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INTERNATIONAL JOURNAL OF PROGRESSIVE RESEARCH IN ENGINEERING MANAGEMENT AND SCIENCE (IJPREMS)
(Int Peer Reviewed Journal)
Vol. 05, Issue 09, September 2025, pp : 685-694

e-ISSN : 2583-1062
Impact Factor : 7.001

ADVANCED VOLTAMMETRIC AND ANALYTICAL TECHNIQUES FOR NANOPARTICLE-BASED DRUG DELIVERY SYSTEMS

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DOI: https://www.doi.org/10.58257/IJPREMS43800

ABSTRACT

When combined with nanotechnology, advanced voltammetric and electroanalytical techniques have greatly improved the sensitivity, selectivity and adaptability of drug delivery systems based on nanoparticles (NDDS). Even at trace levels, these methods—which include cyclic voltammetry, square wave voltammetry and stripping voltammetry—allow precise identification and measurement of medications, biomarkers and environmental pollutants. By increasing surface area, conductivity and functionalization, the use of nanomaterials enhances electrode performance and makes treatment monitoring and real-time point-of-care diagnostics easier. Additionally, advancements like wearable technology, multipurpose hybrid sensors, green synthesis of nanomaterials and artificial intelligence-assisted data analysis are opening the door to scalable, customized and sustainable healthcare solutions. These developments collectively establish voltammetric methods as potent analytical instruments for contemporary clinical diagnostics, environmental safety and pharmaceutical research.

Keywords: Voltammetry, Electroanalytical Methods, Cyclic And Stripping Voltammetry, Nanomaterials, Biosensors And Nanoparticle-Based Drug Delivery Systems (NDDS).

1. INTRODUCTION

In various areas of pharmaceutical, therapeutic and medical research, analytical measurement techniques are essential. Since human biological responses and electrochemical responses at the electrode–solution connection have an identical collection of electron transmission methods, the use of electrically conductive techniques in pharmaceutical and biomedical analysis has developed significantly in the last ten years. The electrochemical oxidation/reduction mechanism provides the basis for many significant physiological, enzymatic and other biochemical activities (1,2,3).

The wide range of the reagent (chemical compounds), superior enantio-selectivity of the metabolites within the example of aromatic drugs, and the ability to clarify the mechanism for novel drug substances make electroanalytical techniques far more significant than other techniques like titrimetry, radiometry, spectrophotometry, chromatography and capillary electrophoresis. While the effectiveness of the techniques mentioned above, the quantification of small and extremely small components in complex analytes has drawbacks with regard to extraction and separation, the substantial impact of the matrix from naturally occurring substances in living things and pharmacological doses.

Because electrochemical technologies are highly sensitive, selective, reproducible, portable and inexpensive, they offer an ideal solution for the detection and analysis of biological fluids, pharmaceutical compounds and enantiomeric drug discrimination. Developed in the 1920s by the famous Czechoslovakian chemist Jaroslav Heyrovsky, voltammetry is an electroanalytical technique that has become a vital tool in the analytical toolbox for the examination of numerous pharmacological compounds (4).

Potential changes continuously as a linear function of time in cyclic voltammetry (CV) and linear sweep voltammetry (LSV). By using an electrochemical method called Differential Pulse Voltammetry (DPV), the cell current between the indicator and reference electrodes is measured as a function of time and potential. A waveform made up of a symmetrical square wave is compared with DPV using the large amplitude differential technique known as square wave voltammetry (SWV). A very quick response and a minimal quantity of electroactive species are achieved by the efficient high scan rate.

The term "stripping voltammetry" (SV) refers to a group of voltammetric techniques that are primarily divided into four types: anodic (ASV), cathodic (CSV), adsorptive (AdSV) and potentiometric (PSV). Through this method, the chemicals produce on the conducting layers for the diluted specimens by a preconcentration phase. The electrical behavior is then measured, allowing for the detection of medicinal substances at the trace level.

Drug delivery techniques based on nanoparticles can increase drug permeability and solubility across lipophilic barriers (5,6,7). Polymeric, metallic and lipid-based nanoparticles are frequently used for medication delivery (8,9). It

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e-ISSN : 2583-1062
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is well known that nanoparticles from metals, such as gold atoms, have great attraction for nerve cells in the brain. (10).

2. VOLTAMMETRIC TECHNIQUES: AN OVERVIEW

The word "voltammetry" comes from "volt-amperometry." The word "polarography" was first used to refer to this technique, which is now frequently used for "voltammetry with a dropping mercury electrode." This process is referred to as "electrochemistry." Since these methods are more numerous than any other electroanalytical method, the term "electro-analysis" is frequently used to describe them. This gives a quick overview of voltammetry, one of the key methods in electroanalysis.

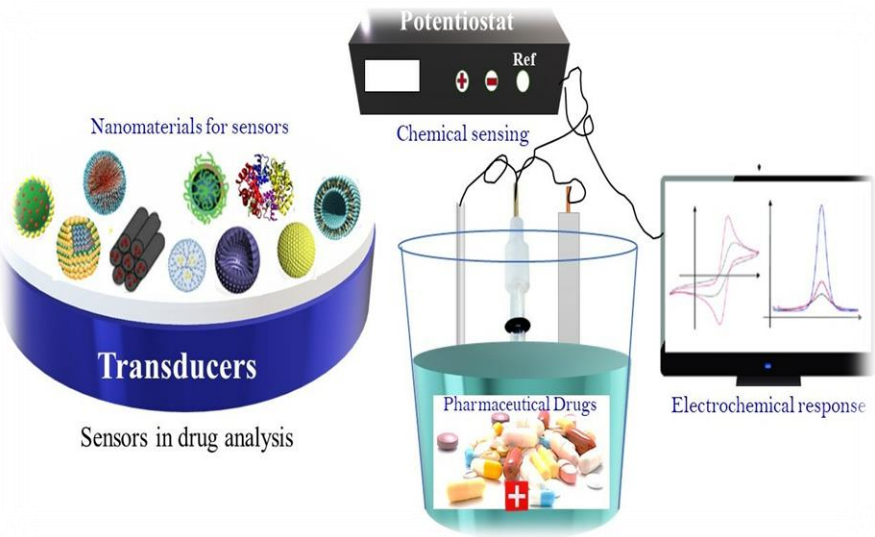

Figure 1: Analysis of nanoparticle-based drugs

The method primarily involves measuring the flow of current (I) using working electrodes immersed in a solution containing an electroactive sample that will be examined by altering voltage (v) in a systematic manner. Due to its ease of use, affordability and speed in identifying biologically and environmentally important species, this approach is becoming more and more significant nowadays. Because the analyte can be easily identified by its voltammetric peak potential, it provides the highest level of selectivity and sensitivity (11).

Basic principles of voltammetry

In the electrochemical procedure known as voltammetry, an electrode immersed in a mixture of electrolytes holding an appropriate component is exposed to a variable potential. The traceable voltage created by the compound's oxidation (reducing to oxidizing) responses at the top of the electrode is measured as an indication of the voltage that is used. During this process, the bioactive molecule undergoes electron transfer, which may result in reduction or oxidation. The current that results is precisely equal to the amount present within the analyte. To make these measurements simple, a three-electrode configuration is typically utilized. Nanomaterials are commonly added to the conducting electrode, which serves as the active site for redox reactions, to increase sensitivity and selectivity.

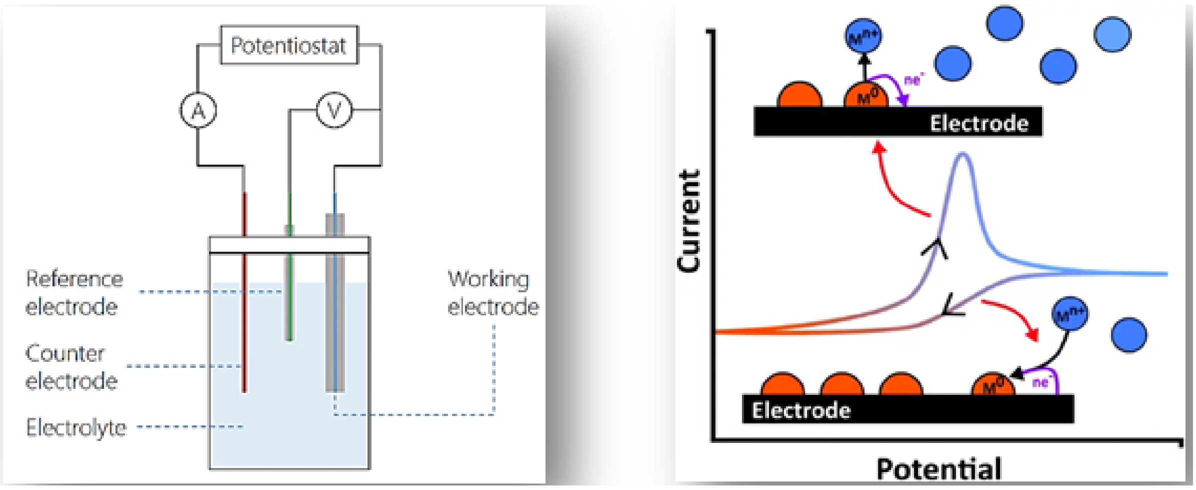

Figure 2: Principles of Voltammetry

In order to guarantee an accurate comparison, the reference electrode maintains a steady and constant voltage while the opposite electrode ends the electrical system and allows current to flow. Essential information for identifying and measuring specific analytes is provided by the relationship between the current being detected and the voltage being used, which is based on their electrochemical properties. Voltammetric sensors' adaptability can be applied to a wide range of analytical applications, enabling precise and reliable detection of the desired molecules within challenging test mixtures (44,55).

2.1 Linear Sweep Voltammetry:

Linear sweep voltammetry (LSV) is a very frequently used potential sweep technique.

Applying a quick, one-way potential scan at the working electrode, which usually ranges from 20 to 100 mV/s and changes linearly with time, is the most basic technique (12). A linear potential waveform, in which the potential E varies gradually over time t, serves as the basis for the working electrode's signal. From the initial potential (Ei), the final potential (Ef) is obtained. In LSV, the possible area under study is scanned. In an LSV experiment, the typical reaction is a peak-shaped curve (13,14).

2.2 Cyclic Voltammetry:

Cyclic voltammetry is a highly utilized technique for potential sweeps (CV). Since the possible scanning's path shifts after the initial scan, CV is amplification of LSV. Accordingly, the final potential becomes the starting point for the next scan and the reversal point is referred to as the switching potential, or Eλ1.

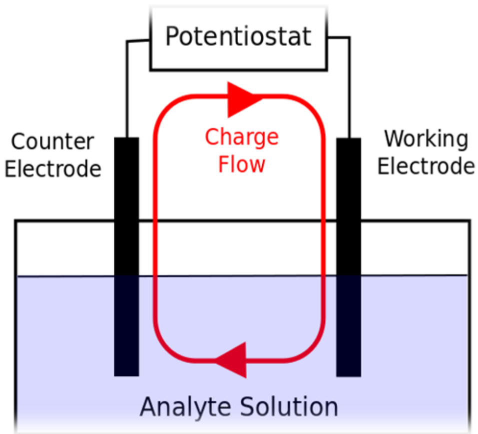

Figure 3: Cyclic Voltammetry (CV)

2.3 Differential Pulse Voltammetry:

The characteristics of linear sweep voltammetry and pulsed voltammetry are combined in differential pulse voltammetry (DPV). Detecting chemicals at concentrations as low as parts per billion or fewer is possible with this extremely sensitive approach. It is very helpful for examining organic chemical traces. However, because to the waveform's many pulses, individual scans can take several minutes, making the procedure comparatively slower (12). A disturbance is produced by superimposing a sequence of pulses with a set amplitude on top of a staircase waveform. The current is initially measured at the beginning of each pulse and then again at the end, in contrast to standard pulse voltammetry (NPV). The symmetric peaks (15,16,17) define the answer. The applied potential, E, is used to record and display the difference between these two current values.

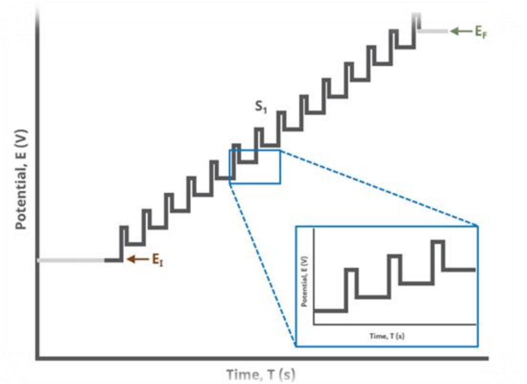

Figure 4: Differential Pulse Voltammetry (DPV)

2.4 Square Wave Voltammetry:

In analytical work, the most modern and popular pulse method is Square Wave Voltammetry (SWV). A square wave is a wave with an elevated wavelength (20–100 Hz) is administered at each step of a rapid potential scan at the electrode in this development of the pulse approach (12).

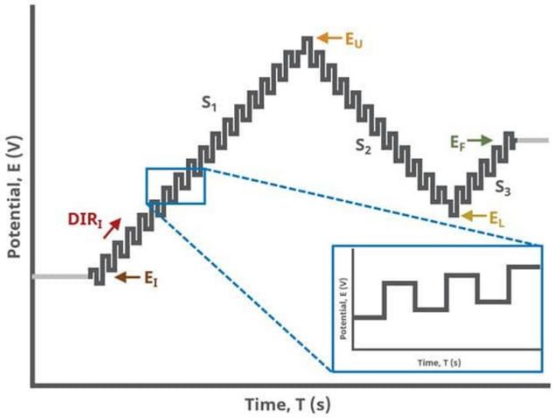

Figure 5: Square Wave Voltammetry (SWV)

2.5 Stripping Voltammetry:

A fluid-filled electrode that looks like a mercury electrode, must first produce electroactive material on its surface or inside its core in order to begin stripped electrical operations. The sort and amount of electrically reactive substances are determined by stripping voltammetry (SV), which is the second stage. It involves polarizing the electrode and recording cathodic or anodic voltammograms (15,18).

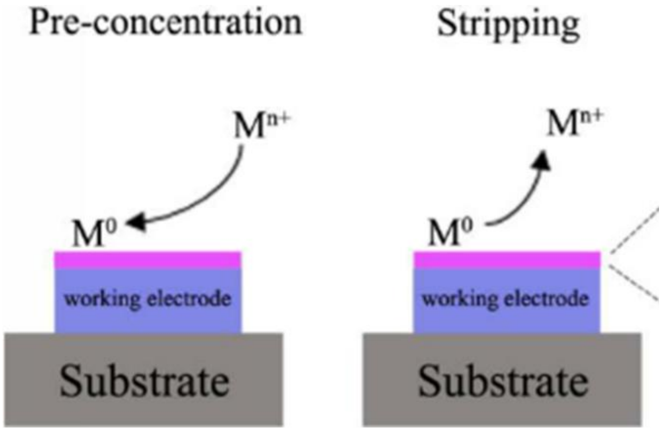

Figure 6: Anodic Stripping Voltammetry (ASV)

2.6 Chronopotentiometry:

Chronopotentiometry is a method for measuring variations in voltage continuously by using a constant current or a voltage step to the electrode. It is better suited for quantifying larger concentrations of substances compared to more common voltammetric or polarographic methods (12).

2.7 Chronoamperometry

Square wave pulses are used in the voltage measuring technique known as chronoamperometry. The proportion of the maximum oxidizing voltage compared to the max reduced voltage provides only a tiny bit of info about the dissolved component. But like other pulsed techniques, chronoamperometry produces powerful charging currents that diminish rapidly with time. Each scan in the delayed pulse mode, which avoids electrode fouling, takes roughly one second. Chronoamperometry has a high signal-to-noise ratio due to its ability to monitor current over extended time periods (12).

3. APPLICATIONS OF VOLTAMMETRY IN NANO DRUG ANALYSIS

3.1 Food Contaminants: Heavy Metals, Pesticides and Toxic Substances:

Food contaminants are harmful substances that are unintentionally introduced into food due to natural sources, environmental factors, or processing methods. The most common method for detecting heavy metals such as lead, cadmium, and mercury in food matrices is differential pulse stripping voltammetry (DPSV). Lead, cadmium and arsenic levels in wholemeal, wheat, and maize have also been analyzed using square wave stripping voltammetry

(SWSV). Alternative DPASV techniques employ a circular gold circle cathode and a Nafion-coated antimony film cathode instead of the suspending mercurial electrode because of its toxicity and inconvenience (15,19,20,21). Food can also contain pesticides, including insecticides, herbicides and fungicides.

Furthermore, cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) using a hemoglobin-modified carbon paste electrode have been effectively employed to assess the amount of acrylamide present in chips made from potatoes (23).

3.2 Trace Essential Elements:

Minerals and small amounts of elements are crucial for healthy human growth and development. On the other hand, deficits or health issues may result from excessive amounts, buildup, or inadequate intake. Some of the most essential substances in food are copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), cobalt (Co), and selenium (Se). Using flame atomic absorption spectrometry is the standard method for analyzing food trace metals. Stripping analysis in conjunction with Cu chelate adsorption buildup has demonstrated good sensitivity among electrochemical techniques. Nevertheless, over time, chelates and metal might firmly adhere onto the semiconductor's outermost layer. A platinum-based rotary plate cathode can be used in anodic stripping voltammetry to measure the Cu levels in alcohol samples eliminating a need for Cu-complex formation (24).

3.3 Food Additives:

Numerous compounds are employed in the food industry as flavoring, coloring, texturizing, nutritious and preservatives. However, while food additives have been reported to provide positive aspects, consuming higher amounts of these substances than is advised can have harmful consequences. To prevent the development of microbes and the discoloration caused by spontaneous aging processes, sulfite, for instance, was initially utilized as an additive to food. Among other things, it is present in pickles, coconut water, vinegar, juices, wine and dried fruits and vegetables. But it has been linked to hypersensitivity that aggravates asthmatic symptoms and causes nausea, diarrhea, gastric irritation, nettle rash or swelling. Titration, photometry and iodometry are the approved methods for identifying sulfites in foods and beverages; these methods require lengthy analytical times and sample pretreatment.

Alternative electrochemical techniques, on the other hand, have recently been put forth that calculate the quantitative reduction of sulfur dioxide and bisulfite that results from acidifying sulfite-containing samples (25,26). Food samples have not been pretreated in order to quantify azo chemicals, amaranth, carmine, ponceau 4R, sunset yellow and tartrazine using electrochemical methods such CV, DPV and adsorptive square wave stripping voltammetry (AdSWSV). For example, sensitivity has been successfully increased using glassy carbon electrodes modified with bismuth/poly (p-aminobenzene sulfonic acid) (27), copper tetrasulfonated phthalocyanine (CuTSPc) and iron (III) tetra-(N-methyl-4-pyridyl)-porphyrin (FeT4MPyP) alternated layers, acetylene black nanoparticles (28,29), magnetic Fe3O4 and gold nanoparticles (32,33).

3.4 Nutraceuticals: Phenolic Acids, Flavonoids and Others:

In addition to providing basic nutrition, organic foods like veggies, fruits, and grain products that are high in biologically active phytochemicals, also referred to as nutritional supplements, may offer positive medical advantages by lowering the incidence of long-term illnesses like tumors, heart disease, and other aging-related pathologies. The observed biological effects are caused by the multiple, additive, antagonic and synergistic actions of nutritional chemicals found in the dietary habits; for this reason, it is essential to accurately detect and measure these substances in food. These organic molecules have been quantified using a range of working electrodes in conjunction with many sweep potential electrochemical techniques, including CV, AdSV and SWV (34).

The number of articles evaluating the anti-inflammatory properties of supplements, pure substances and processed foods has increased significantly due to the possible physiological advantages of dietary antioxidants. Ferric reducing antioxidant power (FRAP) assays, 1,1-diphenyl-2-picrylhydrazyl (DPPH), oxygen radical absorbance capacity (ORAC) and 2,2′-azinobis-3-ethyl benzothiazoline-6-sulfonic acid (ABTS) assays are among the most widely used techniques to assess antioxidant capacity. However, electroanalytical methods are becoming a more dependable, quick and economical way to assess the antioxidant content of intricate biological and dietary samples (34,35). CV and DPV are the two electrochemical methods most frequently used to assess antioxidant capability. Since the oxidation potential and antioxidant capacity are conceptually closely coupled, they have inherent analytical potential.

As a result, it is anticipated that the oxidation potential determined from the testing of the desired substance will decrease with increasing levels of antioxidants. Moreover, the amperometric current and/or charge measured during constant redox situations can be connected to the increase of the antioxidant capacity and the computation of the overall amount of reactive chemical families in the sample. The "electrochemical index" (EI) idea refers to the total amount of antioxidants that are obtained by selectively oxidizing them at different target potentials (36). In this way, CV was implemented to evaluate the anti-aging properties of wines (40), seaweeds (39), cane and palm sugar (38) and dark fruit juices (37). Additionally, the antioxidant activity of red liquor and grape juice has been assessed using DPV and SWV, respectively (41,42).

3.5 Biomarker detection:

Accurately identifying biomarkers is crucial for early illness detection and physiological condition monitoring in medical diagnostics. Voltammetric sensors designed with nanomaterials have shown remarkable efficacy in identifying important biomarkers as serotonin, dopamine, the vitamin C and urea. For example, inside sophisticated cellular environments, GO-modified sensors have demonstrated outstanding sensitivity and selectivity in the simultaneous detection of uric acid and dopamine (44,45,46).

3.6 Monitoring neurotransmitters and metabolites:

Parkinson's disease and depression are linked to abnormalities in neurotransmitters like dopamine and serotonin, which are essential for neurological function. Such neurotransmitters can be easily and precisely monitored in continuous time utilizing voltage-based detectors enhanced with nanostructures (47). The early detection of arthritis and associated problems has also been made possible by the use of modified zinc oxide electrodes to monitor metabolites in serum specimens, such as uric acids (48).

3.7 Detection of pollutants, heavy metals and toxins:

For ecological surveillance to evaluate pollutants and toxins in air, water and soil, extremely sensitive and reliable detection devices are needed. Heavy metals that present serious ecological and health hazards, including zinc (Zn^{2+}), lead (Pb^{2+}), cadmium (Cd^{2+}), copper (Cu^{2+}), strontium (Sr^{2+}) and mercury (Hg^{2+}), can be detected with greater accuracy using voltammetric sensors modified with nanomaterials (49). Lead (50) and cadmium ion detection using AuNP-modified sensors has shown great sensitivity, with detection thresholds exceeding required standards (50,52). Carbon-based products have also been used to monitor biological contaminants, such as phenols and endocrine disruptors, in water systems. These sensors' nanomaterials' strong conductivity and adsorption capacity enable quick and precise detection (53,54).

4. FUTURE DIRECTIONS AND EMERGING TRENDS

Although voltage-based detectors enhanced by nanomaterials have shown remarkable potential for identifying the presence of biologically active substances, there are many chances for additional development given the rapidly changing technological and scientific scene. The main emerging trends covered in this section include the invention of portable and implantable electronics, the integration of detectors with digital platforms, the use of artificial intelligence (AI) for data visualization, the environmentally friendly production of nanomaterials and the investigation of combination and multipurpose sensing technologies.

4.1 Integration with digital and portable devices:

Voltage detector communication with electronic and handheld electronics is a game-changing movement that aims to improve real-time monitoring, accessibility and usability. When paired with wireless connectivity gadgets like Bluetooth and Wi-Fi, portable sensing systems allow for easy data transfer to cloud-based platforms, smartphones and tablets. End users can quickly make decisions in medical testing, environmental surveillance and food quality because to these systems' immediate access to analytical results (44,56). When the use of advanced testing equipment is not available in remote and resource-constrained environments, this kind of integration is especially advantageous. Autonomous operation is made possible by miniature devices with signal processors and microcontroller units (MCUs), which makes sensor deployment in field applications much easier.

4.2 Development of wearable and implantable sensors:

The future of illness management and individualized health monitoring lies on wearable and implanted sensors. With their excellent sensitivity and biocompatibility, nanomaterial-modified voltage detectors are perfect for continuous biomarker detection using non-invasive or minimally invasive techniques. The metabolites like blood sugar, lactate, and urinary acids can be directly monitored from perspiration, saliva or interstitial fluid using wearable technology with sensors, including electronic watches or sticky pads (57). However, implantable detectors provide unmatched accuracy in monitoring biomarkers in the body, allowing for the early identification of diseases like cancer or metabolic problems. Long-term stability and little discomfort can be assured in biological conditions by employing adaptable, compatible substances like graphite and polymeric nanoparticle hybrids (58).

4.3 AI and machine learning (ML) for data analysis:

Voltammetric sensor data processing, analysis and interpretation are being completely transformed by the use of AI and ML. nevertheless with the addition of disturbance or disruption. ML techniques, such as support vector machines and neural networks, can be trained to identify complex trends in electrical data, improving both the accuracy and dependability of finding analyte (59). AI-powered solutions optimize sensor performance in dynamic situations by enabling adaptive calibration, anomaly detection and predictive modeling. The establishment of graphical user interfaces for beginners is made easier by combining machine learning with electronic products, which increases the utilization of these sensors across a variety of industries (60).

4.4 Green synthesis of nanomaterials:

Research on sustainable and eco-friendly production methods has been spurred by growing concerns about the negative ecological effects of nanotechnology development. In order to produce nanomaterials with minimal negative effects, green synthesis techniques employ natural antioxidants, such as plant compounds, proteins, or microbes (61). By reducing environmental harm and enhancing the biocompatibility of the generated nanomaterials, this technique increases their suitability for use in biomedical and food safety applications. In order to coordinate device manufacturing techniques with worldwide ecological demands, efficient ecologically friendly synthesis methodologies must be developed.

4.5 Emerging hybrid technologies and multifunctional sensors:

The creation of combination methodologies, which integrate advanced functional components in nanotechnologies, has opened doors to versatile sensors that can solve difficult analytical problems. Mixed systems, which include metal oxide films that include magnetic polymers or metallic–carbon composites, use the benefits of each of their COM elements to provide greater reactivity, flexibility, and adaptability (62). Several analytes can be analyzed concurrently on only one system because to these sensors' multiplexed detection capability. Dual-function detectors were recently invented to concurrently identify transmitters, vitamins, and toxic substances, indicating their adaptability and efficiency (63). Adding energy-harvesting elements, like piezoelectric material or solar-energy materials, to hybrid sensors improves their capabilities even further and enables self-powered operation in remote applications.

5. CONCLUSION

The analysis and monitoring of nanoparticle-based drug delivery systems has been completely transformed by advanced voltammetric and electroanalytical techniques combined with nanomaterial-based sensors. These methods offer continuous monitoring, high sensitivity, and specificity for a variety of analytical substances, including chemical pollutants, ingredients in food, medicinal compounds, and indicators. Even at trace quantities and in intricate biological matrices, these methods—which include cyclic voltammetry, differential pulse voltammetry and stripping voltammetry—allow for accurate measurement. By increasing conductivity, surface area and selectivity, nanomaterials improve electrode performance and are therefore very useful for environmental monitoring and clinical diagnostics. Future advancements in ecological nanotechnology manufacturing, portable and injectable detectors, machine learning-driven data processing, and versatile mixed sensors technologies could lead to a greater application of these technologies in health care diagnostics, customized treatment, and sustainable sensing.

ACKNOWLEDGEMENTS

"The authors thank the researchers whose work has been cited in this article for their valuable contributions to the field."

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