

Review Article

Quantification of Caffeine Concentration: An Electrochemical Method: A Review

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Abstract: Caffeine is found in coffee bean and leaf, tea, coconut, soft drinks, different food items and pharmaceuticals. Concentration of caffeine found in different samples is not identical. Several conventional techniques have been developed for caffeine (CAF) determination. Due to their high sensitivity, selectivity, and low detection limit, chromatographic techniques such as liquid chromatography (LC), gas chromatography (GC), high performance liquid chromatography (HPLC,) and spectroscopic techniques such as mass spectroscopy (MS), near infrared ray spectroscopy (NIRs,) coupled with detectors such as photodiode array (PDA), detector, Refractive index (RI) detector, diode array detector (DA) All of these procedures, however, are sophisticated, time demanding, and need expensive equipment. In this aspect, the electrochemical technique overcomes those shortcomings due to its low cost, quick response, and use in on-site testing. It offers a number of advantages, including the fact that it requires little time, a little amount of chemicals, and does not yield complicated results. Recent breakthroughs in the electrochemical application of nanoparticle modified electrodes for caffeine detection in food, coffee bean, beverages, and medicinal formulations are discussed. As a result, the primary goal of this work is to discuss the advantages of adopting electro analytical methodologies over traditional methods for caffeine measurement using nanoparticle modified electrodes. For a multiple of advantages, electrochemical methods of caffeine quantifications are preferable.

Keywords: Caffeine, Electrochemical Methods, Modified Electrodes, Nanoparticle

1. Introduction

Caffeine ($C_8H_{10}N_4O_2$, CAF), also known as 1,3,7-trimethylxanthine is one of the naturally occurring xanthine alkaloids found in plant products and beverages such as coffee, cola nuts, cocoa beans, coffee beans, tea leaves, yerbamate, guarana berries, and several other plants. It serves as a central nervous system stimulant, increasing alertness, decreasing sleep, and improving short-term memory. It stimulates the human central nervous system, increases calcium excretion in the urine, and boosts calcium secretion in the small intestine, resulting in bone mass loss and its physiological effects are proportional to its consumption. It can assist to improve focus and raise glomerular filtration rate (GFR), which promotes toxin excretion in moderate doses [1-3]. It also becomes one of the most extensively used medications in the world, with numerous key pharmacological

effects such as central nervous system stimulation, diuresis, and a beneficial influence on the cardiovascular system [4].

However, excessive CAF consumption can result in a variety of negative side effects, including cardiovascular disease, depression, and hyperactivity [5]. As a result, an accurate, simple, fast, and cost-effective technology for determining CAF in regularly eaten goods is required.

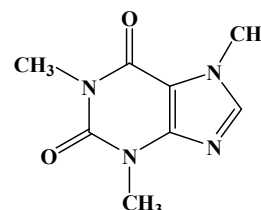


Figure 1. Chemical Structure of Caffeine.

Conventional methods, such as gas chromatography (GC)

or liquid chromatography (LC) interfaced with mass spectrometry (MS) or photodiode array (PDA) detectors [6-8], have been shown to have good sensitivity, selectivity, and detection limits of fewer than 10^{-8} mol L⁻¹. Most of these processes have limitations, such as being costly, time-consuming, and needing sample pre-treatment such as extraction, pre-concentration, and derivatization [9], as well as requiring skilled staff, which often limits their utility in routine analysis [10].

The electrochemical detection of CAF on various electrode materials, mainly bare and nanoparticle modified electrodes, has also been reported in the literature [10-16]. Electrochemical methods have a variety of practical advantages, including a simple approach, inexpensive instruments, and the capacity to miniaturise, in addition to strong sensitivity, a large linear concentration range, a proclivity for real-time detection, and reduced sensitivity to matrix effects [10].

In a range of applications, including electrocatalysis and electrochemical sensors, modified electrodes have distinct benefits over typical normal electrodes. The electrochemical responses obtained when utilizing bare glassy carbon electrodes may not have well-defined peaks in some instances. As a result, the surface of bare electrodes is changed to enhance these groups' electrochemical reactions [17].

Modification and/or functionalization of the electrode surface, in particular, results in an amplification of the relevant electrochemical signal and has proven particularly appealing for developing sensors with high sensitivity and selectivity [18].

This review article discussed the applications of various nanomaterials as electrochemical sensing platforms for caffeine detection. The analytical features of the sensor, such as linearity range, detection limit, and selectivity, are given and highlighted, as well as their potential relevance to real-world samples.

The primary goal of this review was to use and popularize the contribution of electrochemical investigations on caffeine in real samples using nanoparticle modified electrodes, as well as to summarize the performance and advantages of a modified glassy carbon electrode.

2. Electro Analytical Techniques

Electrochemistry offers a wide range of electro analytical methods. A typical electrochemical experiment includes a working electrode made of a solid conductive material, such as platinum, gold, or carbon, a reference electrode, and a counter electrode, which are all immersed in a solution containing a supporting electrolyte to ensure solution conductivity [19].

The most prevalent types of chemical sensors are electrochemical sensors. A chemical sensor is a small device that turns quantitative or qualitative electrochemical information into an analytically meaningful signal as a result of an electrochemical interaction or process between the analyte and the sensing device [20]. The combination of a

nanomaterial and an analyte has been shown to be crucial for sensor sensitivity, selectivity, and stability [21].

Food additives, biological contaminants, and heavy metals have all been detected using electrochemical methods [18]. An electrochemical reaction can provide a range of observable data depending on the electrochemical technique utilised. In fact, a measurable current can be generated, and the accompanying electrochemical techniques are amperometric in this case. When a voltage is measured and/or modulated, the applicable electrochemical techniques are potentiometric. Finally, the electrochemical impedance spectroscopy (EIS) method incorporates electrochemical methodologies including impedance measurements at the electrode in solution interface [22].

Electrochemical impedance spectroscopy (EIS) is an electro analytical tool used to examine the electron-transfer characteristics of altered surfaces and to appreciate surface chemical alterations. Electrochemical impedance spectroscopy (EIS) study provides mechanistic and kinetic data on a wide range of materials, including batteries, fuel cells, corrosion inhibitors, and so on [22].

Voltammetry is an amperometric technique because it measures the current produced by an electrochemical process while altering the potential window. Because there are different ways to modify the potential, we can study a variety of voltammetric procedures. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV) are the most common and frequently used [24]. CV and LSV are widely used voltammetric procedures for investigating the electrochemical behavior of an electro active material.

The two forms of pulse voltammetric methods are DPV and SWV. DPV and SWV, in contrast to CV, can be used to study the redox properties of extremely small amounts of electroactive compounds for several reasons, the most important of which are: (i) the effect of the charging current can be minimized, resulting in higher sensitivity; and (ii) only faradaic current is extracted, allowing electrode reactions to be analyzed more precisely. CA is a potentiostatic approach for recording current as a time function [23]. Figure 2 illustrates a summary of electrochemical analysis methods such as voltammetry, amperometry, electrochemical impedance spectroscopy (EIS), and potentiometry.

The techniques discussed above have been widely used in the creation of electrochemical sensors for a variety of applications. Nano materials, Nanotubes, Nanoparticles, and Nano composites

Recent advances in nanomaterial fabrication have enabled the creation of sophisticated sensing systems [25]. Generally, we have explored changes of the working electrode with diverse nanomaterial, ranging from the traditional nanotubes to Nano composites, among different nanostructures, such as graphene, metal nanoparticles, and/or nanostructured polymers. Non-traditional sensing substrates, such as paper and/or screen-printed electrodes (SPE) that have been modified with various nanomaterial and/or nanostructures, have also been considered [26]. Nanomaterials play a

significant role in the development of electrochemical sensors because they improve sensor stability, sensitivity, and selectivity in the presence of common interferences. In the following sections, we will introduce and describe nanomaterials, as well as examples of related electrochemical sensors, in order to illustrate their use in electrochemical sensing to detect caffeine.

Electro Chemical Sensors

Electrochemical sensors are carbon based nanomaterials, gold nanoparticles, hybrid Nano composite, etc.

Carbon-Based Nanoparticles

Carbon-based nanoparticles (single-walled carbon nanotubes, multi-walled carbon nanotubes, single-walled carbon nano horns, Bucky paper, graphene, fullerenes (e.g., C60), and so on) have very interesting properties, such as high surface-to-volume ratio, high electrical conductivity, chemical stability/durability, and strong mechanical strength, and for these reasons they have attracted considerable attention [26-28].

Carbon nanotubes have several properties linked with their structure, functioning, morphology, and flexibility to be employed in the construction of hybrid or composite materials due to their hollow cylindrical form. Carbon nanotubes are classified into three varieties based on the number of graphite layers: single-walled, double-walled, and multi-walled. Carbon nanotubes with functionalized ends have been used in a range of applications. By altering the tubular structure, chemical functionalities can be easily produced and adjusted [23].

Graphene

Graphene is a nanomaterial that is widely employed in sensing. Several techniques have been employed to produce graphene-based materials (for example, electrochemically and chemically modified graphene) [30]. Graphene has many properties, including high conductivity, rapid electron transport, and a large surface area [18, 30].

Graphene oxide (GO) can be disseminated in aqueous solution due to the presence of hydrophilic functional groups (OH, COOH, and epoxides) along the sheet's edge and on the basal plane. However, due to the lower conductivity of graphene oxide (GO) than graphene, reduced graphene oxide (rGO) is more typically used as an electrode modification in electrochemical sensing/biosensing applications [30].

A caffeine voltammetric sensor built with Nafion and graphene oxide (GO) on a glassy carbon electrode [11]. Because of the presence of Nafion, it possesses a high affinity for caffeine and a high electrochemical sensitivity to caffeine oxidation. Caffeine is detected by the electrode at concentrations ranging from 4.0×10^{-7} to 8.0×10^{-5} M, with a detection limit of 2.0×10^{-7} M. The sensor is extremely stable, repeatable, and sensitive.

Gold Nanoparticles

The first examples of gold nanoparticles (AuNPs) manufacturing, gold nanoparticles have been used in the construction of various sensors. Because of their excellent conductivity, compatibility, and high surface to volume ratio, Au nanoparticles and gold nanomaterials in general have been used in the electrochemical sensing domain from an electro analytical standpoint [31].

In rare situations, gold nanoparticles have been used in selective oxidation and reduction processes. There has been significant progress in the synthesis of Au nanoparticles and nanomaterials for electrochemical sensing. Researchers, on the other hand, face a number of challenges/criticalities, such as size management, morphology, and proper dispersion and/or stabilising agents and/or medium. The recent development of nanoporous gold materials appears to be essential in overcoming these challenges, with hierarchical gold nanoporous materials for biological applications being identified [32].

Masibi, K. K. et al. describe a new caffeine sensor that uses bimetallic Au-Ag nanoparticles generated from low-cost green manufacturing to measure caffeine electrochemically [33]. The sensor is built on a platinum electrode (PtE) that has been modified with polypyrrole (PPY) and green synthesized Ag-Au bimetallic nanoparticles. The paper also details the synthesis of silver nanoparticles (AgNPs), gold nanoparticles (AuNPs), and Ag-Au bimetallic nanoparticles (BMNPs) from citrus sinensis (sweet orange) peel extract. Square wave voltammetry (SWV) results showed that the PPY/Ag-AuBMNPs modified PtE had a detection limit of 2.02 M and a sensitivity of 0.75 A/M in the caffeine concentration range of 0 M to 59 M. The suggested sensor also demonstrated good selectivity and was successful in detecting caffeine in commercial samples. [33].

Table 1. An electrochemical sensors for Caffeine quantification.

Electrochemical Methods	Electrode Material	LOD (mol*L-1)	Application	Reference
DPV	Nafion/GO/GCE, MIS/MWCNTs/VTMS/GCE, electrochemically reduced graphene oxide (ERGO), AuNps/chitosan- ionic liquid /Gr/GCE, gold nanoparticle-chitosan / Gold electrode (AuE), Nano-Cobalt (II, III) oxide modified carbon paste (NCOMCP, CeO2 nanoparticles, Nafion-Gr/GCE, AuNP-GCPE, GORGCPE/SDS	2.00x10-7, 4.42x10-9, 1x10-6, 0.016x10-6, 0.036x10-6, 1.2x10-7, 2.49x10-6,	Cola beverages, energy drinks, cola beverage, teas, black tea, coffee, Nescafé, soluble chocolate, food and pharmaceutical industries Pepsi cola drink, energy, water, instant coffee	[11-14, 16, 34, 35]
CV and DPV	Copper sulphide nanoparticles (CuS NPs MCPE)	0.018x10-6	black tea, green tea, Nescafé, coffee	[15]

Electrochemical Methods	Electrode Material	LOD (mol*L-1)	Application	Reference
SWV	Nanocomposite MIP/PGE, PPY/AgAuBMNPs/PtE	0.9x10-9, 2.02x10-6	tablet, green tea, energy drink, Plasma, coffee	[33]
CV	Nafion/GNPs/LbL film	24x10-6	Coca cola, energy drink	[29]

Caffeine electrochemical determination using PPY/Ag-AuBMNP modified PtE KK Masibi et al., (2020) described electrochemical determination of caffeine utilizing bimetallic Au-Ag nanoparticles derived from low-cost green synthesis [33], and a novel caffeine sensor was built. The sensor is built on a platinum electrode (PtE) modified with polypyrrole (PPY) and green synthesised Ag-Au bimetallic nanoparticles. The review article also discusses the use of citrus sinensis (sweet orange) peel extracts to create silver nanoparticles (AgNPs), gold nanoparticles (AuNPs), and Ag-Au bimetallic nanoparticles (BMNPs). The nanoparticles were utilised to make a nanocomposite material based on polypyrrole (PPY), which was then used to modify PtE via the drop-cast method. The modified electrodes were electrochemically characterised using a ferrocyanide/ferricyanide redox probe produced in PBS. PtE that has been modified with PPY/Ag-AuBMNP functioned better. [33].

Using cyclic voltammetry, the changed electrodes were electrochemically characterised. The experiment was carried out at a scan rate of 25 mVs-1 in a 5 mM $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ solution prepared in 0.1 M PBS to

investigate the electrochemical properties of the bare and modified electrodes. Figure 3 (a) depicted cyclic voltammograms of bare and modified electrodes in 5 mM $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ solution. The electrode PPY/Ag-AuBMNPs modified PtE had a higher current response than the bare and AgNPs, AuNPs, Ag-AuBMNPs, PPY modified PtE electrodes [33].

More cyclic voltammetry tests were performed to investigate caffeine's electrochemical behaviour as well as the electrocatalytic properties of naked and modified PtEs. The experiment was done out in 0.1 M PBS containing 0.2 mM caffeine. A potential window of 0.2 to 2.0 V with reference to Ag/AgCl satd'd KCl and a scan rate of 25 mV s-1 were used in the experiment. Figure 3 (b) depicts the comparative cyclic voltammograms obtained for naked, AgNPs, AuNPs, Ag-AuBMNPs, PPY, and PPY/Ag-AuBMNPs modified PtE in the presence of 0.2 mM Caffeine. Figure 3 (b) shows only the anodic peak at a potential of around 1.6 V vs Ag/AgCl, showing irreversible oxidation. PtE modified with PPY/Ag-AuBMNPs shown higher catalytic activity due to an increase in [36].

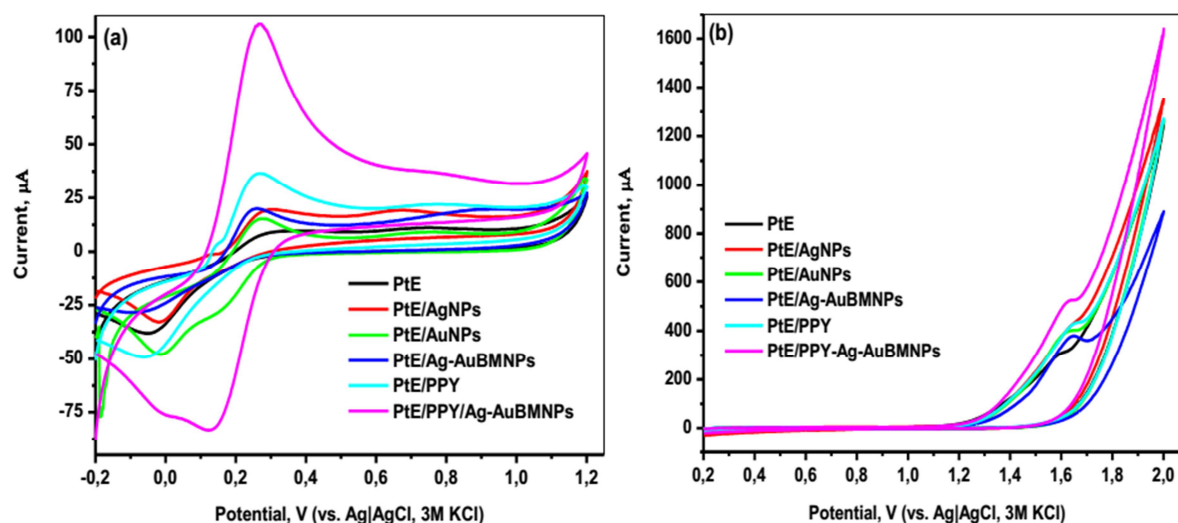


Figure 2. Cyclic voltammograms of bare and modified Pt electrodes in (a) 5 mM $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ solution (b) 0.2 mM CAF produced in PBS at 25 mVs-1 scan rate [33].

Determination of caffeine using graphene-based electrochemical sensor (Nafion-Gr/GCE).

According to J.-Y. Sun et al. (2011), reported to determination of caffeine by used to graphene-based electrochemical sensor [35]. The Nafion-Gr/GCE demonstrated good electrocatalytic activity towards caffeine. Caffeine can be efficiently accumulated at Nafion-Gr/GCE, resulting in a sensitive anodic peak. Gr's unusual physical and chemical properties, including as subtle electronic properties and significant adsorptive capabilities, are related to its

electrocatalytic behaviour. This electrochemical sensor detects caffeine very well, with a detection limit of 1.2107M (S/N = 3), a repeatability of 5.2% relative standard deviation, and a satisfied recovery range of 98.6% to 102.0%. The sensor offers tremendous promise for easy and sensitive caffeine measurement [35].

The electrochemical behaviours of caffeine on a Nafion-Gr modified glassy carbon electrode (Nafion-Gr/GCE) were examined using cyclic voltammetry and differential pulse voltammetry in the following paragraphs.

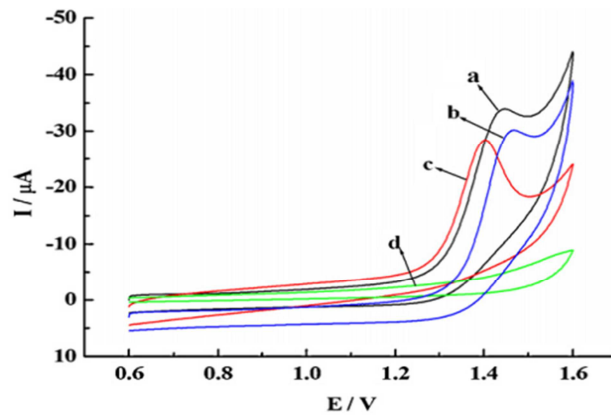


Figure 3. Cyclic voltammograms of the Nafion-Gr modified GCE (a), the Gr modified GCE (b), the Nafion modified GCE (c), and the bare GCE (d) in 0.01 M H₂SO₄ (pH 2.0) medium; scan rate 100 mV s⁻¹ [35].

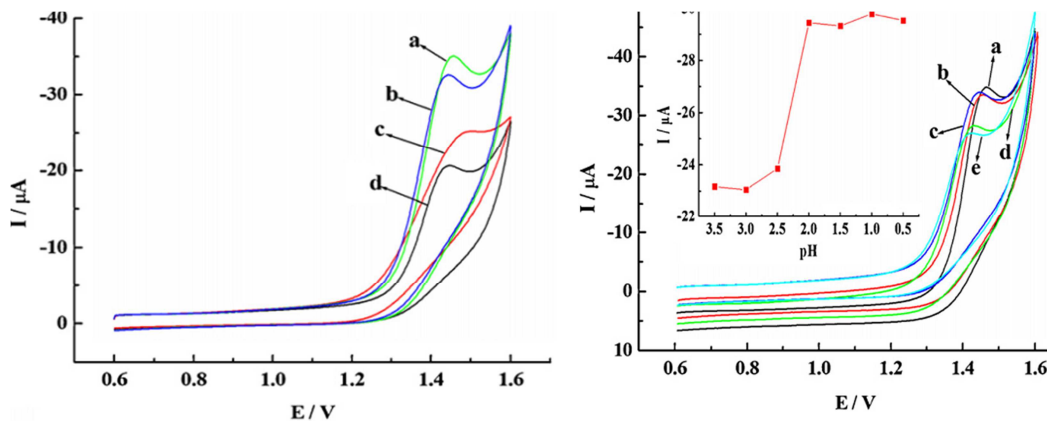


Figure 4. 1.0, 1.5, 2.0, 2.5, 3.0; scan rate 100 mV s⁻¹. Insets: Plot of pH versus oxidation peak current [35].

Because of its great sensitivity and distinct separation from background current, differential pulse voltammetry (DPV) was frequently utilised to do electrochemical measurements. Preliminary studies were carried out in order to select the optimal parameters such as pulse increment, pulse amplitude,

pulse breadth, and pulse time. The optimised circumstances were found to be 6 mV of pulse increment, 49 mV of pulse amplitude, 20 ms⁻¹ of pulse width, and 60 ms⁻¹ of pulseperiod [35].

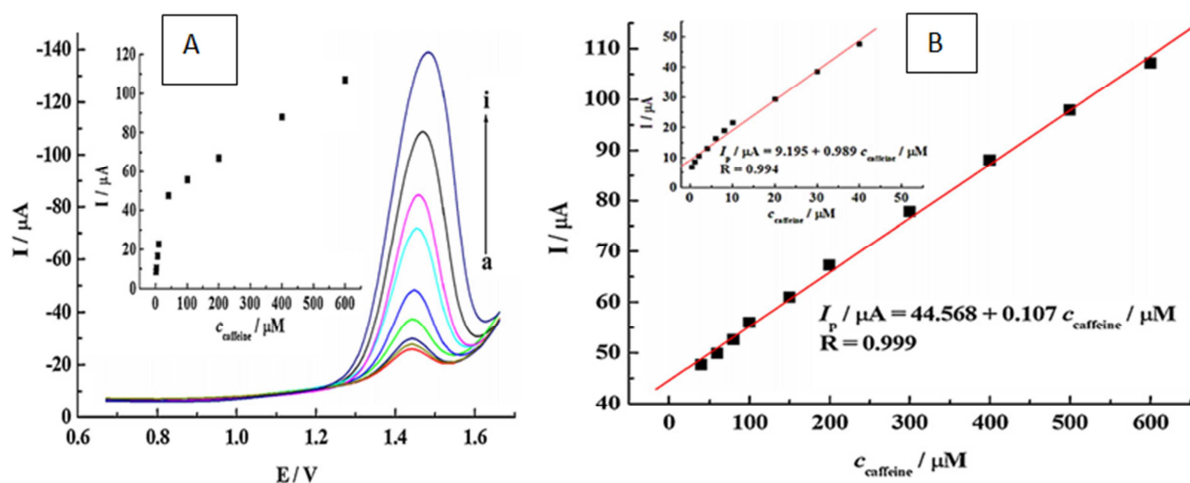


Figure 5. Differential pulse voltammograms (DPV) of Nafion-Gr modified GCE in various caffeine (ai) concentrations: 1.0106, 2.0106, 6.0106, 1.0105, 4.0105, 1.0104, 2.0104, 4.0104, and 6.0104 M; insert is the i_p versus C caffeine plot. Figure 5 shows the linear relationship between the oxidation peak current and caffeine concentration in the range of 4.0105–6.0104M; the inset shows the i_p versus C caffeine in the region of 4.0107–4.0105M [35].

The difference in peak currents with varied caffeine concentrations was studied using DPV. When the caffeine

concentration was adjusted from 4.0107M to 6.0104M, the anodic peak current of caffeine was linearly proportional to

the concentration over the ranges of 4.0105-6.0104M and 4.0107-4.0105M (Figure 4). For the range of 4.0107-4.0105M, the regression equations were $ip/A = 9.195 + 0.989C_{\text{caffeine}}/M$ ($R = 0.994$) and $ip/A = 44.568 + 0.107C_{\text{caffeine}}/M$ ($R = 0.999$) for the range of 4.0105-6.0104M. The detection limit was calculated to be 1.2107M ($S/N = 3$). [35].

3. Conclusion

Conventional analytical methods commonly chromatographic and spectroscopic techniques have been developed for qualitative and quantitative determination and characterization of caffeine with high accuracy, precision, sensitivity, and selectivity. All these methods are complicated, time-consuming and require expensive equipment. All of these approaches are complicated, time-consuming, and expensive. Caffeine detection has traditionally relied on electrochemical techniques. The use of metal and metal oxide nanoparticles for altering electrochemical sensors for voltammetric detection of caffeine appears to be more promising in this scenario. It is owing to the unique features of nanoparticles as well as electrochemical detection above conventional detection techniques due to a faster response time, better sensitivity, very low detection limits, simplified operational processes, and improved reproducibility. The focus of this review was on electrochemical sensors that may be used for caffeine samples using nanoparticle modified electrodes.

Conflicts of Interest

The author declares no conflicts of interest on this paper since it is review article.

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