit, good selectivity, sensitivity, wide detection range, low cost, and ease of implementing automatic measurement, online or in situ, as well as continuous monitoring. These benefits have made them one of the most active and successful areas in contemporary sensor technology. (Saputra, 2023) A sensor measurement, or "reading," is produced when a physical parameter changes in response to a chemical stimulus. Naturally, both the sensor and the sensing environment affect the precise type of physical change. (Janata, 2010)

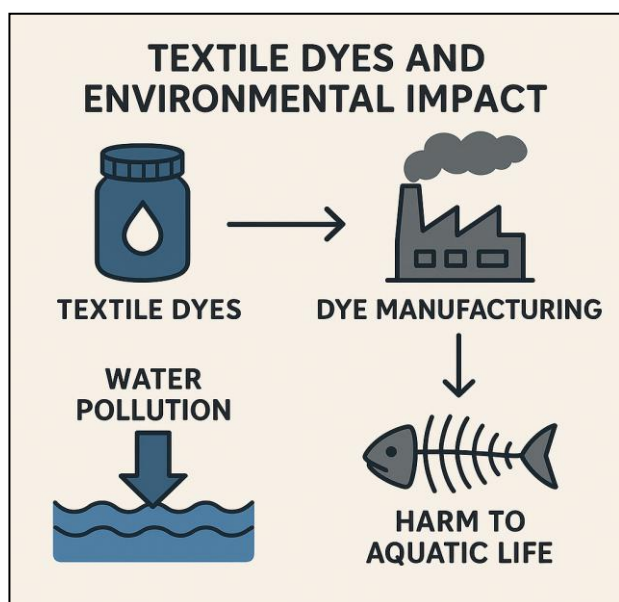


Fig. (1) Textile Dyes and Environmental Impact

Three primary types of sensing modes can be used to identify the electrical signal: voltammetric or amperometric (with the voltage applied, a variation in current is observed for an electrochemical reaction in the first instance, or the alteration of current is observed with time at a fixed potential applied in the latter case), potentiometric (the variation of membrane potential), and impedimetric (the variation of impedance). The creation of an electrochemical sensor should be planned to provide excellent selectivity, minimum detection limits, and the use of a small number of indicator species. (Dzulkurnain et al., 2021)

The amperometric method consists of constant-potential current measurements. The working electrode is maintained at a constant voltage while the analyte undergoes electrochemical (Faradaic) oxidation or reduction. Consequently, the observed current is proportional to the analyte concentration (steady state or transient, depending on mass transfer). Amperometry, including chronoamperometry and pulse-amperometry, is utilized for high-sensitivity assays (e.g., H_2O_2 and glucose). A three-electrode cell and potentiostat are required for instrumentation. When these sensors are combined with electrocatalytic surfaces, they offer simple calibration, fast response, and low detection limits. However, they also have constraints, including interference from co-oxidizable species and the background current. If the system performs effectively under diffusion-limited situations, the limit current is linearly dependent on the analyte concentration, enabling exact measurements at concentrations much lower than one ppm. However, these devices frequently suffer from low selectivity. (Grieshaber et al., 2008) (Baranwal et al., 2022) (Caprioli and Quercia, 2014)

By monitoring the current while applying a working electrode potential, information about an analyte is collected using the voltammetric approach. The final current is generated by the electrochemical reaction occurring on the electrode surface and the electrode or electrolyte interface region. Voltammetric techniques include square wave voltammetry (SWV), differential pulse voltammetry (DPV), cyclic voltammetry (CV), and linear sweep voltammetry (LSV). These tactics offer thorough measurements with a low detection limit and a wide spectrum of efficacy. The current versus potential is measured while applying a time-varying potential waveform (square wave, cyclic, differential pulse, or linear sweep). Information on both qualitative (E_o') and quantitative (peak current $\propto$ concentration) parameters is provided by voltammetric peaks corresponding to the redox activities. Pulse voltammetry (DPV, SWV) reduces the capacitive current, increasing the sensitivity and LOD. This method works well for peak potential-based multi-analyte detection. The drawbacks include the requirement of careful electrode surface conditions and scan/pulse parameter tuning. (Baranwal et al., 2022) (Dzulkurnain et al., 2021)

In contrast, the amperometric approach measures the current over time by applying a constant voltage to the working electrode. The use of a potential measure rather than a potential sweep distinguishes voltammetric and amperometric approaches. Greater selectivity and sensitivity can be achieved using the amperometric technique because the potential of reduction or oxidation used in the measurement is typical for the analyte specimen. (Dzulkurnain et al., 2021)

In contrast, conductometric sensors, also known as impedimetric sensors, use surface impedance variations to identify and measure analyte-specific identification signals on the electrode. Changes in the capacitance values were identified when the sensors were employed to detect extremely small forces. The capacity of a circuit to detect the resistance to the motion of an electrical current is called the impedimetric method or impedance. By applying a tiny sinusoidal potential to the working electrode of an electrochemical cell and monitoring the resulting current response, an electrochemical impedance spectroscopy can be used to measure the impedance. Impedimetric sensing is widely chosen among other alternatives because it provides an extensive range of information about the target analyte. There are certain advantages and disadvantages to this type of sensing. In terms of static sensor characteristics, they have many more benefits than drawbacks, including a short shelf life, a high likelihood of cross-sensitivity, and an increased sensitivity to changes in the surrounding temperature. A reduced detection limit, adequate stability and repeatability of the responses, a broad linear range of response, minimal power usage, compactness, high resolution, consistent performance, and high precision are a few of these. (He et al., 2020) (Dzulkurnain et al., 2021)

Potentiometric sensors have been the most widely used functional sensors since the beginning of the twentieth century because of their affordability and ease of use. A two-electrode system, consisting of a reference electrode and a sensing electrode, is typically considered for potentiometric devices. By using the potential signal value pertaining to the change in surface charge for the target recognition of the sensing electrode, direct target identification was enabled. A liquid contact structure and ion-selective membranes typically characterise potentiometric sensing electrodes. To determine quantitative values, the technique involves recording the potential (E). (Baranwal et al., 2022) (Bocu, 2024)

Overall, we can say that among the many benefits of electrochemical sensors are their superior sensitivity, paving the way for reduced LODs and LOQs; their quick analytical response time, resulting in perfect for flow evaluation and monitoring platforms; their straightforward design, which permits an almost infinite range of geometries, electrode substances, and configurations; and their convenience of operation (easy to integrate as a detection component in a number of

analytical systems, easy to install, and inexpensive equipment). (Baranwal et al., 2022)

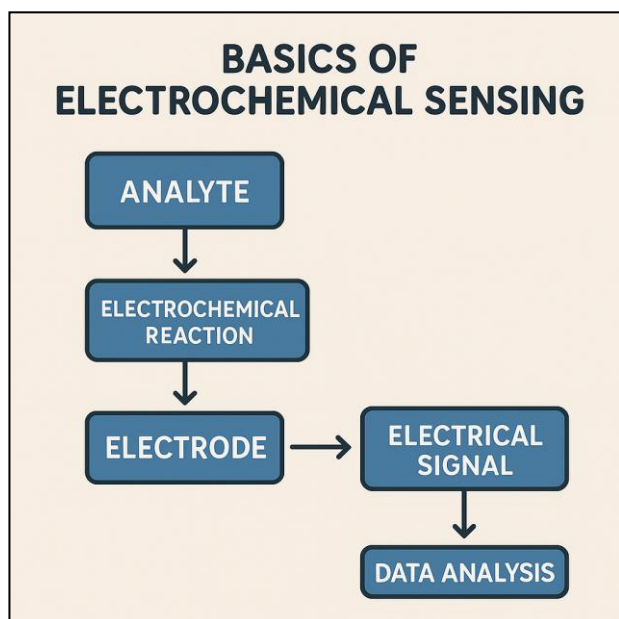


Fig. (2) Basics of Electrochemical Sensing

Because chemically modified electrodes (CMEs) can solve various intrinsic issues and promote interfacial electron transport, they have garnered considerable interest in the development of electrochemical sensors. Chemically modified electrodes are created by bonding or coating a thin layer of mono- or multimolecular, ionic, or polymeric substances onto the surface of a conducting or semiconducting substrate. In Faradaic processes, the response of the changed electrodes demonstrates the chemical or electrochemical characteristics of the modifier materials. Here, undesirable electrochemical characteristics are eliminated, and the desired ones are enhanced. The surface characteristics of bare solid electrodes are limited compared to those of modified electrodes; these include lower specificity, fewer surface functional groups, and smaller specific surface areas. The substance to be analysed cannot adsorb or undergo catalytic oxidation on the electrode surface due to these drawbacks. Consequently, scientists have concentrated on developing chemically modified electrodes. (Ghalkhani and Ghorbani-Bidkorbeh, 2019) (Qin et al., 2024) (Saraksanou et al., 2023)

IV. GRAPHENE OXIDE IN ELECTROCHEMICAL SENSORS

With its characteristic honeycomb configuration, where atoms are joined by sp^2 bonds, graphene has a distinctive two-dimensional, single-layered structure that endows it with remarkable capabilities. Graphene is used as an electrochemical sensor and as an ideal conducting surface with a vast

surface area for the collection of catalytic nanoparticles (NPs). Owing to its remarkable qualities —such as large surface area, high electrical, thermal, and optical conductance, better durability, ease of functionalization, and superior biological compatibility —graphene has attracted considerable interest in electrochemical sensor research. Graphene-based nanomaterials have unique and practical morphological characteristics that make them ideal for sensing applications. Furthermore, graphene exhibits outstanding electrocatalytic activity, enabling improved selectivity and reduced overpotential. Owing to these characteristics, graphene is an ideal material for improving the performance of electrochemical sensors. (Ananda Murthy et al., 2021) (Fu et al., 2023) (Coroş et al., 2020).

In addition, its electrical structure is highly sensitive to the local chemical environment due to its 2D shape, which effectively exposes all delocalized conjugated p -electrons on the surface. Therefore, it is an ideal material for sensing applications. While comparing graphene with carbon nanotubes (CNTs), we find that graphene has two clear advantages over CNTs, which are as follows: Firstly, unlike CNTs, graphene is free of metallic contaminants. These contaminants frequently affect the electrochemistry of carbon nanotubes. Second, graphite, which is comparatively inexpensive and readily available, is used in the synthesis of graphene. (Pumera et al., 2010) (Roy et al., 2011)

Consequently, numerous publications detailing the use of graphene or its composites in electrochemical sensors have been published in the last few years. Graphite is oxidized to create graphene oxide (GO), which is then chemically or thermally reduced. This is the most widely used and scalable method for creating graphene oxide. The only difference between graphene and graphene oxide is that graphene oxide (GO) has epoxy, hydroxyl ($-OH$), carboxyl ($-COOH$), and carbonyl ($-CO$) groups. These groups increase the interlayer distance, thereby creating a more hydrophilic layer. GO is an oxygenated graphene sheet. Reduced graphene oxide (rGO), a reduced graphene-like sheet, is produced when GO undergoes partial reduction. (Roy et al., 2011) (Ananda Murthy et al., 2021)

There are several top-down (destruction) and bottom-up (construction) methods for producing graphene, each with advantages and disadvantages related to cost, scalability, and quality. Flaws, impurities, and functional groups added during manufacturing can change the electrochemical performance and biosensing capabilities of graphene, and the synthesis process has a significant impact on the physical and chemical characteristics of the material. Top-down techniques, such as arc discharge, liquid-phase exfoliation, oxidative exfoliation-reduction, mechanical and electrochemical exfoliation, and unzipping of carbon nanotubes, typically delaminate the layers of larger precursors (graphite or other carbon-based materials) into single-, bi-, and few-layered graphene. Graphene produced by

electrochemically exfoliating graphite has a smaller layer count, a lower degree of oxidation, and superior crystallinity, making it an excellent material for electrodes. This approach shows great promise for the manufacture and processing of graphene. Graphene is created from smaller molecules using bottom-up techniques such as chemical vapor deposition, epitaxial growth, template approach, and complete organic synthesis. Despite having a vast surface area and being nearly flawless, the drawbacks of graphene made using these techniques are poor yield, high manufacturing costs, and complex experimental setups. (Fu et al., 2023) (Coroş et al., 2020)

GO is a carbon-based layered structure that can have one or more layers. It contains oxygen-containing functional groups (such as =O, -OH, -O-, and -COOH) bonded to both its layers and the borders of the sheets. It is called few-layered if it includes more than two GO layers but less than five, and multilayered when there are five to ten layers. It is referred to as graphite oxide if it possesses eleven or more layers. Graphite is oxidized to graphite oxide, which is subsequently exfoliated to produce graphene oxide (GO). The Hummers method, which introduces oxygen-containing functional groups (carboxylic acids, hydroxyl, and epoxy groups) into graphite through oxidation and exfoliation, can be used to create graphene oxide (GO). This breaks the sp^2 hybridized bonds, reducing the conductivity and stopping charge transfer. However, by boosting the catalytic activities unique to various analytes—especially the oxidation of organic molecules—various interactions can be achieved, which could simplify sensing applications. Functionalized carbon atoms with sp^3 hybrid orbitals produce reactive defect sites that allow GO to be used for surface modification, heteroatom replacement, metal nanostructure ornamentation, and size modulation of the GO sheets. (Ramirez et al., 2024)

The type and quantity of oxygen functional groups in the GO structure, which are produced via various synthesis techniques, significantly impact its unique characteristics. Because of its enormous bandgap of approximately 2.2 eV, highly oxidized graphene oxide (GO) has limited conductivity. The most popular method for creating GO is chemical oxidation, which involves modifying the amount of acid, oxidising agents, and reaction conditions to regulate the type and quantity of oxygen functional groups produced. GO, or chemically modified graphene, is produced by the exfoliation and oxidation of graphene, which significantly alters the basal plane. GO is a monolayer with a high oxygen concentration and a C/O ratio of less than 2:1;

Reduced graphene oxide (rGO) is a reduced graphene-like sheet produced when GO is partially reduced. The availability of certain oxygen-containing groups on the surface of the reduced graphene oxide (GO) is thought to be the reason why graphene-based nanomaterials also exhibit increased electrocatalytic activity to decrease O_2 and H_2O_2 . While rGO provides

greater conductivity, GO offers more functional groups for biomolecules to bond covalently. Graphite oxide can be partially exfoliated to create few-layer graphene oxide or exfoliated in solution to create (monolayer) graphene oxide. To lower its oxygen concentration, rGO is characterized as having undergone reductive processing using thermal, chemical, photochemical, microwave, and photo-thermal techniques. (Ananda Murthy et al., 2021)(Rowley-Neale et al., 2018)(Fu et al., 2023)

V. GO-SUPPORTED SENSORS FOR DYE DETECTION

Numerous studies have shown that nanomaterials from the graphene family have the potential to be efficient nanoadsorbents. The adsorption processes include the surface groups. Hydrogen bonding, π - π stacking, van der Waals forces, electrostatic forces, and other mechanisms have been identified as adsorption mechanisms. They also serve as weak sites for the exchange of acid cations. Consequently, these materials have been repeatedly shown to be good adsorbents for the elimination of various contaminants, such as radioactive compounds, dyes and heavy metal ions. For example, a range of graphene-based materials, including GO, rGO, and hybrid GO materials, have been successfully used to remove methylene blue dye over the past ten years. (Vassileva et al., 2023)

The large surface area, hydrophilicity, and abundance of oxygen-based functional groups of GO facilitate intense interactions with a variety of contaminants, including dyes. However, because the adsorption performance is strongly influenced by the degree of oxidation, surface chemistry, and textural characteristics of GO, research on the adsorption mechanisms of GO for various dyes is still underway. According to an increasing amount of research, GO's adsorption ability can be greatly improved by modifications such as functionalization, reduction, and hybridisation with other materials. The carboxyl and carbonyl groups were dispersed toward the G and O margins, whereas the hydroxyl and epoxy functional groups were adorned on the basal plane. Vacancies and sp^3 -bonded atoms are the most prevalent surface defects in rGO. GO and rGO can readily interact with organic and inorganic substances through covalent or non-covalent interactions when these functional groups or defects are present. (Guerrero-Fajardo et al., 2025)(C.R. et al., 2017)

Owing to the presence of aromatic rings in each of the interacting parts, the π - π interaction is yet another significant interaction that is common in dye-graphene systems, in addition to electrostatic attraction. It is anticipated that the partially reduced graphene oxide obtained by eliminating a few oxygen-containing groups from GO exhibits three characteristics that are advantageous for dye adsorption. First, reduction restores the conjugated structure of graphene oxide (GO), which

improves the π - π interaction between the dye and the graphene-based adsorbent. Second, GO undergoes partial reduction, resulting in hydrophobicity that aids the recovery of the graphene-based adsorbent after adsorption. Third, to achieve appropriate adsorption performance, the reduction conditions can be controlled to control the morphology and porosity of GO. (Bulin and Guo, 2023)

The dense and extended aromatic system of a pristine G monolayer, which has a nearly planar shape, extensively interacts with tiny aromatic molecules. However, GO can be characterized as a non-aromatic surface with sp^3 carbon atoms and isolated tiny aromatic regions or sp^2 domains, whereas rGO has fewer aromatic features. Moreover, long-term departures from the planarity of GO are introduced by the presence of sp^3 carbon atoms (bonded with oxygen groups). These two key components are meant to distinguish the behavior of GO and rGO from that of G in relation to interactions with aromatic molecules. However, the behavior of G nanostructures is not necessarily the same as that of other aromatic compounds. The ability of aromatic molecules to donate or remove electrons, as well as their substituents, size, and planarity, all affect π - π interactions. GO adsorbents can achieve improved dye removal efficiency by adjusting their surface functions and oxidation levels, thereby addressing important wastewater treatment issues. GO adsorbents can achieve improved dye removal efficiency by adjusting their surface functionalities and oxidation levels, thereby solving important wastewater treatment issues. (Georgakilas et al., 2016) (Guerrero-Fajardo et al., 2025)

Although the hydrophobic and π - π stacking interactions are weaker than the electrostatic interactions, their predominance is beneficial because they facilitate the desorption and repurposing of graphene materials as adsorbents. Compared to graphene oxides (GOs), reduced graphene oxides (rGOs) often have a larger surface area, more organized graphene sheets with a higher sp^2 carbon content, and altered functional group composition. These features indicate that rGOs often encourage the adsorption of hydrophobic and nonpolar substances on their surfaces. The ability of polar molecules to be adsorbed preferentially onto rGOs controlled by hydrophobic contact is intriguing. (Justino et al., 2023)

Let us consider the case of the interaction between methylene blue (a textile dye) and the surface of GO. The enhanced adsorption ability of the GO materials, with their abundant oxygen-containing functional groups, significantly influenced the adsorption of Methylene Blue. Covalent bonding, electrostatic attraction, and cation exchange with MB dye are all made possible by functional groups that include oxygen. Electrostatic/ionic interactions between the positively charged structure of MB and negatively charged groups, such as $-OH$, $-COOH$, $-C=O$, and epoxy on the base plane and edges of GO, as well as π - π interaction and conjugation based on

the electron donor-acceptor interaction with the hexagonal GO structure, are responsible for the MB adsorption mechanism. The interaction between the π electrons in the $C=C$ bond of the MB structure and the π electrons in the GO hexagonal lattice is the primary mechanism of adsorption. (Ederer et al., 2022)

VI. ANALYTICAL PERFORMANCE

6.1 Detection Limits, Sensitivity, and Selectivity

Conventional methods, including Atomic Emission Spectroscopy (AES), Atomic Absorption Spectroscopy (AAS), and ICP-MS, give accurate results but require large samples, lengthy sample preparation, trained manpower and an expensive instrument. These conventional methods are laboratory-based, non-portable, have low sensitivity, and have limited detection limits. (Jayaraman et al., 2022b; Manami et al., 2025b; Obeidat and Rawashdeh, 2025a; Shan et al., 2022b)

Electrochemical sensors are employed in modern ways to measure voltage or current signals and identify substances. It is inexpensive, easy to use, has a low detection limit, good selectivity, is portable, and can be used for monitoring tasks. (Jayaraman et al., 2022b; Manami et al., 2025b; Obeidat and Rawashdeh, 2025b; Shah et al., 2022; Singh et al., 2022b; Sreelekshmi et al., 2025; Wang et al., 2021). An electrochemical sensor based on graphene can detect heavy pollutants in wastewater by improving selectivity and sensitivity and lowering the limit of detection (LOD). (Benjamin and Miranda Ribeiro Júnior, 2022, 2022; Dutt et al., 2024; Ganie et al., 2023; Khan et al., 2025)

The sensitivity of an electrochemical sensor is its capacity to detect even the smallest shift in electrical signal voltage or current in response to a tiny shift in the analytical concentration. The slope of the calibration curve often serves as its representation. Electrochemical sensors provide a high limit of detection (LOD), fast response, and good sensitivity. When combined with graphene oxide, these sensors offer additional benefits, such as a high surface area, electrical conductivity, oxygen groups, and increased electron transfer sensitivity. (Ahamad et al., 2025; Baranwal et al., 2022; Hayat et al., 2022; Shen et al., 2024; Shirsat and Hianik, 2023; Sinha et al., 2022)

The capacity of a sensor to precisely identify a certain substance, even when other substances interfere, is known as selectivity. Graphene oxide-based electrochemical sensors have great sensitivity and aid in the detection of heavy substances such as lead, cadmium, and arsenic. (Irfan et al., 2022)

6.2 Real wastewater applications and case studies

Wastewater results from water contamination. Pharmaceuticals, pesticides, drugs, personal care items, cosmetics, cleaning supplies, surfactants, industrial solvents and compounds, food packaging materials, food additives, metals, and chemicals with high persistence and toxicity are examples of contaminants. To determine the

harmful effects of potential toxicants on humans, animals, and plants, it is crucial to determine and monitor the contaminants in water. Electrochemical sensors are essential for identifying chemical species, including molecules, ions, and bacteria, in water and other environments. They also assist in providing the Limit of Detection (LOD) and Limit of Quantification (LOQ), which are critical metrics for the detection of water pollution.(Çelik et al., 2025).

Water samples from the food, fertilizer, and battery production industries were used in this case study. Pb^{2+} , Cd^{2+} , Cr^{3+} , Cr^{6+} , Ni^{2+} , Hg^{2+} , Cu^{2+} , Zn^{2+} , and Co^{2+} ions, as well as rocks from agricultural and sewage disposal waste, were found in the collected wastewater. A reduced graphene oxide (rGO)-based electrochemical sensor uses metals, metal oxides, polymers, silica, and other materials. Wastewater can detect the limit of detection (LOD), limit of quantification (LOQ), recovery percentage, stability rate percentage, stability, reproducibility, selectivity, and sensitivity.(Joshi and Gururani, 2022).

6.3 Stability and Reproducibility Issues

Reproducibility refers to the consistency of results under the same settings with multiple sensors, whereas stability refers to the capacity of an electrochemical sensor to provide correct results over time. Electrochemical sensors typically operate in wastewater with high levels of contamination and are inexpensive, portable, and easy to handle. Over time, problems with the stability and sensitivity of electrochemical sensors, along with issues in their repeatability and selectivity, cause them to produce inaccurate data.(Hassan et al., 2022; Liu et al., 2023)

VII. EMERGING TRENDS

7.1 GO–nanocomposites (metal/metal oxides, polymers)

Graphene-based electrochemical sensors use nanocomposites to combine two or more materials, enhancing their benefits. Various metal, metal oxide, and polymer-based nanocomposites have been employed. The large surface area and numerous oxygen functional groups of graphene-based electrochemical sensors are advantageous; however, their low conductivity is a drawback that must be addressed. The use of nanocomposites has several advantages. Benefits include good conductivity, catalytic activity, and stability when using meta-composites such as gold (Au), silver (Ag), platinum (Pt), and copper (Cu); higher selectivity, improved sensitivity, and durability when using metal-oxides such as ZnO and other metal oxides in combination; and high strength, high thermal activity, and flexibility when using polymers such as Nafion and PPY. (Gautam et al., 2024; Ibrahim et al., 2021; Pengsomjit et al., 2025; Saeed et al., 2024).

7.2 Integration with portable and wearable devices

Combining electrochemical sensors with portable and wired devices can make the system lighter,

reduce power consumption, improve detection, enhance user-friendliness, and maintain high selectivity and sensitivity. Graphene-based electrochemical sensors are the best option because of their high surface area, sensitivity, flexibility, and compatibility with other electronics. Traditional methods, such as chromatographic and spectroscopic techniques, are primarily laboratory-based, costly, and non-portable.(Alves et al., 2021; Sainz-Urruela et al., 2021).

7.3 Microfluidics, lab-on-chip, IoT-enabled sensing

Microfluidics, lab-on-a-chip, and Internet of Things (IoT)-enabled technologies are being used in the most recent emerging trends in sensing. When combined with graphene-based electrochemical sensors, these technologies provide cost-effective, portable, and easy-to-handle results. They also provide high sensitivity and selectivity, enabling them to detect heavy contaminants in wastewater. These technologies are superior to traditional methods, which are lab-based, time-consuming, and inconvenient to handle.(Battat et al., 2022; Queijo et al., 2025; Sunaina et al., 2022)

VIII. CHALLENGES AND LIMITATIONS

Although graphene-based electrochemical sensors offer numerous advantages, they also have certain drawbacks, such as problems with stability, repeatability, selectivity, and sensitivity, as well as difficulties with fabrication and integration. Long-term use of electrochemical sensors can be difficult and can result in electrode fouling. Other stability difficulties include repeatability, where various sensors produce different results that can affect reproducibility, and interaction with compounds in wastewater that can impact sensitivity and selectivity. Employing nanocomposites and wearable and portable electronics can be expensive.(Anik et al., 2022; Liu et al., 2023; Verma et al., 2023).

IX. FUTURE PERSPECTIVES

High selectivity, sensitivity, detection limit, and fast response time are all areas where electrochemical sensors have great potential for future improvement. They can also be made more cost-effective, stable, and reproducible by combining them with various nanocomposites, polymers, metals, and metal oxides. They can also be enhanced by combining them with portable and wireless devices. These recent, trendy additions to electrochemical sensors aid in wastewater monitoring.(Alves et al., 2021; Anik et al., 2022; Pengsomjit et al., 2025; Sainz-Urruela et al., 2021; Singh et al., 2022a).

X. CONCLUSION

The goal of this research is to create an electrochemical sensor that is far more effective than

conventional techniques in detecting heavy substances. Given the many advantages of graphene, this review discusses graphene-based electrochemical sensors. High surface area, mechanical strength, and electrical conductivity; combining electrochemical sensors with nanocomposites of metals, metal oxides, and polymers to enhance their benefits; and utilising wearable technology, portable devices, microfluidics, lab-on-a-chip, and the Internet of Things to further enhance their benefits and future developments. Electrochemical sensors provide fast response, enhanced stability, reproducibility, and enhanced selectivity, sensitivity, and detection limit.

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