

**NANOCOMPOSITE MATERIALS IN THE DEVELOPMENT OF
ELECTROCHEMICAL SENSORS FOR PHARMACEUTICALS
AND HEAVY METAL IONS**

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY**

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ELECTROCHEMICAL SENSORS FOR PHARMACEUTICALS
AND HEAVY METAL IONS**

BY

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Submitted

In partial fulfillment of the requirement of the Degree of Doctor of Philosophy in
Chemistry of Mizoram University, Aizawl



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Certificate

This is to certify that the thesis entitled '*Nanocomposite materials in the development of electrochemical sensors for pharmaceuticals and heavy metal ions*' submitted by **Ms. Melody Lalhrualtuangi** for the degree of **Doctor of Philosophy** in the Mizoram University, Aizawl, Mizoram, embodies the record of original investigations carried out by her under my supervision. She has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D. degree. This work has not been submitted for any degree in any other university.

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I, **MELODY LALHRUAITLUANGI**, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1. BACKGROUND

Every single form of life, from the smallest microbes to the largest mammals, including humans, needs water for their survival (Rao et al., 2024). The conservation of ecosystems, the assistance of agricultural implementation, the support of industrial monitoring, and the preservation of life all depend on its very presence (Harrop, 2007). The fact remains, however, that this essential resource is under growing pressure from a wide variety of contaminants primarily due to anthropogenic activities (Holdren & Ehrlich, 1974). Water pollution occurs when harmful substances -such as chemicals, waste, plastics, and pathogens—enter various water bodies, *viz.*, rivers, lakes, oceans, and underground aquifers, degrading their quality and rendering them unsafe for use (Mishra et al., 2019). The adverse effects of water pollution are extensive. In natural ecosystems, pollution can disrupt fragile equilibria, leading to the mortality of fish and aquatic flora, habitat destruction, and a decline in biodiversity (Kolawole & Iyiola, 2023). Contaminated water causes severe health issues, including gastrointestinal infections, reproductive problems, and neurological disorders in humans. In communities where access to clean water is limited, waterborne diseases such as cholera, typhoid, and dysentery remain persistent threats. Beyond health and ecological impacts, water pollution also jeopardizes food security. Polluted water used in agriculture contaminates crops, while the decline in fish populations affects both food supplies and the livelihoods of millions of people who depend on fishing. Economically, polluted waterways drive up water treatment costs, reduce tourism and recreational value, and impose financial burdens on governments and local communities struggling to mitigate the damage. It is estimated that approximately 25% of the global population does not have reliable access to a sufficient supply of clean and safe water, which means that one in every four people around the world struggles to receive water that is free from contaminants and suitable for daily use, including drinking, cooking, and personal hygiene (Abdulameer et al., 2025). Furthermore, about 50% of the world's population lacks access to basic sanitation facilities (Niza-Ribeiro, 2022), including toilets, sewage systems, and other waste-disposal

infrastructure that help prevent the spread of various diseases. Without these facilities, individuals are often forced to resort to unsafe and unsanitary practices, increasing the risk of infection and contamination. In addition to the lack of sanitation, 30% of people globally lack access to basic hygiene resources, and around 2.4 billion people use low-quality or contaminated water (Prüss-Ustün et al., 2019). This leads to a continued exposure to contaminated water that may contain harmful bacteria, viruses, or parasites. The consumption and use of such water significantly increase the risk of contracting serious waterborne diseases, including cholera, typhoid fever, and various gastrointestinal infections. Moreover, over 1.15 billion people worldwide still lack access to clean, safe drinking water (Reader, 2023). This shortage not only affects their health but also impacts education, productivity, and overall quality of life, as individuals - often women and children must spend hours each day collecting water from distant or unreliable sources. Moreover, more than 2 million people are suffering from diarrheal diseases each year as a direct result of consuming contaminated water or lacking proper sanitation and hygiene, where children are the most vulnerable group, making up the majority of those affected (Martínez-Santos, 2017).

As the global population grows and industrialization expands, the pressure on clean water sources continues to increase. Without immediate and sustained action, water pollution could become one of the most critical environmental and public health challenges of the 21st century. The use of pharmaceuticals continued to grow as the world became more urbanized and industrialized. In modern civilization, pharmaceutical compounds play an important and crucial role, especially for therapeutic uses, but their indiscriminate use and poor disposal systems by hospitals and manufacturing enterprises have raised serious concerns for human health and the environment in general (Qian et al., 2021). Although the concentrations of pharmaceutical compounds were found to be low in surface water, they still have a negative impact on the environment (Gonzalez *et al.*, 2022). It has been reported that human health is at risk if these pollutants are consumed continuously, even at trace levels (Blunt *et al.*, 2018; Marlinovic *et al.*, 2021). The pharmaceutically active compounds, such as non-steroidal anti-inflammatory drugs (i.e., diclofenac and ketoprofen), beta-blockers (e.g., atenolol), antibiotics (like tetracyclines,

fluoroquinolones, and sulfamides, etc.), neuroleptics (mainly carbamazepine, diazepam, fluoxetine), hormones (e.g., ethinylestradiol, 17 beta-estradiol), and lipid regulators (e.g., bezafibrate, clofibric acid, and gemfibrozil) are often detected in the wastewater, surface water, and in groundwater (Szymoniak *et al.*, 2017; Jones *et al.*, 2002). Pharmaceutical concentrations are recorded in treated wastewater even in developed countries such as the United Kingdom, the United States, and Germany, in the range of ngL^{-1} and, in some cases, μgL^{-1} (Fent *et al.*, 2006). Similarly, pharmaceutical concentrations in developing countries such as India are much higher, in the range of mgL^{-1} (with ciprofloxacin having the highest concentrations of around 28 to 31 mgL^{-1}) (Larsson *et al.*, 2007; Li *et al.*, 2008). A review revealed widespread occurrence of pharmaceuticals in the environment, with 631 out of 713 compounds found above analytical thresholds in 71 countries (Patel *et al.*, 2019). According to a study conducted by Mahmoudi *et al.* (2018), pharmaceuticals are detected in the surface and groundwater, showing numerous hazardous effects such as mortality and illness outbreaks, respiratory and pulmonary ailments, cancer, neurological disorders, etc.

The utilization of antibiotics, including both human and animal care medications, has become essential in health management, control, and prevention (Mackul'ak *et al.*, 2019). These compounds often enter the environment through the discharge of treated wastewater, sewage overflows, and effluents from manufacturing facilities (Gavrilescu *et al.*, 2015; Mofijur *et al.*, 2024). Humans or livestock excrete a significant amount of the antibiotics through the feces and urine since liver enzymes such as glucuronidation, sulfation, and methylation contribute to a partial breakdown of various medications in the body (Almazroo *et al.*, 2017; L. Du & Liu, 2012; Lucas-Torres & Wong, 2019). Therefore, these compounds, or even their active metabolites, enter sewage waters, are often not eliminated in wastewater treatment plants, and escape as residuals in effluents, entering the aquatic environment (Aemig *et al.*, 2021; X. Li *et al.*, 2023). Although the concentration of these compounds was found at low levels in surface water, however, higher potential to change the microecological system, which ultimately affect the food chain, resulting in several health complications which may include several allergic reactions, chronic toxic

consequences from extended exposure, and disruptions in the normal functioning of the digestive system (Ben et al., 2019; Polianciuc et al., 2020).

On the other hand, heavy metal contamination in ecosystems is a global concern due to its severe health effects on natural media and is considered a primary source of environmental pollution (Ali et al., 2021). These toxins enter from both natural and man-made sources, such as volcanic eruptions, fossil fuel burning, mining, industrial, and agricultural operations, such as the use of fertilizers and pesticides (Angon et al., 2024). They are defined as heavy metals because of their relatively high densities (5 g/cm^3), significantly surpassing that of water (1 g/cm^3), and are, in general, major environmental concerns that threaten both ecosystems and human health (Rigueto et al., 2022). These include arsenic, cadmium, chromium, lead, mercury, iron, copper, etc. These heavy metals are highly toxic and are detected in the environment, posing a severe health hazard to marine life (Zirliannigura et al., 2017). It has been reported that some of these metal ions are essential for certain biological processes (Goswami & Neog, 2023), but their continuous discharge beyond permissible levels becomes toxic to both terrestrial and aquatic environments. A review on heavy metal contamination in drinking water emphasized the presence of cadmium, chromium, copper, iron, lead, cobalt, manganese, mercury, nickel, and zinc across various sources such as groundwater, surface water, and tap water. In numerous cases, the observed concentrations exceeded the maximum allowable and preferred thresholds set forth by regulatory bodies, including WHO (2008), USEPA, EUC, and EPA (Mohod & Dhote, 2013). For these reasons, it is vital to accurately detect the presence of pharmaceuticals and heavy metal ions in the aquatic environment. With adequate monitoring of these contaminants, appropriate preventive measures could be adopted to ensure their safe disposal and removal from the source. Efficient detection could also help prevent their introduction into the food chain. The accumulation of heavy metals in biological systems poses a serious threat to human health. The presence of heavy metals in the environment over long periods results in their continuous cycling through ecosystems and accumulation in living organisms (Ayangbenro & Babalola, 2017). Lead, mercury, arsenic, cadmium, chromium, and zinc are naturally occurring heavy metals known to be highly toxic. Bioaccumulation of these ions in the biosystem poses severe,

prolonged health hazards to living beings (Angon et al., 2024; Nnaji et al., 2023). Human activities, including mining, industrial operations, agricultural practices, and improper waste management, significantly contribute to heavy metal contamination of aquatic environments, adversely affecting natural ecosystems by diminishing soil fertility, polluting water sources, and harming aquatic organisms (Haghighizadeh et al., 2024). Detecting and continuously monitoring heavy metals and pharmaceuticals in aqueous solutions is essential for safeguarding public health and preventing their entry into the food chain.

Although the analytical techniques *viz.*, AAS (atomic absorption spectroscopy), atomic emission spectroscopy (AES), chromatography, ICP-MS (inductively coupled plasma mass-spectroscopy), laser-induced breakdown spectroscopy (LIBS) (Fang et al., 2016; Haider et al., 2014; Karthika et al., 2019; Kumaresan & Riyazuddin, 2001; Pistón et al., 2012), LC-MS/MS, HPLC/MS, and GC/MS (Isaac-Olivé & Navarro-Frómata, 2019; Patial & Singh, 2024) These systems are highly efficient in detecting these heavy metals and pharmaceuticals at very low levels. These detection systems have inherent drawbacks, such as high instrument costs, sophisticated instrumentation, and *off-site* detection. Therefore, the search for robust, miniaturized devices for efficient *on-site* detection is inevitable. The electrochemical devices are efficient and found promising over several other detection systems (H. Hu et al., 2022). However, the efficiency and selectivity of electrochemical devices are key challenges to achieving real-world applications. The role of advanced and engineered materials has gained momentum in detection systems, opening new areas of research for device development.

1.2. SOURCES AND HARMFUL EFFECTS OF POLLUTANTS

The persistence of heavy metals in the environment is a serious environmental concern. Unlike organic pollutants, which can degrade over time, heavy metals persist in the environment for extended periods, cycling through ecosystems and accumulating in living organisms (Ayangbenro & Babalola, 2017). Heavy metals, including lead, mercury, arsenic, cadmium, chromium, and zinc, are naturally occurring elements that must be detected at low levels because they are highly toxic at

low concentrations. Although zinc is an essential ion, toxic at higher concentrations (Angon et al., 2024; Nnaji et al., 2023). Human activities, such as mining, industrial operations, agricultural practices, and improper waste management, significantly contribute to heavy metal contaminations, and once these metals enter soil, water, and air, they can adversely affect ecosystems by diminishing soil fertility, polluting water sources, and harming aquatic organisms (Haghighizadeh et al., 2024). Alongside heavy metal pollution, the contamination of aquatic habitats by micro-pollutants, specifically hormones and pharmaceuticals, has recently emerged as a significant environmental concern. These micro-pollutants have been found to be harmful to aquatic ecosystems and a potential threat to human health. In the following sections, a brief description is provided of the sources, toxic effects, and health hazards associated with a number of heavy metal toxic ions and some of the micro-pollutants.

1.2.1. Cadmium

Cadmium is a widespread toxic substance that is found in the environment and has shown several negative effects on human health. Exposure to cadmium occurred through the consumption of contaminated food or drink, as well as through inhalation and the smoking of cigarettes (Genchi et al., 2020). Natural processes and human activities are both responsible for the rise in cadmium concentrations (M. T. Hayat et al., 2019). Natural activities, including volcanic eruptions, rock weathering, soil erosion, abrasion of mineral-rich soil, and forest fires, released cadmium into the environment (Ankush et al., 2024). During volcanic activity, cadmium-laden gases and ash are released and deposited in terrestrial or aquatic environments. Likewise, as rocks and minerals containing cadmium undergo weathering, the metal is released into adjacent soils and aquatic environments (Kubier, 2019). Furthermore, industrial activities such as mining and smelting of non-ferrous metals (especially zinc and lead) are among the primary contributors, as cadmium often occurs as a by-product of these processes (Du et al., 2020). During the extraction and refining of these metals, cadmium is released into the air, soil, and waterways, and agricultural practices like the use of phosphate fertilizers, which often contain trace amounts of cadmium, lead to its accumulation in agricultural soils over time (Ćwieląg-Drabek et al., 2020). This

poses a risk of uptake by crops, which then enter the food chain, impacting human and animal health.

Cadmium is known to be potentially carcinogenic, and exposure to cadmium results in renal impairment, bone demineralization, and respiratory disorders (Davidova et al., 2024). The respiratory system is the principal pathway of cadmium (Cd) absorption and is deposited in the lungs (Qu & Zheng, 2024). It also enters the body via the bloodstream, where it is absorbed by the kidneys, liver, and intestines after being transported by erythrocytes and albumin (Satarug et al., 2018). The body gradually eliminates cadmium via the kidneys, urine, saliva, and breast milk during lactation. Cadmium exposure resulted in numerous detrimental effects in humans, including adrenal and hepatic dysfunction, testicular injury, and damage to the hematopoietic system and adrenal glands (Tinkov et al., 2018). Prolonged exposure to cadmium poses a substantial risk to the nervous system, resulting in oxidative stress, disruption of calcium homeostasis, and interference with neurotransmission, all of which contribute to cognitive and behavioural disorders (Rezaei et al., 2024)

1.2.2. Mercury

Mercury is a hazardous pollutant that is often present in our environment at alarmingly high concentrations (Ashima Bhan & N. N. Sarkar, 2005). Based on the findings of the United States Agency for Toxic Substances and Disease Registry (ATSDR), mercury is categorized as a bioaccumulative toxin, which places it in the third position among the most hazardous heavy metals on Earth, following arsenic and lead (Clifton, 2007). In its natural form, it occurs in several forms, including elemental mercury, which is liquid at room temperature, and inorganic and organic mercury compounds, such as methylmercury (Beckers & Rinklebe, 2017). In contrast to natural mercury emissions, which tend to remain stable over time, anthropogenic emissions have surged dramatically, leading to a notable accumulation in the atmosphere (Driscoll et al., 2013). The increase in human activities has led to a nearly threefold rise in atmospheric mercury levels, significantly disrupting the natural mercury cycle (Qiu et al., 2025). Industrial activities, including coal combustion, artisanal and small-scale gold mining, cement production, metal smelting, and the improper disposal of

mercury-containing products such as batteries, fluorescent lamps, and electronics, have increased mercury levels in the environment (Kung et al., 2024). Once in the environment, mercury is chemically converted to methylmercury (MeHg), a highly toxic substance that accumulates in the food chain (Beauvais-Flück et al., 2016). In aquatic environments, bacteria convert mercury into MeHg, the most dangerous and accessible form of mercury. Different fish species exhibit elevated MeHg levels, which may be bioaccumulated (Jeong et al., 2024). The gastrointestinal system absorbs approximately ninety-five percent of ingested MeHg, facilitating its entry into red blood cells and the brain through covalent attachment to glutathione and cysteine protein groups (Rice et al., 2014). This indicates that even minimal quantities can accumulate to significant levels in predatory species, such as large fish, which are subsequently ingested by humans and wildlife, thereby posing potential health hazards.

Increased levels of mercury in the atmosphere posed a serious threat to human health globally. Mercury is transported by air; even distant places are not safe from its harmful effects. The kidney is highly vulnerable due to its crucial role in eliminating toxins from the body. Certain studies show that mercury exposure increases blood pressure and the risk of heart disease (Miller et al., 2013). Furthermore, mercury significantly suppresses the immune system, thereby hindering the body's ability to combat illnesses (Gardner et al., 2010). Exposure to mercury during pregnancy leads to its passage across the placental barrier, resulting in accumulation within the brain and disruption of typical neurological development (Dack et al., 2022). It is associated with cognitive deficits, including a lower intelligence quotient (IQ) and challenges with memory and attention span. Children experience difficulties in language development, struggle with the processing and comprehension of spoken and written language, and exhibit delays in speech (Cusick & Georgieff, 2016). Mercury toxicity also impacts visual-spatial skills, which are needed for reading, sketching, and recognizing spatial relationships, as well as fine motor skills like grasping small objects, writing, and coordinating movements (Walker et al., 2007). These deficiencies affect a child's independence, academic, and social success throughout life. In adults, mercury exposure results in symptoms such as tremors, mental disorders, muscular

weakness, and cognitive deterioration (Chamoli & Karn, 2024). The most significant risk arises when exposure occurs during early brain development, necessitating the protection of pregnant women, babies, and young children from harmful mercury exposure.

1.2.3. Lead

Lead is among the most hazardous metals and is recognised worldwide as a highly toxic substance that is widely dispersed and persistent in the environment (Arias et al., 2010). The utilization of lead was traced back to ancient civilizations, attributed to its distinctive physico-chemical characteristics, while its essential traits like softness, malleability, ductility, low electrical conductivity, and robust corrosion resistance render it extremely valuable in multiple sectors, including construction, batteries, paints, and plumbing (Kumar et al., 2020). Moreover, these properties pose challenges to phasing out their use in many applications, such as leaded pipe, solders, grids, battery manufacturing and recycling, and refining (Duzgoren-Aydin, 2007). These applications often involve high-temperature processes or direct human contact, which resulted in the release of lead particles or lead-laden fumes into the environment (Liu et al., 2013). Consequently, individuals working in or living near areas are at heightened risk of lead exposure. Waste streams produced during battery manufacturing, especially lead-acid batteries, significantly contribute to the issue, and acid metal plating and finishing operations release lead into the environment, similar to the production and disposal of ammunition, which frequently includes lead-based components (Bača & Vanýsek, 2023). The processes of printing, painting, and dyeing significantly contribute to elevated environmental lead levels, particularly when waste management practices fail to remove lead before final disposal (Naja & Volesky, 2017). Poor management, disposal, and recycling in many low- and middle-income countries worsen this problem, causing environmental degradation with increased human exposure (Kordas et al., 2018). The continued utilization of materials containing lead is a significant public health issue, especially lead's cumulative toxic effects and its capacity to persist within biological systems over extended periods (Kumar et al., 2020). Furthermore, lead is non-biodegradable, meaning it does not decompose naturally in the environment. Plants cultivated in contaminated soils

apparently take up lead via their roots, resulting in the accumulation of lead in edible tissues (Emetere & Aimudo, 2020). This bioaccumulation allows lead to enter the food chain and affect not just local communities dependent on the produce, but also broader populations through the distribution of contaminated crops (Kumar et al., 2020).

Lead exposure resulted in neurological, developmental, and reproductive issues in humans, especially in children (Sanders et al., 2009). The persistence and mobility of lead in the environment underscore the need for safer, more effective remediation strategies to prevent its entry into biological systems. Exposure to even low levels of lead in young children and infants interferes with normal brain development, resulting in lasting cognitive and behavioural impairments (Assi et al., 2016). Extended exposure to lead results in developmental delays and cognitive impairments. The underdevelopment of a child's blood-brain barrier allows lead to infiltrate brain tissue more readily, thereby worsening its detrimental impact on cognitive and neurological growth (Naranjo et al., 2020). The accumulation of lead over time disrupts haemoglobin production, leading to anaemia. The lead causes an increase in blood pressure, particularly among middle-aged and older adults, which subsequently heightens the risk of cardiovascular disorders (Obeng-Gyasi, 2019). Adults experience neurological symptoms such as memory loss, confusion, irritability, muscle weakness, and, in severe instances, paralysis (Gudadhe et al., 2024). Exposure to lead has the potential to adversely affect kidney function, resulting in chronic kidney disease and a range of systemic complications (Jalili et al., 2021). In pregnancy, the continued exposure may lead to spontaneous miscarriages, while exposure to lead has been linked to a decrease in sperm count and diminished fertility in men (Kumar, 2018). The World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA) have specified that a maximum allowable concentration of lead in the drinking water is as low as $10 \mu\text{gL}^{-1}$ and $15 \mu\text{gL}^{-1}$, respectively (Hakonen & Strömberg, 2018).

1.2.4. Zinc

Zinc (Zn) is a trace element that is crucial to various biological processes in plants, animals, and humans (Patil et al., 2023). Zinc supports gene expression,

immunological function, wound healing, growth, protein synthesis, and cell membrane structure via participating in more than 300 enzymes. Zinc is essential for chlorophyll synthesis, enzyme activation, and protein metabolism in plants. Although zinc is crucial in trace quantities, high concentrations are potentially harmful and pose serious threats to environmental and public health (Gondal et al., 2021). Zinc occurs naturally in the Earth's crust and enters the environment through weathering of rocks and minerals, during which zinc-bearing minerals gradually decompose and release zinc into soil and water systems (Navratil & Minarik, 2005). Moreover, volcanic eruptions release zinc-containing ash and gases into the atmosphere, while forest fires and soil erosion also introduce small yet quantifiable amounts of zinc into the surrounding environment (Nieder & Benbi, 2024).

Several human-induced sources encompass mining and smelting activities, during which the extraction and processing of zinc and various metals produce zinc-containing wastes (Chowdhury & Rahman, 2024). Industrial manufacturing units, such as galvanization (the zinc coating of iron and steel), paint production, rubber, ceramics, and electronics industries, contribute to the release of zinc in the environment. However, the application of agricultural activities, especially the incorporation of zinc-based fertilizers, pesticides, and animal feed additives, caused the accumulation of zinc in the soil (Qu et al., 2012). A significant number of individuals across the globe are presently exposed to zinc from a range of sources, such as dietary supplements, food additives, pharmaceuticals, personal care items, and dental materials (Ayenimo et al., 2010; Roney et al., 2006). The ubiquity of zinc in consumer products has raised concerns about potential overexposure and its long-term effects on human health, making it a subject of considerable interest and debate within toxicology and human nutrition.

Prolonged consumption of excessive zinc, well over the recommended dietary allowances (RDAs), typically ranging from 150 mg/day to 1–2 grams per day, can lead to serious health repercussions (Schoofs et al., 2024). The most notable among these are anaemia, immune system dysfunction, and trace mineral abnormalities. Direct skin exposure to zinc powders or concentrated zinc solutions (e.g., zinc chloride or zinc sulfate) may cause significant corrosive damage (Plum et al., 2010). Therefore,

excessive exposure to zinc has been reported to cause ulceration, blistering, inflammation, and, in certain instances, permanent scarring. The symptoms are frequently attributable to the caustic properties of zinc salts, which harm the skin and underlying tissues (Schwartz et al., 2005). Moreover, zinc phosphide (Zn_3P_2) is a highly toxic rodenticide, posing significant poisoning risks to humans, including symptoms such as abdominal pain and diarrhoea. In more extreme instances, pulmonary edema and liver damage, chest tightness, nausea, agitation, coldness, unconsciousness, coma, and death (Parhizgar et al., 2020)². The United States Environmental Protection Agency (US EPA) has established a reference dose of 0.3 mg/kg-day for zinc, derived from the lowest observed adverse effect level (LOAEL) used in clinical studies that investigate the impact of oral zinc supplements on copper and iron levels in the human body (Nriagu, 2007).

1.2.5. Chloramphenicol

Chloramphenicol (CRP) is a broad-spectrum antibiotic synthesized in 1947 by David Gottlieb, rapidly becoming one of the most prevalent antimicrobial medicines in human and veterinary medicine (Balbi, 2004; Gottlieb et al., 1954). Due to its therapeutic efficacy, it has been utilized in the treatment of numerous bacterial illnesses and has been utilized to treat severe illnesses, including typhoid fever, dysentery, anthrax, meningitis, and various eye infections (Dasopang et al., 2019; Tatli et al., 2003). Moreover, it is efficient against both Gram-positive and Gram-negative bacteria (Pacifici, 2018). Moreover, owing to its affordability, accessibility, and potent antibacterial properties, chloramphenicol (CRP) has been widely misused and overused across multiple domains, including healthcare, animal husbandry, and aquaculture (Andleeb et al., 2020). The misuse of CRP has generated significant public health and environmental issues, prompting various nations to establish rigorous controls and the maximum permissible residue level of CRP at 0.5 ngg^{-1} or ngmL^{-1} in commonly consumed food matrices, including meat, milk, honey, and eggs (Viñas et al., 2006). CRP readily infiltrates into the environment and food chain via various pathways. The extensive and indiscriminate use of chloramphenicol has led to harmful effects, necessitating stringent regulations on its use. In some countries, an outright prohibition is imposed on its application in food-producing animals. Moreover, a

significant quantity of CRP is excreted unchanged in urine and faeces after administration, potentially leading to contamination of soil and water systems. In aquaculture, the frequent use of CRP to manage bacterial diseases in fish and prawns has led to excessive, unregulated application, resulting in elevated CRP concentrations in aquatic ecosystems and contamination of rivers, ponds, and drinking water supplies (Nguyen et al., 2022). The persistence of CRP in the environment poses hazards to both human health and microbial ecology, as it facilitates the development of antibiotic-resistant microorganisms. In humans, prolonged or excessive exposure to CRP residues is linked to hypersensitive reactions, gastrointestinal difficulties, and severe haematological diseases, including bone marrow suppression and aplastic anaemia (Nyamagoud et al., 2025; Singhal et al., 2020). Similarly, it induces allergic reactions, gastrointestinal difficulties, and other detrimental health effects (Hanekamp & Bast, 2015). This jeopardizes food safety and presents enduring dangers to public health.

1.2.6. Ibuprofen

Ibuprofen, chemically known as 2-(4-isobutylphenyl)propanoic acid, is a weakly acidic compound that belongs to the class of nonsteroidal anti-inflammatory drugs (NSAIDs) (Adams et al., 1967). Its pharmacological action is primarily attributed to the reversible inhibition of cyclooxygenase (COX-1 and COX-2) enzymes, which play a critical role in prostaglandin biosynthesis (Chavez & DeKorte, 2003). By suppressing prostaglandin production, ibuprofen effectively reduces inflammation, alleviates pain, and lowers fever, making it a highly versatile therapeutic agent (K. D. Rainsford, 2013). Owing to these properties, ibuprofen is extensively used in the management of arthritis-related pain, musculoskeletal disorders, and other clinical conditions characterized by inflammation and pyrexia (Bushra & Aslam, 2010). It is also frequently prescribed or self-administered for the relief of mild to moderate pain, including headaches, dental pain, dysmenorrhea (menstrual cramps), muscular pain, postoperative discomfort, and pain linked to trauma or injury (Bhushan & Martens, 1998; Dawood & Khan-Dawood, 2007; Moore & Hersh, 2001). Additionally, its antipyretic effect makes it a first-line choice for treating fever in both adults and children (Evers et al., 2006).

Commercially, ibuprofen is available in a wide range of dosage forms, including tablets, capsules, oral suspensions, chewable formulations, gels, and topical preparations, enabling flexible administration tailored to age, condition, and patient preference (Potthast et al., 2005). This versatility, combined with its well-established efficacy, relatively low cost, and over-the-counter (OTC) accessibility, has made ibuprofen one of the most widely consumed medications worldwide. Moreover, ibuprofen is considered one of the safest NSAIDs when used at recommended therapeutic doses, which has further enhanced its widespread clinical and household use (H. Chen et al., 2005). Nonetheless, despite its prevalent application, prolonged consumption or misuse of ibuprofen can lead to considerable unfavourable health consequences. A prevalent problem comes from its effect on the gastrointestinal (GI) system (Tsokos & Schmoldt, 2001). Extended or excessive usage might harm the gastric mucosa by diminishing prostaglandin-mediated protective mechanisms, resulting in irritation, gastritis, peptic ulcers, gastrointestinal haemorrhage, or even perforation in severe instances (Rainsford & Bjarnason, 2015). The hazards are heightened in elderly people, individuals with peptic ulcer disease, or those also utilizing other NSAIDs, corticosteroids, or anticoagulants (Monteiro et al., 2022). Ibuprofen use can lead to gastrointestinal problems and disrupt renal function by affecting prostaglandin-mediated blood flow, potentially resulting in acute kidney injury, fluid retention, and severe hypertension or heart failure (Ellepola et al., 2020). Significantly, extended or high-dose usage of ibuprofen is associated with cardiovascular problems, indicating an increased risk of myocardial infarction, cerebrovascular accident, and thrombotic occurrences, especially in individuals with pre-existing cardiovascular risk factors (Volans, 2015).

1.2.7. Sulfamethoxazole

Sulfamethoxazole (SFX), with the chemical name of 4-amino-N-(5-methylisoxazol-3-yl) benzenesulfonamide, is a synthetic antimicrobial agent, categorized in the sulfonamide class of antibiotics (Wu et al., 2022). Clinically, SFX is widely utilized to prevent a variety of bacterial infections. It is often paired with trimethoprim, a complementary medication that disrupts the subsequent step in folate

metabolism by inhibiting dihydrofolate reductase (Kemnic & Coleman, 2025). The fixed-dose combination of these drugs, commonly referred to as co-trimoxazole, is utilized in the treatment of respiratory tract infections, including bronchitis and pneumonia, as well as urinary tract infections, gastrointestinal infections, and specific systemic infections (Chen et al., 2020; Tang & Wang, 2018). Notably, it continues to be a preferred option for preventing and treating infections in individuals with compromised immune systems, especially those affected by HIV/AIDS (Andrade et al., 2009). Due to its broad antibacterial spectrum and low cost, sulfamethoxazole is also used in veterinary medicine and is sometimes added to livestock and poultry feed to prevent or treat bacterial infections, thereby improving animal health and productivity at large (Rabello et al., 2020; Suwanpakdee et al., 2025). However, residual quantities of SMX and its metabolites persist in animal-derived food products, surface water, soil, and sediments, raising concerns about the widespread use of SMX in veterinary treatment (Khalifa et al., 2024). In recent years, several antibiotics, such as sulfonamides, have been detected in various environmental compartments, including surface water, drinking water, effluents, and soil. The presence of sulfamethoxazole in various aquatic environments is well documented, with concentrations above 10 mg L⁻¹ detected in river water samples in Germany (Adeleye et al., 2022; Lalmalsawmi & Tiwari, 2021). Several studies have demonstrated that sulfamethoxazole (SMX) is toxic to microalgae, primarily due to its effects on chloroplasts, the organelles that facilitate photosynthesis. SMX disrupts translation in chloroplasts, thereby interfering with the synthesis of proteins crucial for proper chloroplast function (Välitalo et al., 2017). Moreover, sulfamethoxazole inhibits the bacteria responsible for nitrate removal in wastewater. This results in the accumulation of nitrates, contributing to water pollution. Excessive nitrate levels lead to algal blooms and reduced oxygen levels, negatively impacting fish and other aquatic organisms (Roose-Amsaleg & Laverman, 2016).

Sulfamethoxazole showed several side effects that limit its therapeutic uses. Gastrointestinal disturbances such as nausea, vomiting, abdominal pain, and diarrhoea, caused by mucosal irritation or changes in the gut microbiota, are the most common side effects (Balakrishnan et al., 2006). Another concern is hypersensitivity reactions,

which range from moderate skin rashes, urticaria, and photosensitivity to life-threatening reactions (Farrell et al., 2003). Sulfamethoxazole also causes haematological issues due to its effects on folate metabolism. Among these conditions are thrombocytopenia, characterized by a low platelet count that increases the risk of bleeding; agranulocytosis, defined as a severe reduction in white blood cell count that heightens susceptibility to infections; and megaloblastosis involving the presence of abnormally large red blood cells resulting from impaired DNA synthesis (Abou-Eisha et al., 2004; Nakamura et al., 1995). Moreover, the presence of sulfamethoxazole residues in food items such as milk, meat, and other animal-derived products intensifies these issues (Tegegne et al., 2024). These residues are associated with allergic reactions in susceptible individuals, the emergence of antibiotic resistance in microbial populations, and, in certain instances, long-term health repercussions, including an increased risk of carcinogenesis (Bacanli, 2024).

1.3. LITERATURE REVIEW

Precise, rapid, and cost-effective analytical detection systems have attracted growing interest in recent years for monitoring emerging contaminants in aquatic environments. Such pollutants include pharmaceuticals, personal care products, pesticides, endocrine-disrupting chemicals, and heavy metals, which, although often present at trace concentrations, pose serious health risks to ecosystems and human health. The detection and monitoring of these substances in water bodies are therefore crucial for protecting public health and preventing their accumulation within the food chain. Electrochemical sensors are gaining prominence as highly efficient analytical tools for detecting and quantifying these contaminants in aqueous solutions. Electrochemical techniques, including voltammetry, amperometry, and potentiometry, are particularly advantageous for on-site use due to their high sensitivity, cost-effectiveness, and portability (Jalalvand & Karami, 2025). These techniques detect trace levels of heavy metals simultaneously with high accuracy, making them suitable for real-time monitoring in environmental settings (García-Miranda Ferrari et al., 2020). Moreover, electrochemical techniques are distinguished by low operational costs, high sensitivity, rapid response times, and comparatively robust instrumentation

(Shao et al., 2010). Additionally, the potential for miniaturization and integration with portable devices demands their enhanced applicability in field-based and real-time monitoring systems (Lalmalsawmi et al., 2022). Advancements in electrochemical sensors primarily focus on replacing traditional electrodes with advanced materials to enhance sensing performance. As a result, the performance of electrochemical sensors requires suitable working electrodes made from appropriate, efficient materials that enhance sensitivity and selectivity (Lalawmpuia et al., 2024).

Carbon-based nanomaterials, particularly graphene oxide (GO), are employed in sensor technologies since they possess a large surface area and high electrical conductivity, along with robust mechanical strength (Jayaraman et al., 2022). Many sensitive electrochemical sensors are designed for the detection of pollutants using graphene or graphene-based composites (Lü et al., 2013; Lv et al., 2013, 2014). It possesses an array of functional groups that include oxygen, like hydroxyl, epoxide, and carboxyl groups, making it highly versatile in chemical and biological sensing applications (Roy et al., 2011). Biosensors, which use graphene-based materials, are gaining interest in recent times due to their high sensitivity towards the target biomolecules (Szunerits & Boukherroub, 2018). Graphene oxide (GrO) is found to be an efficient adsorbent owing to the porous structure, excellent chemical stability, large specific surface area, tunable properties for targeted applications, ease of functional modification, and affinity to remove a wide range of pollutants (Liu et al., 2011). Graphene-based materials are also utilized in biosensors, which receive much attention in sensor platforms for analyzing target biomolecules with high sensitivity (Suvarnaphaet & Pechprasarn, 2017). An efficient electrochemical-based sensor was developed for the detection of amoxicillin using a glassy carbon electrode (GCE) modified with reduced graphene oxide (RGO) nanosheet (Pham et al., 2021). The modified electrode exhibited a large surface area, a high charge-transfer rate, and increased catalytic activity compared to the bare electrode, resulting in a low detection limit of 0.193 μM for amoxicillin.

1.3.1. Electrochemical detection of heavy metal ions

Electrochemical methods are highly effective for *in situ* and real-time monitoring of heavy metals in aquatic ecosystems. Voltammetric technologies have demonstrated significant advancements, providing rapid, sensitive, and reliable detection of several heavy metal ions, making them suitable alternatives to traditional analytical techniques. In a line, a sensitive electrochemical sensor for Pb^{2+} detection was developed by modifying a glassy carbon electrode (GCE) with $\text{Bi/Bi}_2\text{O}_3@\text{C}$ nanoparticles. The sensor attained a detection limit of 6.3 nM by square-wave anodic stripping voltammetry (SWASV), demonstrating high stability, consistent repeatability, and adequate selectivity (Wang et al., 2023). A polyamide-amine dendrimer/nickel metal-organic framework (PAMAM/Ni-MOF) nanocomposite was utilized as an electrochemical sensing platform for the concurrent measurement of Pb^{2+} and Cu^{2+} in aquatic environments. The sensor demonstrated a wide linear response range of 1–100 $\mu\text{g L}^{-1}$ using SWASV and attained low detection limits of 1.21 $\mu\text{g L}^{-1}$ for Pb^{2+} and 0.77 $\mu\text{g L}^{-1}$ for Cu^{2+} , underscoring its exceptional sensitivity and appropriateness for trace-level monitoring (Wang et al., 2025). Recently, a disposable dual-screen-printed carbon electrode (SPCE) modified with a composite of polypyrrole (PPy), gold nanofoam, and tungsten disulfide nanosheets (SPCE/PPy/Au-nano/WS₂NSs) was developed for the sensitive electrochemical detection of Hg^{2+} , Pb^{2+} , and As(III) via differential pulse voltammetry (DPV). This sensing platform exhibited remarkable sensitivity and selectivity, attaining limits of detection (LODs) as low as 0.127, 0.241, and 0.193 ppb for Hg^{2+} , Pb^{2+} , and As(III), respectively (Mejri et al., 2026). Carbon nanomaterials, including graphene and graphene oxide, are extensively utilized in conjunction with other functional materials to modify the glassy carbon electrodes. Their elevated conductivity, extensive surface area, and proficient electron-transfer capability enhance electrode performance by facilitating charge transport and promoting electrocatalytic reactions (Chalupniak & Merkoçi, 2017; Chang et al., 2014; Gontrani et al., 2021). A nanocomposite electrode containing Fe_2O_3 and graphene (G), combined with *in situ* plated bismuth (Bi), was reported for the simultaneous electrochemical detection of trace amounts of Zn^{2+} , Cd^{2+} , and Pb^{2+} . The sensor exhibited an extensive linear concentration range of 1–100 $\mu\text{g L}^{-1}$ and attained

low detection limits of $0.11 \mu\text{gL}^{-1}$, $0.08 \mu\text{gL}^{-1}$, and $0.07 \mu\text{gL}^{-1}$ for Zn^{2+} , Cd^{2+} , and Pb^{2+} , respectively (Lee et al., 2016). The detection performance of ZIF-67/rGO was evaluated for Pb^{2+} and Cd^{2+} in aqueous solutions. The sensor demonstrated a linear response across a wide concentration range ($0.05\text{-}0.1 \text{ mgL}^{-1}$), with a limit of detection (LOD) of $5 \times 10^{-3} \text{ mgL}^{-1}$ for Pb^{2+} and $2 \times 10^{-3} \text{ mgL}^{-1}$ for Cd^{2+} (Garg et al., 2023). Further, A fluorinated graphene oxide (GO) electrode was developed for the concurrent detection of Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} using square-wave anodic stripping voltammetry. The inclusion of fluorine in GO markedly improved sensitivity due to robust interactions between electron-donating fluorine atoms and electron-deficient heavy metal ions (Thiruppathi et al., 2017). Further, AgNPs/rGO nanocomposites were synthesized using an *in situ* approach and employed to modify a glassy carbon electrode, facilitating the simultaneous electrochemical detection of Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} , showing low LOD of 0.141, 0.254, 0.178, and 0.285 μM , respectively (Yukird et al., 2018b). The concurrent detection of Cd^{2+} and Pb^{2+} was accomplished utilizing a glassy carbon electrode modified with BiOCl-decorated multiwalled carbon nanotubes (BiOCl/MWCNTs). The sensor achieved detection limits of $4.0 \mu\text{gL}^{-1}$ and $1.9 \text{ f } \mu\text{gL}^{-1}$ for Cd^{2+} and Pb^{2+} , respectively, using square-wave anodic stripping voltammetry under optimized conditions (accumulation at -1.20 V for 120 sec, pH 4.0) (Cerovac et al., 2015). Moreover, Pb^{2+} in drinking water was detected via a screen-printed electrode enhanced with β -cyclodextrin-functionalized multiwalled carbon nanotubes (MWCNTs). The sensor demonstrated enhanced sensitivity (98 nA/ppb) and a minimal detection threshold (0.9 ppb), achieving 90% repeatability after repeated applications of the fabricated electrode (Alam et al., 2019). Moreover, ZnO nanotube/reduced graphene oxide modified GCE was synthesized for detecting Pb^{2+} ions, and it shows a low LOD of $4.8 \times 10^{-10} \text{ M}$ within a straight-line variation of Pb^{2+} concentration from 2.4×10^{-9} to $4.8 \times 10^{-7} \text{ M}$ (Lu et al., 2015). Further, ZnO nanorods mixed with graphene efficiently detect Cd^{2+} and Pb^{2+} simultaneously using anodic stripping voltammetry (ASV), with LOD values of $0.6 \mu\text{gL}^{-1}$ and $0.8 \mu\text{gL}^{-1}$ for Cd^{2+} and Pb^{2+} , respectively (Yukird et al., 2018b). A recent study demonstrates the excellent catalytic performance of ZnO-electrochemically reduced graphene oxide for detecting Pb^{2+} and Cd^{2+} simultaneously. The LOD values of $1.69 \mu\text{gL}^{-1}$ for Cd^{2+} and $0.45 \mu\text{gL}^{-1}$

for Pb^{2+} are achieved using the ZnO-GO/GCE, and the thin film electrode exhibits remarkable stability (Luyen et al., 2024).

Mercury (Hg^{2+}) was identified with a polypyrrole (PPy)-coated graphene/ β -cyclodextrin (GR-CD) composite modified screen-printed carbon electrode (SPCE). DPV revealed that the GR-CD/PPy/SPCE displayed an enhanced sensitivity for Hg^{2+} relative to unmodified electrodes. The sensor attained a detection limit of 0.47 nM and exhibited excellent selectivity against interfering metal ions (Palanisamy et al., 2017). A bismuth molybdate/graphene (BiM/GR) nanocomposite was synthesized for the electrochemical detection of Hg^{2+} , exhibiting superior electrocatalytic performance (Sakthi Priya et al., 2022). The sensor demonstrated an extensive detection range (0.02–149 μM), exceptional sensitivity (9.5 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^2$), and an ultra-low detection limit of 5.0 nM. The BiM/GR-modified electrode was effectively utilized for the measurement of Hg^{2+} in river water, corn, and fish samples, yielding good recoveries. Further, an eco-friendly, single-use electrochemical sensor utilizing herbal silver nanoparticles (AgNPs) was utilized for the detection of Hg^{2+} (Eksin et al., 2019). The sensor was fabricated by altering the surface of a pencil graphite electrode (PGE) with silver nanoparticles (AgNPs) and folic acid (FA). The sensor, utilizing cyclic voltammetry, attained a detection limit of 8.43 μM and exhibited remarkable selectivity. A novel magnetic electrochemical sensing method detects Hg^{2+} in aqueous solutions utilizing a nanocomposite of halloysite nanotubes, iron oxide, and manganese oxide (HNTs- Fe_3O_4 - MnO_2), synthesized by depositing Fe_3O_4 nanoparticles onto HNTs. The sensor showed a linear response to Hg^{2+} from 0.5 to 150 $\mu\text{g L}^{-1}$, with a detection limit of 0.2 $\mu\text{g L}^{-1}$ and was effectively utilized on actual water samples, attaining recoveries ranging from 96.0 to 102.7% (Fayazi et al., 2016). Moreover, the electrochemical detection of mercury in aqueous solutions was studied utilizing glassy carbon (GC) and indium-tin oxide (ITO) electrodes enhanced with gold nanoparticles (AuNPs). The integration of uniformly distributed AuNPs on GC and ITO substrates demonstrated significant efficacy for Hg detection, achieving the detection limit of 1 $\mu\text{M L}^{-1}$ (Ratner & Mandler, 2015a).

The identification of Zn^{2+} in environmental and biological systems is increasingly significant, as high zinc levels can pose ecological risks and potential

health issues, even though zinc plays a crucial role in biological processes (Fosmire, 1990). A liquid crystal polymer (LCP)-based bismuth film electrode was reported for *in situ* Zn^{2+} detection. The LCP substrate offers significant benefits, including improved operational reliability, mechanical durability, and flexibility, enabling its use on both flat and uneven surfaces. The sensor demonstrated a detection limit of 1.22 nM using square-wave anodic stripping voltammetry with a deposition time of 180 s, indicating its exceptional sensitivity and effectiveness for monitoring trace levels of zinc in practical scenarios (N. Wang et al., 2017). On the other hand, electrochemically reduced graphene oxide (ERGO)-modified glassy carbon electrodes (GCEs) were utilized for the detection of Zn^{2+} . The ERGO-modified GCE, prepared via the modified Hummers process (Tan et al., 2025) and reduced *in situ* via cyclic voltammetry, exhibited a threefold increase in electrocatalytic activity relative to the bare electrode, along with elevated reduction currents and a negative potential shift. A detection limit of $5 \text{ ng} \cdot \text{mL}^{-1}$ was attained using differential pulse voltammetry (Kudr et al., 2016). However, the simultaneous detection of various toxic metals, including Zn^{2+} , is essential for monitoring environmental samples. A $\text{Ti}_3\text{C}_2/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite-based electrochemical sensor was identified as a highly sensitive platform for the detection of Zn^{2+} in conjunction with Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} . Under optimized conditions, the $\text{Ti}_3\text{C}_2/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ modified GCE exhibited remarkable electrochemical performance, featuring a broad linear range (0.005–0.5 μM) and an exceptionally low detection limit of 0.26 nM for Zn^{2+} . Moreover, Zn^{2+} was detected along with Cd^{2+} , and Pb^{2+} employing dendritic bismuth/graphdiyne (Bi/GDY) film-modified glassy carbon electrode (GCE). Furthermore, the fabricated electrode efficiently detected Cd^{2+} and Zn^{2+} in aqueous media. The sensor exhibited ultralow detection limits (0.115 nM for Zn^{2+} , 0.171 nM for Cd^{2+} , and 0.146 nM for Pb^{2+} , $\text{S/N} = 3$) and an extensive linear concentration range of 10.0 nM–100.0 μM . As a result, it demonstrated outstanding repeatability, reproducibility, and stability and was effectively utilized for the sensitive detection of these metals in actual seawater samples (Ai et al., 2023). A bismuth-film electrode was utilized for the concurrent detection of Hg^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , and Cu^{2+} in tap water. The *in situ* Bi-deposited films facilitated the study of metals oxidised at potentials both below and above those of

bismuth, enabling versatile multi-metal detection with limits of detection of 2.5, 2.7, 1.1, 2.2, and 0.6 nmol L⁻¹, respectively (Cesarino et al., 2010).

1.3.2. Electrochemical detection of pharmaceuticals

Electrochemical sensing has gained considerable attention as a reliable and efficient method for antibiotic detection due to its advantages of rapid response, portability, and cost-effectiveness. These attributes make such platforms highly suitable for monitoring pharmaceuticals in various environmental matrices. Nevertheless, only a limited number of studies have specifically addressed the challenges of achieving ultra-sensitive and reproducible detection of chloramphenicol (CAP) and related antibiotics. The presence of these compounds, even at trace concentrations, poses serious concerns by inducing ecotoxicological effects and facilitating the spread of antimicrobial resistance. This has highlighted the critical need for the development of sensitive and selective detection strategies. The integration of nanomaterials, particularly nanoparticles and carbon-based nanostructures, has played a pivotal role in enhancing electrochemical platforms by improving conductivity, enlarging surface area, and enhancing catalytic activity (Hong et al., 2023; Torrinha et al., 2020). Considering these, several nanomaterial-assisted electrochemical sensors for CAP detection have demonstrated outstanding analytical performance. For instance, Lu et al. (2021) reported the fabrication of an electrochemical aptasensor based on polyethyleneimine-functionalized reduced graphene oxide combined with gold nanocubes (PEI-rGO/AuNCs). Using a single-stranded DNA-binding protein as the recognition element, the sensor achieved a broad linear range of 5 pmolL⁻¹–1 μmolL⁻¹ with a remarkably low detection limit of 2.08 pmolL⁻¹, and was successfully validated in spiked chicken samples (M. Lu et al., 2021a). Similarly, chitosan–multi-walled carbon nanotube (CS–MWNT) composite incorporated with gold nanoparticles (AuNPs) was investigated as an efficient electrode modifier for the sensitive detection of chloramphenicol (CAP). The combined influence of the conductive MWNT network, the biocompatible chitosan matrix, and the electrocatalytic characteristics of AuNPs markedly improved the sensor's analytical efficacy. After optimising experimental conditions, the sensor exhibited a wide linear detection range from 10⁻⁸ to 10⁻² g/L and attained a remarkably low detection limit of 3.3 × 10⁻⁹ g/L,

underscoring its capability for trace-level monitoring of CAP (Geng et al., 2024). In another study, Wu et al. (2025) developed a molecularly imprinted electrochemical sensor utilizing polyaniline (PANI) nanorods combined with reduced graphene oxide (RGO). The device enabled selective adsorption of CAP within 6 minutes and exhibited a linear range of 5.0×10^{-9} – 1.0×10^{-6} M, with a detection limit of 1.0 nM. In addition, the sensor showed excellent stability, reproducibility, and satisfactory recoveries in pork and milk samples, further confirming its potential for practical applications in food safety monitoring (Wu et al., 2025). Conversely, for the electrochemical detection of sulfamethoxazole (SMX), Zhang et al. (2019) introduced a molecularly imprinted electrochemical sensor, fabricated using electropolymerization utilizing sulfamethoxazole as the template and o-phenylenediamine as the functional monomer. The device showed a linear response between analyte concentrations of 0.2 to 1.4 μ M, with a detection limit of 0.05 μ M. The sensor showed high selectivity, repeatability, and stability (Zhang et al., 2019). An electrochemical sensor with excellent sensitivity was obtained using the *in situ* synthesis of covalent organic framework materials on polyaniline (TFAB-COF@PANI) for the microanalysis of sulfamethoxazole (SMX). The sensor demonstrated an extensive linear detection range of 1–450 μ M, with a minimal detection limit of 0.107 μ M under optimized experimental conditions (Pan et al., 2023a). However, in addition to single-analyte detection, the determination of sulfamethoxazole using electrochemical techniques is frequently conducted in conjunction with trimethoprim (TMP), given that these two antibiotics are typically co-formulated and used together in combination therapy to improve antibacterial effectiveness (Martins et al., 2021a; Mendes et al., 2019; Yue et al., 2020a). In this context, multiwalled carbon nanotubes functionalized with Prussian Blue nanocubes (MWCNT/PBnc) were created for the simultaneous determination of SMX and TMP utilizing differential pulse voltammetry. The altered electrode exhibited remarkable sensitivity and selectivity, reaching detection limits of 38 nmolL⁻¹ for SMX and 60 nmolL⁻¹ for TMP (Sgobbi et al., 2016).

Nanostructured materials are showing increased attention in the advancement of scientific and technological developments, or in the development of miniaturized devices. The unique properties, viz., the physical, chemical, electrical, biological, and

optoelectrical, have attracted interest in diverse areas of research. Moreover, the green synthesis has recently gained attention for synthesizing the nanomaterials or their respective composites (Ameta et al., 2021). Platinum nanoparticles were synthesized using the leaf extract of *Cerbera manghas* (as a reducing agent) (Rajathi & Nambaru, 2014). Plant extracts provide opportunities for precise control of nanoparticle formation, allowing for well-defined sizes and morphologies achieved in a single-step, facile method (Mittal et al., 2013). The synthesis of gold nanoparticles was reported using *Persea americana* (Avocado) as a reducing agent (Lalhrualtuangi et al., 2025). Using jambul seed extract, a straightforward and environmentally safe method was introduced for the synthesis of silver-reduced graphene oxide nanocomposites (Ag/rGONCs). *In situ* decoration of silver ions on graphene oxide was achieved in a single step by utilizing the green precursor of jambul seed extract in a one-pot approach. With detection limits of 50 nM, 15 nM, and 500 nM, the resulting nanocomposite showed good selectivity for the detection of Pb^{2+} , Hg^{2+} , and Cr^{6+} ions (Onkar Patil et al., 2020).

In a line, the metal oxide nanoparticles were utilized extensively because of their size, high surface area, biocompatibility, chemical stability, surface reaction activity, and rapid electron transport; hence, they are widely used in the electroanalysis of analytes (Kumar et al., 2024). Traditionally, the synthesis of metal nanoparticles has primarily relied on chemical methods, such as chemical vapour deposition (CVD) (Khan et al., 2019), thermal decomposition (Unni et al., 2017), or chemical reduction (Szczyglewska et al., 2023). These methods of synthesizing high-quality nanomaterials, however, pose several drawbacks, such as high energy consumption, toxic chemicals that may pose environmental and health risks, and the generation of chemical waste; they are devoid of sustainable implications (Chopra et al., 2022; Jamkhande et al., 2019). Therefore, alternative environment-friendly and sustainable approaches are attracting attention in material synthesis. ‘Green Chemistry’ principles emphasize using environmentally friendly and non-toxic reagents, energy-efficient processes, and reduced waste production (Ahmed et al., 2022; Gupta et al., 2023). *Acmella oleracea*, the most well-known species within this genus, is valuable for its traditional medicinal uses and potential in developing metal nanoparticles,

contributing to sustainable nanotechnological inputs. *Acmella oleracea* synthesizes the silver nanoparticles using the phytochemicals of the *Acmella oleracea* leaf extract, viz., glycosides, flavonoids, phenolic compounds, alkaloids, amino acids, tannins, terpenoids, and saponins. These compounds potentially reduce the silver ions and stabilize the nanoparticles (Bhardwaj et al., 2022). Similarly, *Spilanthes acmella* extract synthesizes the iron oxide nanoparticles (IO-NPs). The UV-Vis spectroscopy data infer the formation of nanoparticles, and the FT-IR reveals that the biosynthesized IO-NPs are capped with different phytochemicals, contributing to their antioxidant activity and adsorption effectiveness (Sharma et al., 2023).

ZnO exhibits distinct advantages as an electrochemical sensor material resulting from its large band gap energy, intense binding energy, high excitability, and exceptional biocompatibility (Ahmed et al., 2022). Their high mechanical strength and stability ensure durability in testing conditions, making them highly suitable for various sensing applications. The nanoceria ($\text{CeO}_2(\text{NP})$) has shown broad applicability in sensor research due to its biocompatibility, chemical and thermal endurance, high oxygen storage capacity, and excellent surface electrical conductivity (Finny et al., 2020; Wahyuni Hartati et al., 2021). Similarly, the CeO_2 nanoparticle-modified screen-printed electrodes ($\text{CeO}_2\text{-SPEs}$) were synthesized for the simultaneous analysis of codeine (COD), acetaminophen (APAP), and caffeine (CAF), where the $\text{CeO}_2\text{-SPEs}$ exhibited low detection limits of 0.051, 0.043, and $2.4 \mu\text{molL}^{-1}$ for COD, APAP, and CAF, respectively (Khairy et al., 2018). Dopamine was detected efficiently with a low detection limit of 80 nmolL^{-1} using the ultra-small cerium oxide nanoparticles (USCeONPs) (Gomes-Junior et al., 2024). Moreover, researchers explored the use of nanoceria in the electrochemical sensors for the detection of various pollutants (Kusuma et al., 2022; Z. Wang et al., 2022; J.-W. Zhang & Zhang, 2020). These research findings demonstrated the remarkable electrochemical behaviour of CeO_2 modified electrodes for their simple design, high durability, and efficient detecting capabilities.

1.4. SCOPE OF PRESENT INVESTIGATION

Aquatic ecosystems are facing serious threats from a variety of pollutants, particularly toxic heavy metals and emerging micro-pollutants. Rapid industrialization, unregulated urban growth, agricultural runoff, and the extensive use of pharmaceuticals and personal care products have collectively contributed to the continuous influx of these hazardous substances into water bodies. The accumulation of such contaminants has reached their threshold levels in the aquatic environment, endangering aquatic biodiversity and posing severe risks to human health, irrigation, and food chains. Heavy metals, being non-biodegradable, persistent, and bioaccumulative across trophic levels, lead to long-term ecological imbalance and adverse health impacts such as neurotoxicity, organ damage, and carcinogenic effects. Similarly, micro-pollutants, even at trace concentrations, are capable of disrupting endocrine systems, impairing reproduction, and destabilizing aquatic ecosystems. To address these pressing environmental challenges, there is an urgent need for rapid, sensitive, and cost-effective detection technologies. Electrochemical sensing techniques have emerged as powerful alternatives to conventional analytical methods owing to their simplicity, high sensitivity, rapid response, and low operational cost. The current study aims to develop electrochemical methods for highly selective and ultrasensitive sensing of heavy metal ions and pharmaceuticals in an aqueous environment. A glassy carbon electrode (GCE) was employed as the working electrode due to its broad potential window, chemical stability, and facile surface modification. Further, the graphene oxide possesses a high surface area, rich oxygen functionalities, and the ability to form stable nanocomposites with suitable materials, thereby improving electrical conductivity and mechanical robustness. Moreover, a greener route synthesizes the metal oxide nanoparticles, such as zinc oxide (ZnONPs) and cerium oxide (CeONCs) synthesized using an *Acmella oleracea* leaf extract. These nanoparticles serve as efficient catalytic sites, accelerating electron transfer and significantly enhancing sensor sensitivity and selectivity. A simple and robust method impregnates these ZnONPs and CeONCs with the GrO substrates and yields multifunctional nanocomposites. Further, the drop casting method casted the nanocomposite materials at the GCE surface and was employed for the ultra-trace

detection of heavy metal ions, including Hg^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} , and pharmaceutical contaminants such as chloramphenicol (CRP), ibuprofen (IBP), and sulfamethoxazole (SFX) in aqueous medium. The detection of these pollutants at trace levels will demonstrate the high analytical potential of the proposed method. The fabricated electrode was assessed for its stability and enhanced shelf life for greater applications. Furthermore, the practical applicability of the developed sensor is evaluated using real water samples collected from various locations across Aizawl City, India.

CHAPTER 2

METHODOLOGY

2. METHODOLOGY

2.1. CHEMICALS AND APPARATUS

Table 2.1 presents a detailed and comprehensive list of all the chemicals and reagents utilized throughout the present study. This includes the materials required for synthesis, characterization, and analytical procedures.

Table 2.1: A detailed list of chemicals and reagents utilized in the present study.

Sl. No	Chemicals	IUPAC Name	Formula	Company	CAS No./ID
1	Amoxicillin	(2S,5R,6R)-6- {[(2R)-2- Amino-2-(4- hydroxyphenyl) acetyl]amino}- 3,3-dimethyl-7- oxo-4-thia-1- azabicyclo[3.2.0]]heptane-2- carboxylic acid	$C_{16}H_{19}N_3O_5S$	Sigma Aldrich, USA	26787-78-0
2	Cerium nitrate	Cerium(III) nitrate hexahydrate	$Ce(NO_3)_3 \cdot 6$ H_2O	Sigma Aldrich, USA	10294-41-4
3	Diclofenac	2-[2-(2,6- dichloroanilino) phenyl]acetic acid	$C_{14}H_{11}Cl_2NO_2$	Sigma Aldrich, USA	15307-79-6
4	Graphite powder	Carbon	C	Sigma Aldrich, USA	7782-42-5
5	Ibuprofen	2-[4-(2- methylpropyl)ph enyl]propanoic acid	$C_{13}H_{18}O_2$	Sigma Aldrich, USA	15687-27-1
6	Paracetamol	N-(4- hydroxyphenyl) acetamide	$C_8H_9NO_2$	Sigma Aldrich, USA	103-90-2

7	Tetracycline	(4S,4aS,5aS,12aS)-4-(Dimethylamino)-1,4,4a,5,5a,6,11,12a-octahydro-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamide	$C_{22}H_{24}N_2O_8$	Sigma Aldrich, USA	64-75-5
8	Sulfamethoxazole	4-amino-N-(5-methyl-1,2-oxazol-3-yl)benzene-1-sulfonamide	$C_{10}H_{11}N_3O_3S$	Sigma Aldrich, USA	723-46-6
9	Chloramphenicol	2,2-dichloro-N-[(1R,2R)-1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl]acetamide	$C_{11}H_{12}Cl_2N_2O_5$	SRL, India	56-75-7
10	Cobalt nitrate	Cobalt(II) nitrate hexahydrate	$Co(NO_3)_2 \cdot 6H_2O$	SRL, India	10026-22-9
11	Phosphoric acid	trihydroxidooxidophosphorus	H_3PO_4	SRL, India	7664-38-2
12	Cadmium nitrate tetrahydrate	Cadmium nitrate tetrahydrate	$Cd(NO_3)_2 \cdot 4H_2O$	Merck, Mumbai, India	10022-68-1

13	Calcium chloride	Calcium chloride	CaCl_2	Merck, Mumbai, India	7440-70-2
14	Copper sulphate	Copper sulphate	CuSO_4	Merck, Mumbai, India	7759-98-7
15	Ethyl alcohol	Ethanol	$\text{C}_2\text{H}_5\text{OH}$	Merck, Mumbai, India	64-17-5
16	Lead nitrate	Lead nitrate	$\text{Pb}(\text{NO}_3)_2$	Merck, Mumbai, India	10099-74-8
17	Magnesium sulphate	Magnesium sulphate	MgSO_4	Merck, Mumbai, India	7487-88-9
18	N, N-dimethylformamide (DMF)	N, N-dimethylformamide	$\text{C}_3\text{H}_7\text{NO}$	Merck, Mumbai, India	68-12-2
19	Nickel chloride	Dichloronickel	NiCl_2	Merck, Mumbai, India	7718-54-9
20	Potassium ferricyanide	Potassium hexacyanoferrate (III)	$\text{K}_3[\text{Fe}(\text{CN})_6]$	Merck, Mumbai, India	13746-66-2
21	Potassium ferrocyanide	Potassium hexacyanoferrate (II) trihydrate	$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	Merck, Mumbai, India	14459-95-1

22	Potassium chloride	Potassium chloride	KCl	Merck, Mumbai, India	7447-40-7
23	Sodium chloride	Sodium chloride	NaCl	Merck, Mumbai, India	7647-14-5
24	Sodium nitrate	Sodium nitrate	NaNO ₃	Merck, Mumbai, India	7631-99-4
25	Sulphuric acid	Sulphuric acid	H ₂ SO ₄	Merck, Mumbai, India	7664-93-9
26	Zinc chloride	Zinc chloride	ZnCl ₂	Merck, Mumbai, India	7446-20-0
27	Chloride reagent	Chloride	Cl ⁻	Hanna Instruments, India	Hi-93753
28	Fluoride low-range reagent	Fluoride	F ⁻	Hanna Instruments, India	Hi-93729
29	Nitrate reagent	Nitrate	NO ₃ ⁻	Hanna Instruments, India	Hi-93728
30	Phosphate reagent	Phosphate	PO ₄ ³⁻	Hanna Instruments, India	Hi-93713
31	Sulfate reagent	Sulphate	SO ₄ ²⁻	Hanna Instruments, India	Hi-93751

32	Acetic acid	Acetic acid	CH_3COOH	HiMedia Chemical, Mumbai, India.	64-19-7
33	Ferric chloride	Iron trichloride hexahydrate	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	HiMedia Chemical, Mumbai, India.	10025-77-1
34	Hydrogen peroxide	Hydrogen peroxide	H_2O_2	HiMedia Chemical, Mumbai India.	7722-84-1
35	Mercuric chloride	Mercury dichloride	HgCl_2	Himedia, India	7487-94-7
36	Sodium phosphate dibasic heptahydrate	Disodium; dihydrogen phosphate; heptahydrate	$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$	HiMedia Chemical, Mumbai India.	7558-79-4
37	Sodium phosphate monobasic monohydrate	Sodium dihydrogen phosphate	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	HiMedia Chemical, Mumbai India.	10049-21-5.
38	Sodium acetate anhydrous	Sodium acetate	CH_3COONa	HiMedia Chemical, Mumbai India.	127-09-3
36	Sodium hydroxide	Sodium hydroxide	NaOH	HiMedia Chemical, Mumbai India.	1310-73-2

The Arium Mini Plus UV Lab (Germany) water purification system was utilized to obtain purified water with a water resistivity of $18.2 \text{ M}\Omega \times \text{cm}$, and the conductivity was less than $20 \text{ }\mu\text{Scm}^{-1}$. All solutions were prepared using the purified water. Acetate buffer and phosphate buffer solutions were prepared as described by Hamed and wang (Hamed et al., 2018; Wang et al., 2013). Standard working solutions were then obtained by diluting the stock solutions with either acetate buffer or phosphate buffer, supporting electrolyte.

2.2. INSTRUMENTS

An electronic balance (HPB220, Wensar, India) was utilized for weighing the chemicals. The pH of solutions was measured utilizing a Microprocessor pH meter (Labtronics India Ltd., India; Model No.: LT-16). The centrifuge (REMI-23, Vasai, India) operates at a maximum rotating speed of 6900 revolutions per minute (RPM) and was employed for centrifugation applications. A bath sonicator (LMUS-4, Wensar, India) is utilized for sonication applications.

The surface morphology and surface roughness of the materials were analyzed using an Atomic Force Microscope (AFM, Ntegra Aura, NT MDT, Russia). A Field Emission Scanning Electron Microscope coupled with Energy Dispersive X-ray spectroscopy (FESEM/EDX, JEOL JSM 7100F; Oxford Xmax, Japan) was employed under operating conditions of 15 kV, with a magnification range from $10\times$ to $1,000,000\times$, an accelerating voltage between 0.2 and 30 kV, and a probe current varying from 1 pA to 400 nA. Furthermore, High-Resolution Transmission Electron Microscopy (HRSTEM, JEOL JEM 2100; Oxford Xtreme, Germany) was operated at an acceleration voltage of 200 kV with a magnification of 40K.

X-ray diffraction (XRD) examination of the nanocomposite materials was conducted utilizing a PANalytical X'Pert PRO MPD diffractometer (Netherlands) to acquire their powder diffraction patterns. The device was utilized at a scan rate of $0.033^\circ (2\theta)$, using generator settings of 30 mA and 40 kV. Copper served as the anode material, emitting $\text{Cu K}\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$) and $\text{K}\alpha_2$ ($\lambda = 1.54443 \text{ \AA}$) radiations. X-ray photoelectron spectroscopy (XPS, ESCA 3500, Japan) was utilized to ascertain the elemental composition of the synthesized material and to identify the oxidation states of its constituent elements. The Brunauer-Emmett-Teller (BET) analyzer

(Micromeritics ASAP 2000 V2.04, USA) determines the surface volume, area, and pore size of the materials.

A TOC analyzer (TOC-VCPH/CPN, Shimadzu, Japan) was employed to quantify the non-purgeable organic carbon (NPOC) and inorganic carbon (IC) levels in water samples. A multiparameter photometer (Hanna, model: HI83300, USA) is utilized for acquiring diverse parametric data from water samples. An Atomic Absorption Spectrometer (AAS) (Shimadzu, Inc., AA-7000, Japan) and a multiparameter waterproof meter (probe) from Hanna, USA (model: HI98194) were utilized to measure the pH, ORP (Oxidation-Reduction Potential), conductivity, resistivity, TDS (Total Dissolved Solids), and salinity of the natural water samples. Zinc oxide and cerium oxide nanoparticles colloidal solution were analyzed by the UV-Visible spectrophotometer (UV-1800; Shimadzu, Japan). An LED (light-emitting diode) bulb (Havells- Adore LED 9W, India) was used as a light source for photo-Fenton-like reactions. A Modular Thermo Scientific Vanquish™ Core HPLC system (Thermo Scientific, Germany) was used to estimate the degradation percentage of CRP and SFX.

The electrochemical investigations were performed utilizing an electrochemical workstation (Biologic Instruments electrochemical workstation, Model SP-200, France). The reference electrode (Ag/AgCl/NaCl (3.5M)) sourced from BaSi, USA (Model: RE-5B), a platinum counter electrode (outer diameter: 6 mm, inner diameter: 1.6 mm; Model: A-002013, Allum, USA), and a glassy carbon working electrode (GCE) (outer diameter: 6 mm, inner diameter: 3 mm; Model: A-002421, Allum, USA). The electrochemical data were examined using the integrated software EC-Lab. EC-Lab is an extensive software specifically engineered for BioLogic Potentiostat/Galvanostat/FRA equipment utilized in comprehensive electrochemical studies.

2.3. ELECTROCHEMICAL TECHNIQUES

Electrochemical methods were widely employed to investigate the interfacial interactions between analytes and electrode materials, as well as to evaluate the kinetics of charge transfer processes. These approaches provide essential insight into the fundamental principles of electron transfer, adsorption, and mass transport reactions, therefore improving the assessment of electrode properties and allowing for the precise detection of target analytes. The detection behind electrochemical techniques is based on observing changes in measurable electrical properties when electroactive species interact with the electrode. These techniques are categorized based on the measured signal, which includes potentiometry that observes potential variations, voltammetry and amperometry that examine current responses to applied potential, and electrochemical impedance spectroscopy (EIS) that assesses interfacial resistance and capacitance. The widely employed methods involve systematic regulation of either potential or current. When the potential is regulated and the resulting current is quantified, the method is known as potentiostatic (e.g., voltammetry, amperometry). Therefore, voltammetry techniques like cyclic voltammetry (CV) offer valuable insights into the redox processes, reversibility, and electrode stability, whereas differential pulse voltammetry (DPV) enhances sensitivity and resolution for detecting trace levels of analytes. Furthermore, EIS is useful for investigating interfacial characteristics, charge transfer resistance, and interaction with analytes. The study employs the sensitive detection and quantification of target analytes.

2.3.1. Cyclic voltammetry (CV)

Cyclic voltammetry is an electrochemical technique in which the potential of a working electrode is linearly swept back and forth using a potentiostat, and the resulting current from redox-active species in the solution is measured as a function of the applied potential. The potential of the working electrode is controlled relative to a reference electrode, commonly a saturated silver/silver chloride electrode (Ag/AgCl). This method employs a triangular potential waveform, oscillating the electrode potential between two predetermined limits, i.e., lower potential and upper potential.

Therefore, the working electrode potential is linearly varied between two specified switching potentials in a saw tooth manner, facilitating sequential oxidation and reduction of the electroactive species in solution. This produces separate anodic and cathodic peak currents, reflecting electron transport from the solution to the electrode and vice versa. The intensity of the resultant faradaic currents elucidates the kinetics of electron transfer and interfacial phenomena at the electrode surface. The reversibility of the redox pair is assessed by analyzing the anodic and cathodic peak potentials (E_{pa} and E_{pc}) and their respective peak currents (i_{pa} and i_{pc}). In a reversible system, the peak-to-peak separation ($\Delta E_p = E_{pa} - E_{pc}$) is around $59/n$ mV at 25 °C, where 'n' represents the number of electrons transported, and the anodic and cathodic currents are approximately equivalent, signifying rapid electron exchange in equilibrium with the applied potential. When ΔE_p exceeds $59/n$ mV and increases with the scan rate, the process is described as quasi-reversible, indicating slower electron transfer kinetics. The absence of a reverse peak in the cyclic voltammogram indicates chemical irreversibility, typically resulting from subsequent reactions or product instability, though it does not typically suggest total irreversibility of electron transfer reactions.

2.3.2. Differential pulse voltammetry anodic stripping voltammetry (DPASV)

Differential pulse voltammetry (DPV) is a pulse technique that aims to enhance sensitivity by reducing background charging currents and improving the detection of faradaic signals. This method involves superimposing a series of small potential pulses onto a linear potential sweep, with the current being recorded twice for each pulse, once immediately before its application and again at the end of the pulse. The measured signal is the difference between these two current values, thereby eliminating the non-faradaic (charging) component and emphasizing the faradaic (electron transfer) response of the analyte. Each pulse possesses a constant amplitude, and the response is graphed against the applied potential, resulting in a voltammogram characterized by distinct, peak-shaped signals, whose peak height is directly proportional to the concentration of the analyte. Differential pulse anodic stripping voltammetry (DPASV) enhances sensitivity using the preconcentration phase, when the analyte is initially deposited onto the electrode surface at a negative potential and

subsequently stripped during a positive potential scan. The stripping process generates a distinct anodic peak current that correlates precisely with analyte concentration, rendering DPASV exceptionally effective for the ultra-trace detection of heavy metals and specific chemical molecules.

2.3.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a multifaceted method employed to examine interfacial properties and charge transfer dynamics at the electrode–electrolyte interface. The technique involves applying a little sinusoidal potential change over an extensive frequency spectrum while observing the resultant current response. The system's impedance is derived from the ratio of the applied potential to the measured current, analysed across varying frequencies. The sinusoidal perturbation in electrochemical impedance spectroscopy results in a wave-like system response. This wave-like behaviour necessitates the characterization of impedance through two parameters: (i) total impedance (Z), denoting the amount of opposition to current flow, and (ii) phase shift (Φ), reflecting the delay between the applied voltage and the resultant current. These characteristics are often shown in impedance spectra as Nyquist plots (real vs imaginary impedance) and Bode plots (impedance magnitude and phase versus frequency). The impedance is mathematically represented as a complex function of angular frequency, $Z(\omega)$, where $\omega = 2\pi\nu$ (ν = frequency). $Z(\omega)$ comprises two components: the real part (resistive behaviour) and the imaginary part (capacitive or inductive behaviour). The amalgamation of these elements offers an extensive representation of the electrochemical phenomena taking place at the electrode interface. A Nyquist plot is obtained by graphing the real part of impedance ($R_e(Z)$) on the X-axis and the imaginary part on the Y-axis ($I_m(Z)$). Every point on the Nyquist plot represents the impedance at a particular frequency. By correlating experimental EIS data from electrolytic cells to a suitable equivalent circuit, electrochemical parameters such as solution resistance, double-layer capacitance, and mass transport processes are amicably demonstrated. The EIS is also employed to quantify the charge transfer resistance (R_{ct}), which acts as a metric for assessing the efficiency of electron transfer between the analyte and the electrode surface. A reduced R_{ct} value indicates rapid electron transfer kinetics.

2.4. PREPARATION OF MATERIALS

2.4.1. Preparation of *Acmella oleracea* aqueous leaf extract

Fresh leaves of *Acmella oleracea*, also known as the toothache plant, were collected in the vast campus of Mizoram University, Aizawl, meticulously washed with purified water to eliminate any dust or surface impurities, and then air-dried at room temperature in shaded conditions for one week. Shade-drying maintains the phytochemical constituents of the leaves, since direct sunlight exposure may lead to evaporation or degradation of heat- or light-sensitive phytochemicals. Upon achieving complete dryness, the leaves were carefully ground into a uniform powder utilizing a mortar and pestle. 10 g of the dried leaf powder was placed into a clean beaker, mixed with 100 mL of purified water at a ratio of 1:10 (w/v). The solution mixture was subjected to heating on a hot plate at a temperature of 80°C for a duration of 30 min, accompanied by continuous stirring to facilitate the effective extraction of phytoconstituents into the aqueous medium. The extract was permitted to cool slowly at room temperature, and the cooled extract was then filtered using Whatman filter paper (mesh size: 11 µm) to eliminate particulate matter and plant debris, resulting in a clear aqueous leaf extract. The filtrate was stored in a cleaned glass bottle, appropriately labelled, and stored in the refrigerator for subsequent experiments.

2.4.2. Phytochemical screening

The aqueous extract of *Acmella oleracea* leaves underwent preliminary phytochemical analysis to identify the presence of significant classes of secondary metabolites. The screening was conducted qualitatively, focusing on colour changes and/or the formation of precipitates that arise from specific chemical reactions. Established protocols documented in the literature were adhered to for each test.

1. **Test for Flavonoids:** 1 mL of extract was treated with 2 mL of a 2% NaOH solution. The emergence of an intense yellow hue that vanished upon the introduction of a few drops of conc. HCl signified the presence of flavonoids (Audu et al., 2007).
2. **Test for Tannins:** 1 mL of the aqueous extract was added to 3 mL of purified water and treated with 3 drops of 10% ferric chloride solution. The mixture was

vigorously stirred. The emergence of blue-green colour inferred the presence of tannin in the extract (Singh & Kumar, 2017).

3. **Test for phenolic compounds:** 2 mL of extract was mixed with a few drops of a 5% ferric chloride solution. The emergence of a bluish-black or greenish hue signified the presence of phenolic compounds (Nortjie et al., 2022).
4. **Test for saponins:** 5 mL of plant extract was stirred with 10 mL of distilled water in a test tube. Prolonged foaming (exceeding 10 minutes) suggested the existence of saponins (Shaikh & Patil, 2020).
5. **Test for Terpenoids:** Approximately 5 mL of aqueous plant extract was transferred to a cleaned test tube and combined with 2 mL of chloroform. The mixture was thoroughly agitated and boiled in a water bath until the chloroform fully evaporated, resulting in a residue. To the residue, 3 mL of concentrated H_2SO_4 was meticulously introduced along the interior wall of the test tube. The tube was subsequently heated at around 60°C in a water bath for several minutes. The manifestation of a reddish-brown hue signified the existence of terpenoids (Shaikh & Patil, 2020).

2.4.3. Synthesis of Graphene Oxide (GrO)

Hummer's modified method synthesized the graphene oxide (GrO) (Zaaba et al., 2017). The detailed synthesis followed: 27 mL of sulfuric acid (H_2SO_4) and 3 mL of phosphoric acid (H_3PO_4) are mixed and agitated for about 15 min. 0.225 g of graphite powder is added to the mixed acid solution under stirring. The solution is then gradually supplemented with 1.32 g of potassium permanganate (KMnO_4), and the solution mixture is further agitated for 6 hrs until it turns dark green. To remove the excess KMnO_4 , 0.675 mL of hydrogen peroxide is gently added and stirred for 10 min. The exothermic reaction is allowed to cool down, and 10 mL of hydrochloric acid and 30 mL of purified water (PW) are added and centrifuged for 15 min at 1000 rpm. The supernatant is then decanted, and the residuals are washed three times with PW. The cleaned GrO powder is dried in a drying oven at 90°C for 24 hrs.

2.4.4. Synthesis of metal oxide nanoparticles

To synthesize zinc oxide nanoparticles, a 100 mL solution of 0.01 M zinc chloride (ZnCl_2) was freshly prepared in purified water (PW). 5 mL of *Acmella oleracea* aqueous leaf extract is steadily added with constant stirring to ensure the intimate mixing of phytochemicals with the metal precursor solution. The pH of the solution was carefully adjusted to around 6 using dilute sodium hydroxide. The reaction mixture was kept under continuous stirring at 70 °C for 24 hrs. The method resulted in a discernible alteration in the colour from colourless to pale off-white, accompanied by the formation of a colloidal suspension, indicating the successful formation of ZnO nanoparticles. The whitish precipitate ZnO(NP) was collected, rinsed with 30 mL purified water, and then dried at 400°C for 12 hrs.

A 0.05 M solution of cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was freshly prepared by dissolving the necessary quantity of the salt in 100 mL of PW. In this procedure, 7.5 mL of the pre-filtered plant extract was added dropwise while maintaining continuous stirring to achieve uniform mixing. The reaction mixture was kept under continuous agitation for 2 hrs at 60°C to promote the reduction and stabilization processes. Throughout the reaction, a noticeable colour change from its original colour to a yellowish hue occurs. The UV–Visible absorption spectra of the synthesized metal oxide nanoparticle colloidal solutions were measured within the wavelength ranges of 200–600 nm. The precipitate CeONC was collected, rinsed with 30 mL purified water, and dried at 400°C for 12 hrs.

2.4.5. Synthesis of Nanocomposite materials

To synthesize the zinc oxide nanoparticles incorporated graphene oxide (ZnO(NP)@GrO) and cerium oxide nanoparticles incorporated graphene oxide (CeONC@GrO) nanocomposite material, 300 mg of freshly prepared graphene oxide (GrO) was first dispersed in 50 mL of ethanol. The suspension underwent ultrasonication for 45 min, an essential procedure for attaining good exfoliation of the multilayer GrO structure. Thereafter, 900 mg of pre-synthesized zinc oxide nanoparticles (ZnO NPs) was dispersed in 100 mL of PW, which was further introduced dropwise to the graphene oxide (GrO) suspension while maintaining

continuous agitation. The gradual addition facilitated consistent nucleation and formation of nanoparticles on the GrO surface, reducing agglomeration and ensuring close interfacial contact. The mixture was subsequently refluxed for 6 hrs at 90 °C, and then cooled to 24°C, during which a discernible colour transformation to a blackish tint was noted. This transition signified a good interaction between the GrO sheets and the nanoparticles. The nanocomposite material was then filtered and washed repeatedly using approximately 30 mL of PW, followed by 30 mL of ethyl alcohol. Additionally, ZnO(NP)@GrO product was subjected to drying at 80°C for 24 hrs.

Likewise, the synthesis of CeONC@GrO nanocomposite material was carried out. Briefly, 300 mg of freshly prepared GrO material was dispersed in 50 mL of ethanol and subjected to ultrasonication for 45 min. Subsequently, 900 mg of cerium oxide dispersed in 100 mL PW is added dropwise to the GrO suspension, refluxed for 6 hrs at 90°C, resulting in a colour change to a blackish hue. After being cooled at 24°C, the composite solution was centrifuged at 3000 rpm and thoroughly rinsed with 30 mL of both purified water and ethyl alcohol. Finally, the product was dried at 80°C for 24 hrs, subsequently crushed into powder, and the CeONC@GrO nanocomposite material was obtained and kept in a cleaned glass bottle.

2.5. FABRICATION OF ELECTRODE

The glassy carbon electrode (GCE) was modified using a systematic approach to ensure the formation of uniform thin-film electrodes with stable surface properties. The GCE surface was initially polished in combination with polishing diamond (1µm) and alumina (0.5 µm) slurry to achieve a clean and contaminant-free surface. This mechanical polishing procedure increases the active surface area and guarantees homogeneity of the electrode surface. Subsequent to polishing, the electrode underwent sonication for 5 min to eliminate the residual polishing particles from the surface. The electrode was meticulously rinsed with purified water followed by ethyl alcohol, which effectively removes any organic or particle impurities from the electrode surface. For the preparation of the modifying suspensions, 5 mg of CeONC@GrO, ZnO(NP)@GrO powder, and pristine GrO powders were each dispersed in 10 mL of dimethylformamide (DMF) and agitated for 1 hrs to achieve a

homogenous solution. Upon attaining a homogeneous dispersion solution, 0.025 mL of each prepared solution was meticulously drop-cast onto the surface of the pretreated GCE to create thin and well-adhered films. The coated electrodes were subsequently dried at 45°C in a drying oven, where the solvent evaporates. The resultant ZnO(NP)@GrO, or CeONC@GrO, or pristine GrO modified electrodes modified glassy carbon electrodes were then utilized for electrochemical investigations.

2.6. CHARACTERIZATION OF NANOCOMPOSITE

The surface morphology of the synthesized ZnO(NP)@GrO and CeONC@GrO nanocomposite materials was characterized using field emission scanning electron microscopy (FE-SEM; Model: JSM 7100F, JEOL, JAPAN). The percentage elemental composition of elements in the samples was analyzed using energy-dispersive X-ray (EDX) spectroscopy coupled with scanning electron microscopy (SEM). The particle shape and size of the synthesized ZnO(NP)@GrO and CeONC@GrO nanocomposite materials were characterized using transmission electron microscopy (TEM; Model JEM 2100, JEOL, JAPAN). An atomic force microscope (AFM) (NTEGRA Aura instrument from NT MDT, Russia) was used for analysis of the material's surface roughness, and measurements were conducted under the tapping mode. The composition and oxidation states of Zinc (Zn 2p) and Cerium (Ce3d) were analyzed using X-ray photoelectron spectroscopy (XPS) with the ESCALAB Xi+ model from Thermo Fisher Scientific Pvt. Ltd., UK. Similarly, the X-ray Diffraction (XRD) analysis of ZnO(NP)@GrO and CeONC@GrO nanocomposites was carried out to confirm their crystalline structure.

Furthermore, the ecotoxicity evaluation of the synthesized nanocomposite materials is done against *Daphnia magna* (*D. magna*), which was sourced from the National Institute of Environmental Research in the Republic of Korea. The culturing of *D. magna* was conducted in an M4 medium using a 2 L glass beaker, following the OECD Guideline No. 211. (*Test No. 211*, 2012) The temperature was controlled at 20±1°C under a 16 h illumination and 8 h darkness daily cycle. The organisms were provided with *Chlorella vulgaris* each day at a concentration of 5×10^5 cells/mL, while the M4 medium was replaced twice every week.

The acute toxicity of nanocomposite materials was conducted following the protocols outlined in OECD Guideline 202. (*Test No. 202*, 2004) For the test solutions, different concentrations of CeONC@GrO solutions (0 - 10 mgL⁻¹) and ZnO(NP)@GrO (5.0, 30.0, 90.0, and 120.0 mgL⁻¹) were prepared and stirred in ISO medium (pH: 8, hardness: 250 mgL⁻¹, DOC: 9.1 mgL⁻¹) for 24 hr. All the test solutions were passed through a filter (Whatman, 0.45µm). All the experiments, including the control, were performed in 4 replicates, where 20 neonate individuals were subjected to 50 mL of the ISO solution for 48 hrs without food. The experiment is conducted at 20±2°C under a 16-hrs and 8-hrs dark photoperiod cycle, without feeding. The toxicity was evaluated by measuring the percentage of immobilized and mortality (motionless after 15 s after shaking). Throughout all experiments, the control group exhibited no mortality. The median effective concentration (EC₅₀) and its 95% confidence interval (CI) were determined using the trimmed Spearman-Kärber method (Hamilton et al., 1977).

The point of zero charge (pH_{PZC}) pH is the pH at which a solid surface exhibits no net charge, as the effects of its acidic and basic functional groups on the solution pH are equilibrated. At pH levels below the pH_{PZC}, surface functional groups often undergo protonation, imparting a positive charge to the surface; conversely, at pH levels above the pH_{PZC}, these groups dissociate, releasing the protons, leading to a negative surface charge. The pH_{PZC} of ZnO(NP)@GrO and CeONC@GrO nanocomposites was done using a drift approach (Saha et al., 2020). Initially, CO₂-free water was acquired by boiling purified water for 20 min to remove dissolved carbon dioxide, and thereafter sealing the flask immediately to avert reabsorption of the CO₂. 0.01 molL⁻¹ NaCl solutions were prepared using the same water, and their initial pH values were adjusted to 2, 4, 6, 8, 10, and 12 with 0.1 molL⁻¹ HCl or NaOH solutions. Subsequently, 100 mg of the solid was added to each water sample, and the suspensions were securely sealed and agitated for 24 hrs at 25°C to attain equilibrium between the solid/solution interface. Following equilibration, the final pH of each solution was recorded. A graph depicting initial pH (pH_{Initial}) against final pH (pH_{Final}) was subsequently plotted. The pH_{PZC} was determined at the point where the curve

intersects the line $\text{pH}_{\text{Initial}} = \text{pH}_{\text{Final}}$, indicating the pH at which the surface possessed no net charge.

2.7. SPECIATION STUDIES

The speciation of cadmium, lead, mercury, zinc, chloramphenicol, ibuprofen, and sulfamethoxazole was simulated using Visual MINTEQ (v3.1 software) at 25°C. The software utilizes various equilibrium constants of these metal ions along with the physical parameters, *viz.*, metal concentration, pH, ionic strength, and temperature. The percentage distribution of various species was graphed against pH, offering insights into the stability of free ions, hydroxo-complexes, and carbonate complexes. The dissociation constants (pK_a values) of organic compounds like chloramphenicol, ibuprofen, and sulfamethoxazole were utilized to model their ionization states across various pH levels. Chloramphenicol ($\text{pK}_a \approx 5.5$) (Khelifa et al., 2023) predominantly exists in its neutral form at acidic pH, whereas a partial deprotonation of the hydroxyl groups takes place under alkaline conditions. Ibuprofen ($\text{pK}_a \approx 4.9$) (Bjarnason et al., 2018) remained primarily in its neutral form at pH levels below 5, transitioning to the anionic carboxylate form when the pH exceeded the pK_a values. Sulfamethoxazole, characterized by its amphoteric nature ($\text{pK}_{a1} \approx 1.6$, $\text{pK}_{a2} \approx 5.7$) (H. Wang et al., 2024), exists in a cationic form under strongly acidic conditions, as a neutral species at intermediate pH, and as an anionic species in alkaline media. The anticipated speciation profiles offered valuable insights into the stability, solubility, and environmental mobility of these analytes throughout the pH range.

Table 2.2. Equilibrium constants utilized for the speciation of Cd^{2+} , Hg^{2+} , Pb^{2+} , Zn^{2+} , CRP, IBP, and SFX in aqueous solutions.

Species	Reaction/Ionization	Log K/pK _a
Cadmium (Cd^{2+})	$\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})^+ + \text{H}^+$	-10.09
	$\text{Cd}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_2 + 2\text{H}^+$	-19.3
	$\text{Cd}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_3^- + 3\text{H}^+$	-28.7
	$\text{Cd}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_4^{2-} + 4\text{H}^+$	-36.0
	$2 \text{Cd}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cd}_2(\text{OH})^{3+} + 3\text{H}^+$	-8.6
Lead (Pb^{2+})	$\text{Pb}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_2 + 2\text{H}^+$	-16.91
	$2\text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Pb}_2(\text{OH})^{3+} + 3\text{H}^+$	-6.36
	$\text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})^+ + \text{H}^+$	-7.56
	$\text{Pb}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_3^- + 3\text{H}^+$	-28.08
Mercury (Hg^{2+})	$\text{Hg}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Hg}(\text{OH})^+ + \text{H}^+$	-3.40
	$\text{Hg}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Hg}(\text{OH})_2 + 2\text{H}^+$	-5.96
	$\text{Hg}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Hg}(\text{OH})_3^- + 3\text{H}^+$	-21.1
Zinc (Zn^{2+})	$\text{Zn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{OH})^+ + \text{H}^+$	-8.96
	$\text{Zn}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{OH})_2 + 2\text{H}^+$	-17.0
	$\text{Zn}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{OH})_3^- + 3\text{H}^+$	-28.0
	$\text{Zn}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{OH})_4^{2-} + 4\text{H}^+$	-40.1
Chloramphenicol (CRP)	$-\text{OH} \text{ (phenolic group)} \rightleftharpoons -\text{O}^- + \text{H}^+$	pK _a $\approx$ 5.5
Ibuprofen (IBP)	$-\text{COOH} \rightleftharpoons -\text{COO}^- + \text{H}^+$	pK _a $\approx$ 4.9
Sulfamethoxazole (SFX)	$-\text{NH}_2^+ \rightleftharpoons -\text{NH}_2 + \text{H}^+$ (aniline group)	pK _{a1} $\approx$ 1.6
	$-\text{SO}_2\text{NH} \rightleftharpoons -\text{SO}_2\text{N}^- + \text{H}^+$ (sulfonamide group)	pK _{a2} $\approx$ 5.7

2.8. REAL WATER SAMPLES

Water samples were obtained from two specific sites in Aizawl City, Mizoram, India: (i) effluent from the sewage treatment facility at SIPMIU (23°43'49"N, 92°44'10"E), and (ii) hospital wastewater released into Tuikual Lui next to Ebenezer Hospital (23°43'51"N, 92°42'29"E). The samples were subjected to filtration through 11 μm filter paper and subsequently analyzed for various physicochemical parameters utilizing a pH meter, multiparameter photometer, TOC analyzer, and AAS. For electrochemical analyses, the filtered samples were augmented with known concentrations of cadmium (Cd^{2+}), lead (Pb^{2+}), mercury (Hg^{2+}), zinc (Zn^{2+}), chloramphenicol (CRP), ibuprofen (IBP), and sulfamethoxazole (SFX).

2.9. ELECTROCHEMICAL PROCEDURE

2.9.1. Electrochemical characterization of electrodes

All modified glassy carbon electrodes (GCE) fabricated with nanocomposite materials, in addition to the unmodified electrode, were characterized by electrochemical methods. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were utilized using the standard redox probe of $0.004 \text{ molL}^{-1} \text{ Fe}^{2+}/\text{Fe}^{3+}$ prepared in $0.1 \text{ molL}^{-1} \text{ KCl}$ solution as the supporting electrolyte. Cyclic voltammograms were obtained for each electrode within the potential range of -0.5 V to $+1.0 \text{ V}$ at scan rates of 50 to 150 mVs^{-1} . The application of various scanning rates facilitated the evaluation of redox process kinetics, allowing distinction between diffusion-controlled and surface-confined electron transport mechanisms. Electrochemical impedance spectroscopy (EIS) measurements for the fabricated electrodes were also conducted under identical electrolyte conditions in a frequency range of 80 kHz to 100 mHz , utilizing six data points per frequency decade and an AC amplitude of 10 mV . The obtained Nyquist plots were examined by fitting the experimental data to the corresponding Randles circuit expressed as $R_1 + Q_2/(R_2 + W_2)$, where, R_1 represents the solution resistance (R_s), Q_2 signifies the constant phase element linked to the double-layer capacitance (C_{dl}) at the electrode–electrolyte interface, R_2 indicates the charge transfer resistance (R_{ct}), and W_2 encompasses the

Warburg impedance (W), which reflects diffusion-controlled processes. The equivalent circuit fitting and extraction of electrochemical parameters were obtained using EC-Lab software, utilizing the least-squares fitting approach for precise parameter optimization.

2.9.2. Electrochemical detection of pharmaceuticals and heavy metal ions

A glassy carbon electrode (GCE) modified with ZnO(NP)@GrO was used for the electrochemical detection of heavy metal ions (Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+}). Standard solutions of these metal ions were prepared in a 0.1 molL^{-1} sodium acetate buffer solution (AcBS). Cyclic voltammetry (CV) was initially conducted to assess the electrochemical behaviour of the target ions at a metal concentration of 1.0 mgL^{-1} . The optimized potential window for each ion is as follows: Cd^{2+} (-1.4 to 0.3 V), Hg^{2+} (-0.6 to 0.8 V), Pb^{2+} (-1.0 to -0.1 V), and Zn^{2+} (-1.4 to 0.1 V). Differential pulse anodic stripping voltammetry (DPASV) was subsequently utilized for the individual and concurrent detection of these ions throughout the potential range of -1.3 to 0.6 V . Optimization tests were conducted by adjusting the pH from 3.5 to 5.5, the deposition potential from -1.4 to -0.9 V , and the deposition period from 30 to 180 sec. In single detection, concentration studies were done within a concentration range of 1.0 to $50.0 \text{ }\mu\text{gL}^{-1}$, while for simultaneous detection, concentration studies were performed within a concentration range of 1.0 to $40.0 \text{ }\mu\text{gL}^{-1}$. Interference investigations were conducted by introducing a tenfold excess of prevalent ions (Ca^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Mg^{2+} , and Ni^{2+}) in relation to $5.0 \text{ }\mu\text{gL}^{-1}$ of the target analytes. Repeatability was analyzed using five consecutive measurements of $30.0 \text{ }\mu\text{gL}^{-1}$ metal ion solutions, while stability was studied over a 0–48 hrs period with measurements conducted at 12 hrs intervals, during which the fabricated electrode was maintained at room temperature. Analysis of a real sample was undertaken using hospital wastewater spiked with known amounts (5.0 – $30.0 \text{ }\mu\text{gL}^{-1}$) of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} , and recovery experiments were carried out based on these values.

In the case of pharmaceutical detection, a CeONC@GrO modified GCE was employed for chloramphenicol (CRP), ibuprofen (IBP), and sulfamethoxazole (SFX) detection. A phosphate buffer solution (PhBS, 0.1 molL^{-1}) served as the supporting electrolyte for CRP and SFX, whilst a sodium acetate buffer solution (AcBS, 0.1

molL⁻¹) was utilized for IBP detection. CV scans were performed within the potential window: -0.5 to 0.5 V for CRP, -0.2 to 0.7 V for IBP, and -0.3 to 0.1 V for SFX. The pH optimization was conducted within the pH range of 5.0 to 9.0 for CRP and SFX, and from 3.0 to 5.5 for IBP. Deposition potential and time were optimized in the ranges 1.4 to 0.6 V and 30 to 280 s, respectively. Concentration studies were done within the micropollutant concentration range of 10.0 to 100.0 µgL⁻¹. Interference experiments were conducted by introducing a tenfold excess of prevalent inorganic ions, including Ca²⁺, Mg²⁺, NO₃⁻, and SO₄²⁻, alongside structurally analogous medicinal drugs such as amoxicillin (AMX), ciprofloxacin (CFX) and tetracycline (TTC) for CRP and SFX. Similarly, for the detection of SFX, in addition to inorganic ions, the presence of paracetamol (PRT), diclofenac (DFN), and tetracycline (TTC) were studied. Repeatability was analysed by five consecutive measurements of pharmaceutical solutions, while stability was studied for a duration of 1 to 5 days with measurements conducted at 24-hour intervals, during which the fabricated electrode was kept at room temperature for successive measurements. Real sample analysis was undertaken utilizing outlet sewage water samples collected from the sewage treatment facility, SIPMIU, which were spiked with known quantities (1.0–50.0 µgL⁻¹) of CRP and SFX, whereas for the detection of IBP, hospital wastewater was used for real water analysis, and recovery tests were conducted based on these spiked concentrations.

Calibration data for both heavy metal ions and pharmaceuticals were acquired by measuring peak currents under optimized parametric conditions. The limit of detection (LOD) and limit of quantification (LOQ) were determined from five duplicate DPASV measurements employing the equation $3 \times (SD)/m$ and $10 \times (SD)/m$, where SD represents the standard deviation of the blank signal and m denotes the slope of the calibration plot. DPASV measurements were conducted under uniform pulse amplitude, incremental steps, and frequency parameters to ensure dependable detection. Moreover, precision was further assessed by calculating the relative standard deviation (RSD) using the formula $RSD (\%) = (s/m) \times 100$, where 's' represents the standard deviation and m denotes the mean.

2.10. PHOTO-FENTON LIKE DEGRADATION (PFD) OF CHLORAMPHENICOL (CRP) AND SULFAMETHOXAZOLE (SFX) USING CeONC@GrO

Stock solutions of chloramphenicol (CRP) and sulfamethazine (SMZ), both at a concentration of 10.0 mgL⁻¹, were formulated using purified water. The solutions were sonicated for 10 minutes to improve the solubility of these chemicals. Subsequent dilutions of the stock solutions yielded the working concentrations. The pH of the prepared solutions was modified to fall between 3.0 and 9.0 with the incremental addition of 2.0 molL⁻¹ HCl or 2 molL⁻¹ NaOH solutions.

During the PFD process, the temperature was maintained at 25±1°C utilizing a water bath inside a dark box. The PFD process is performed in a 100 mL beaker, with continuous stirring, in which 10 mgL⁻¹ CeONC@GrO is added into the antibiotic solutions, and to ensure sorption equilibrium, the solution was maintained in dark conditions with constant agitation for 60 min. Subsequently, 0.02 mL of H₂O₂ is introduced, along with visible light, to initiate the PFD process. The concentrations of CRP and SFX are monitored throughout the reaction using a Modular Thermo Scientific Vanquish™ Core HPLC system (Thermo Scientific, Germany). The treated antibiotic samples are analyzed at specific time intervals after filtration through a 0.45 µm membrane (Whatman, USA).

A calibration curve for the HPLC analysis was created by plotting peak area against pollutant concentration, which varied from 0.01 to 20.0 mgL⁻¹ for each constituent. The HPLC parameters utilized for quantification are detailed in Table 2.4. Pollutant samples were obtained from the reactor at specified time intervals, and the calibration curve was employed to ascertain the unknown pollutant amounts. The percentage reduction of each pollutant was determined using Equation (1.1).

$$\text{Percentage degradation} = \frac{C_i - C_t}{C_i} \times 100 \quad \dots(1.1)$$

where C_i represents the initial pollutant concentration and C_t denotes the concentration at time t . All experiments were performed in triplicate, and the corresponding standard errors were recorded.

Furthermore, the solution pH serves as a crucial factor influencing the degradation behaviour of pollutants in aqueous media. To evaluate this effect, the pH-dependent degradation of the selected micropollutants was examined over a broad pH range of 3.0 to 9.0. The results were expressed in terms of the percentage degradation of pollutants as a function of solution pH.

Hydrogen peroxide (H₂O₂) generates highly reactive hydroxyl (•OH) radicals, which non-selectively attack and cleave the bonds present in pollutant molecules. These radicals disrupt the conjugated systems within macromolecules, leading to the formation of smaller intermediate compounds. The intermediates are subsequently mineralized into CO₂ and H₂O. To confirm the involvement of •OH radicals in the degradation mechanism, additional experiments were conducted using well-known •OH radical scavengers. Accordingly, photo-Fenton-like degradation of 2.0 mgL⁻¹ of each target pollutant (100.0 mL) was carried out in the presence of 10.0 mL of 0.1 molL⁻¹ isopropanol, silver nitrate, and sodium azide, employing the synthesized nano Fenton-like catalyst under optimized reaction conditions. A reduction in the degradation percentage in the presence of these scavengers verified the active participation of •OH radicals in the pollutant degradation process.

Table 2.3. Different parameters for the determination of CRP and SFX in HPLC.

Name of pollutants	Mobile phase	Wavelength (nm)	Injection volume (μL)	Flow rate (mL/min)	Retention time (min)
Chloramphenicol (CRP)	0.1% Acetic Acid: Methanol (55:45)	280.0	10.0	1.0	2.0
Sulfamethoxazole (SFX)	Acetonitrile: Phosphate buffer: Methanol (38:58:4)	260.0	10.0	1.0	1.2

The toxicity of CRP, SFX, and their degradation products was examined to identify the toxic compounds formed from the degradation process. The toxicity of degraded products, as determined using LC-MS analysis, was assessed using ECOSAR V2.2 software. The software predicts the acute (LC₅₀/EC₅₀) and chronic toxicity (ChV) of intermediates produced towards three organisms, viz., fish, daphnia, and green algae, which estimate the acute toxicities in line with European Union

criteria (defined in Annex VI of the Directive 67/548/ECC), i.e., $LC_{50} > 100$ or $EC_{50} > 100$ is not harmful, $10 < LC_{50} < 100$ or $10 < EC_{50} < 100$ is harmful, $1 < LC_{50} < 10$ or $1 < EC_{50} < 10$ is toxic, and $LC_{50} < 1$ or $EC_{50} < 1$ is very toxic and chronic toxicities were evaluated as per Chinese hazardous compounds evaluation standards (HJ/T154-2004), i.e., $ChV > 10$ is not harmful, $1 < ChV < 10$ is harmful, $0.1 < ChV < 1$ is toxic, and $ChV < 0.1$ is very toxic (Iqbal et al., 2020).

CHAPTER 3

RESULTS AND DISCUSSION

3. RESULTS AND DISCUSSION

3.1. MATERIALS CHARACTERIZATION

3.1.1. Phytochemical screening of *Acmella oleracea*

Table 3.1 illustrates the phytochemical constituents of *Acmella oleracea* (toothache plant) leaf extract, revealing the presence of phenolic compounds, terpenoids, flavonoids, saponins, and tannins. These phytochemicals are not only pharmacologically important but also play a crucial role in the green synthesis of zinc oxide (ZnO(NP)) and cerium oxide (CeONC) nanoparticles. Comparable phytochemicals were identified in the pharmaceutical and phytochemical investigation on *Acmella oleracea* (Aktar et al., 2024; Uthpala et al., 2018). The presence of these metabolites offers *Acmella oleracea* an effective, environmentally sustainable precursor for nanoparticle synthesis. Phenolic compounds and flavonoids serve as principal electron donors, whilst terpenoids, tannins, and saponins stabilize the nanoparticle, therefore inhibiting agglomeration and promoting uniform dispersion (Jeevanandam et al., 2016). The importance of these phytochemicals in the synthesis of nanoparticles. The leaf extract of *Mimusops elengi* has demonstrated the use of phenolics and flavonoids as the primary reducing agents in the environmentally friendly synthesis of silver and zinc oxide nanoparticles (Rakhman et al., 2022). Similarly, the phenolic groups present in *Mangifera indica* extract are primarily utilized for the synthesis of copper oxide nanoparticles, as they act as natural reducing and stabilizing agents during nanoparticle formation (Selvi et al., 2019).

Table 3.1. Phytochemical screening of *Acmella oleracea* leaf extract.

SL. NO.	PHYTOCHEMICALS	RESULTS
1.	Flavanoids	Present
2.	Tanins	Present
3.	Phenolic compounds	Present
4.	Saponins	Present
5.	Terpenoids	Present

3.1.2. UV-Vis spectroscopic analysis of metal oxide nanoparticles

The absorption spectra of the synthesized ZnO(NP) nanoparticles were recorded at room temperature within the wavelength range of 200–800 nm to examine the optical characteristics, and the resultant spectrum is depicted in Figure 3.1 (a). The appearance of the UV absorption peak around 370 nm in Figure 3.1. (a) ZnO nanoparticles signify the typical near-band-edge absorption of ZnO, resulting from the electronic transfer of electrons from the valence band to the conduction band, confirming the semiconducting nature of ZnO. The absorption properties of the green-synthesized ZnO nanoparticles were consistent with those of ZnO produced using *Jatropha curcas* latex, as extensively documented in previous studies, thereby affirming the reliability of the synthesis method and the characteristic optical behaviour of ZnO nanostructures (Sharma et al., 2025). Similarly, the appearance of the UV absorption peak at around 378 nm confirms the presence of zinc oxide nanoparticles. These results validate that the phytochemical-mediated synthesis route employed effectively produces ZnO(NP).

On the other hand, the absorption spectrum of the CeONC nanostructure, measured at room temperature within the 250–800 nm range, is presented in Figure 3.1(b). The phytochemicals in the plant extract form the CeONC nanostructures.

Bioactive chemicals initially reduce Ce^{3+} ions to zero-valent Ce atoms as reducing agents. The nucleation process starts with the partial reduction of Ce^{4+} ions to Ce^{3+} species, and subsequent redox equilibrium facilitates the generation of oxygen vacancies and the formation of Ce–O–Ce networks, resulting in the formation of CeONC nuclei, which further form stable clusters of nanostructured CeONC (Arumugam et al., 2015). The UV-Vis absorption spectra of green-synthesized nanostructured CeONC show a broad band at 317 nm and a smaller peak at 258 nm in the ultraviolet range. The peak at 317 nm corresponds to the $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$ charge transfer transition, while the absorption at 258 nm is attributed to the presence of Ce^{3+} species (Elaziouti et al., 2015). This absorption mostly arises from the charge transfer transition between the O^{2-} (2p) orbitals of lattice oxygen and the vacant Ce^{4+} (4f) orbitals in CeO_2 (Altaf et al., 2021; Z. Wang et al., 2007). Such charge transfer processes are characteristic of cerium oxides and are responsible for their strong optical response in the UV range. Furthermore, the acquired spectral profiles indicate that the charge transfer transition of Ce^{4+} is not an isolated phenomenon; rather, it overlaps with the intra-ionic $4f^1 \rightarrow 5d^1$ electronic transition of Ce^{3+} ions (Yin et al., 2002). The occurrence of Ce^{3+} species generally results from oxygen vacancies and the partial reduction of Ce^{4+} to Ce^{3+} . The intersection of these two transitions, the $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$ charge transfer and the Ce^{3+} ($4f^1 \rightarrow 5d^1$) excitation, results in a broad yet intense absorption band (Ansari, 2010). This behaviour suggests a mixed valence state ($\text{Ce}^{3+}/\text{Ce}^{4+}$) and indicates the existence of oxygen vacancy defects. The present result is in agreement with earlier reports, where cerium oxide nanoparticles synthesized using *Pisonia alba*, exhibited a UV–Vis absorbance maximum at 258 and 317 nm (Sharmila et al., 2019).

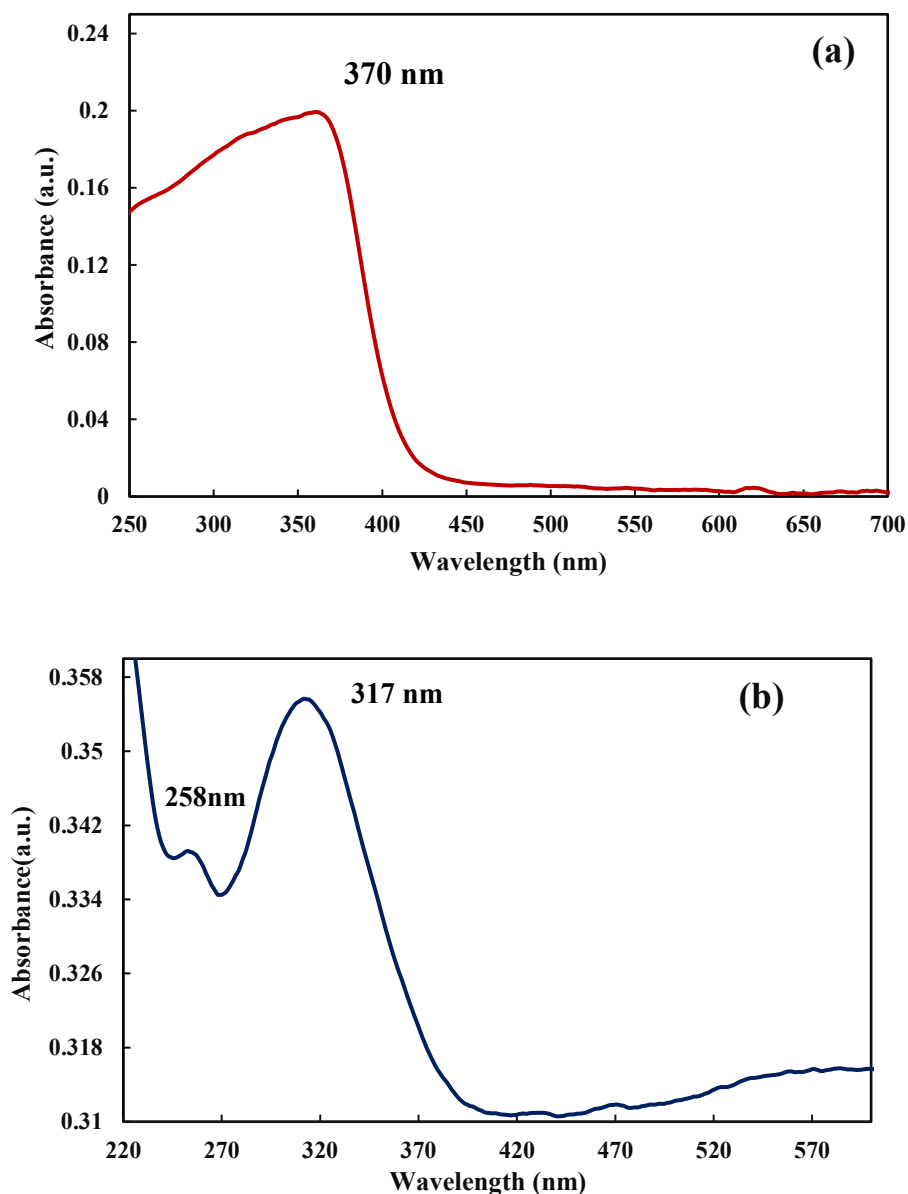
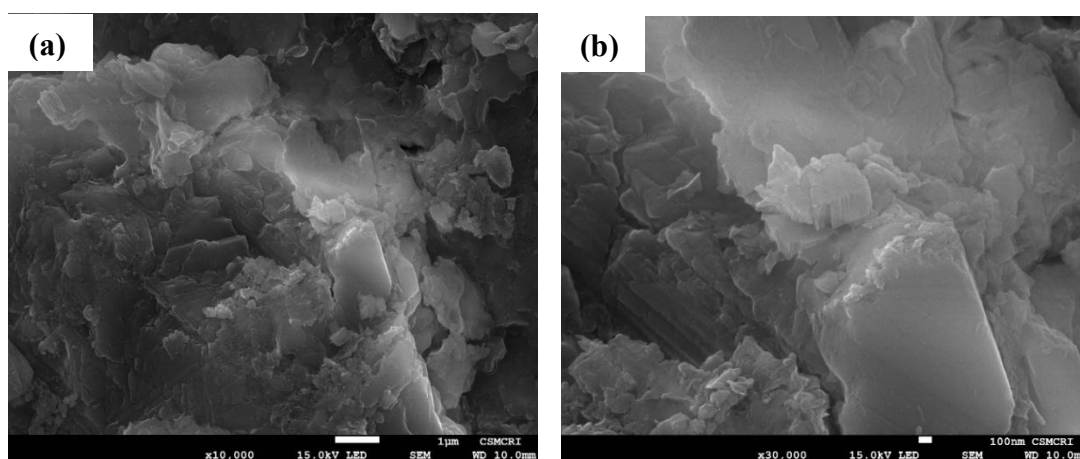


Figure 3.1. UV Visible spectra of: (a) ZnO(NP) and (b) CeONC colloidal solutions.

3.1.3. Surface morphology of synthesized materials

Scanning Electron Microscopy (SEM) was utilized to examine the surface morphology of the synthesized nanocomposites. Figure 3.2 (a-b) displays the SEM micrographs of graphene oxide (GrO), characterized by its conventional layered, sheet-like structure with a crumpled or wrinkled paper-like appearance. The results indicate that graphene oxide (GrO) possesses the inherent flexibility of its ultrathin, two-dimensional sheets. The sheets frequently appear as flat or elongated layers that

are stacked, overlapped, or folded as a result of van der Waals interactions and the prevalence of several oxygen-containing functional groups, including hydroxyl, epoxy, and carboxyl moieties, on their basal planes and borders. The observed structure of layers and wrinkled structure validate the synthesis of GrO, which offers high surface area and active binding sites, making it an appropriate substrate for nanoparticle deposition in the synthesis of composite materials. Further, the SEM picture of zinc oxide nanoparticles incorporated with graphene oxide (ZnO(NP)@GrO) [Cf Figure 3.2 (c-d)] clearly illustrates the effective incorporation of ZnO nanoparticles on the GrO sheets. The nanoparticles have a clear, well-defined hexagonal shape, characteristic of the wurtzite crystal structure of ZnO, hence affirming the crystalline nature of the synthesized material. Similarly, the SEM image of cerium oxide nanoparticles incorporated with graphene oxide (CeONC@GrO) is shown in Figure 3.2 (e-f). The figure illustrates that the green-synthesized cerium oxide nanoparticles (CeONC) consist of small nanoscale particles with distinct morphology, uniformly dispersed over the graphene oxide sheets. The ZnO(NP) and CeONC particles are uniformly distributed across the surface of the GrO layers rather than forming agglomerates at the GrO surface.



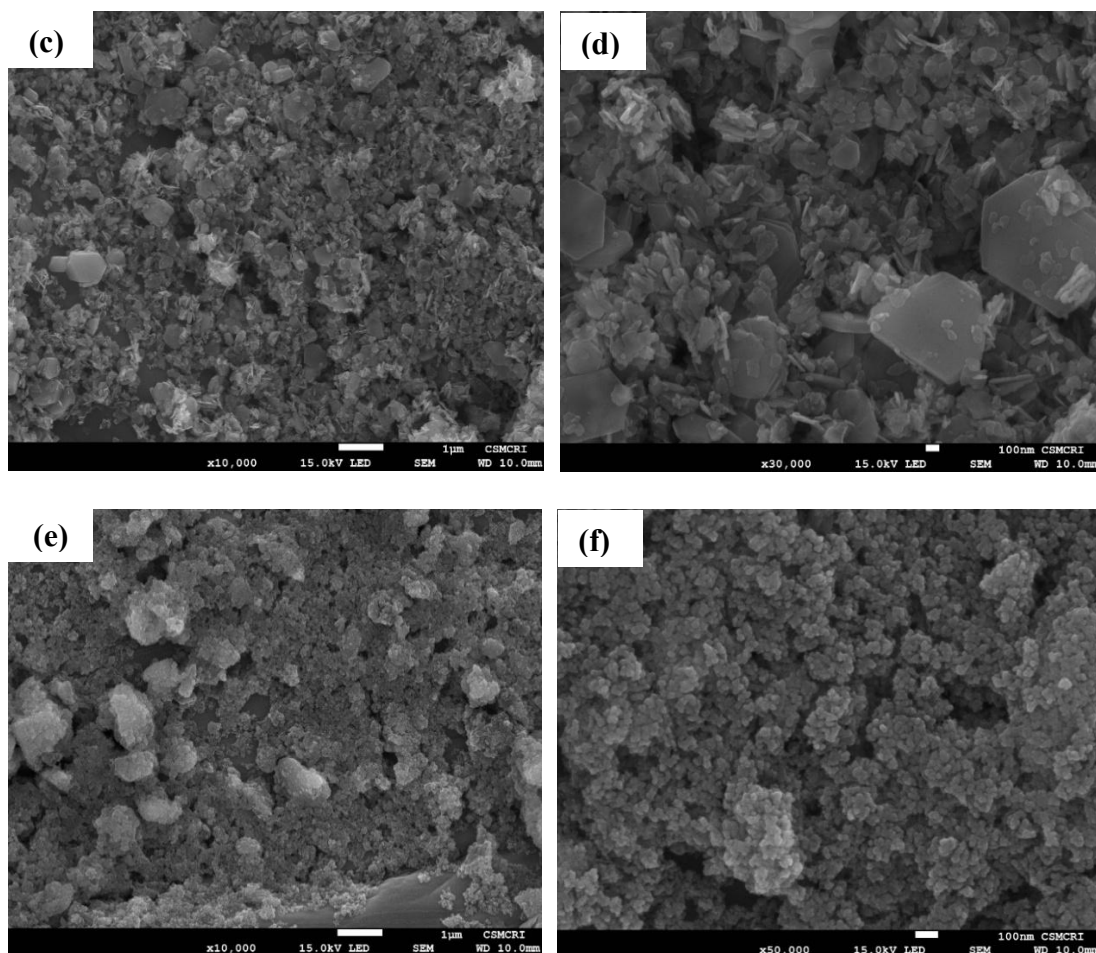


Figure 3.2. Scanning electron micrographs of: (a & b) Graphene oxide (GrO); (c & d) ZnO(NP)@GrO and (e & f) CeONC@GrO.

Additionally, Figure 3.3 (a–d) displays the energy dispersive X-ray (EDX) spectra of the GrO, ZnO(NP)@GrO, and CeONC@GrO. The pristine GrO exhibited the peaks of carbon and oxygen, so affirming its conventional composition (*Cf* Figure 3.3 (a)). However, the ZnO(NP)@GrO showed a distinct peak of Zn along with the C and O peaks (*Cf* Figure 3.3 (b)). Similarly, the CeONC@GrO composite exhibited distinct peaks of Ce, C, and O (*Cf* Figure 3.3 (c)). Furthermore, the observed increase in oxygen weight percentage in both composites, *viz.*, ZnO(NP)@GrO and CeONC@GrO, indicates the presence of metal oxides in addition to the corresponding metal species (*Cf* Table 3.2). This infers the incorporation of ZnO and Ce-based oxide nanoparticles into the GrO matrix.

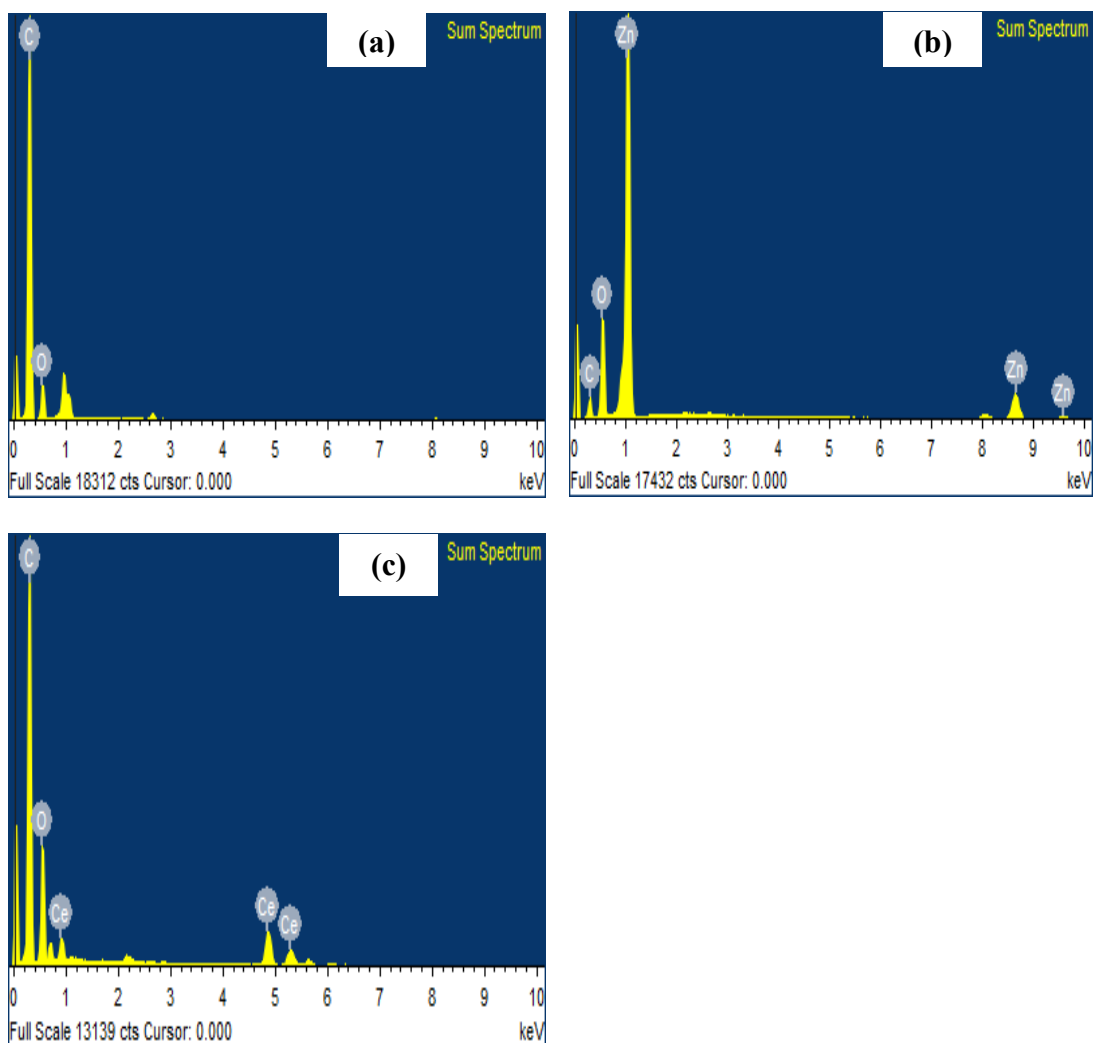


Figure 3.3. EDX elemental spectra of: (a) pristine graphene oxide (GrO); (b) ZnO(NP)@GrO nanocomposite; and (c) CeONC@GrO nanocomposite.

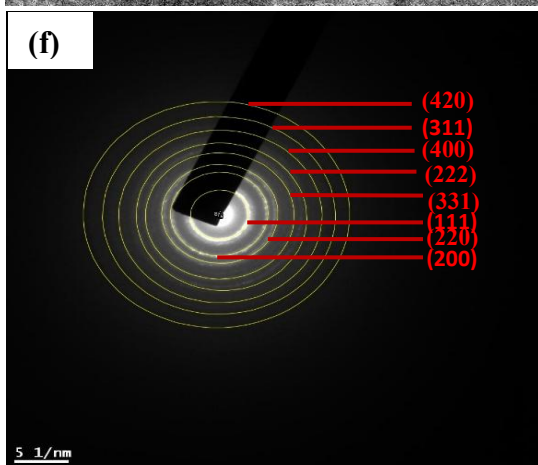
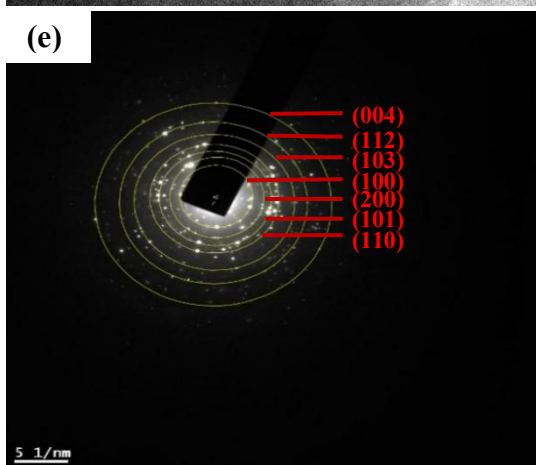
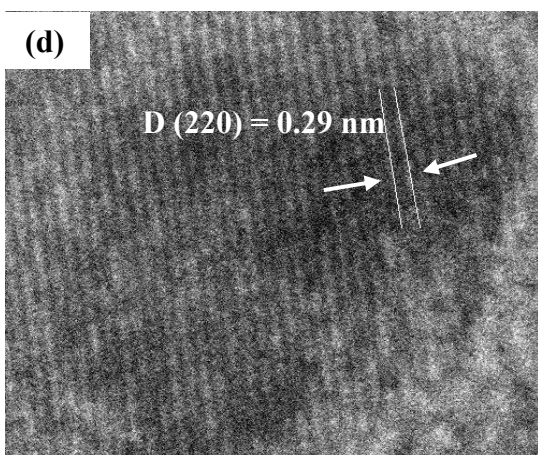
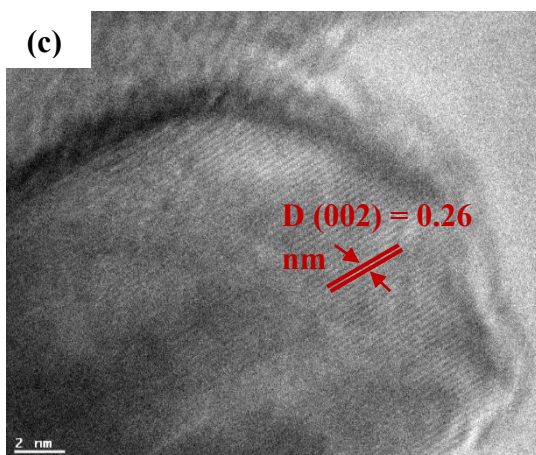
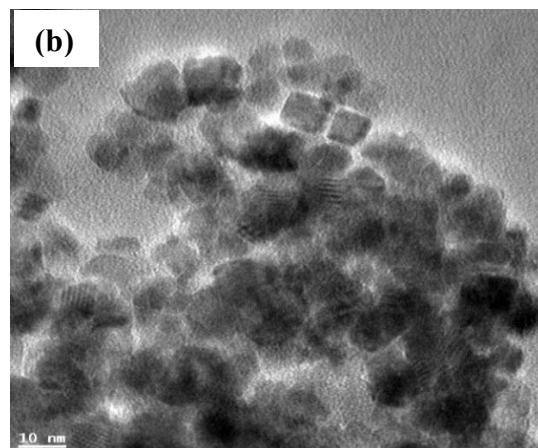
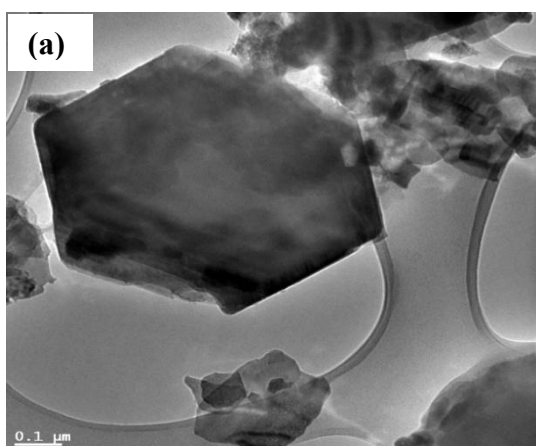
Table 3.2. EDX elemental compositions of GrO, ZnO(NP)@GrO, and CeONC@GrO.

Sample	Elements present	Weight (%)	Atomic (%)
GrO	C	77.20	81.85
	O	22.80	18.15
ZnO(NP)@GrO	C	13.87	32.27
	O	23.44	40.94
	Zn	62.69	26.80
CeONC@GrO	C	54.13	72.73
	O	24.61	24.82
	Ce	21.26	2.45

Transmission electron microscopy (TEM) further provides the morphology of the synthesized nanocomposites. Figure 3.4 (a) shows the TEM images of ZnO(NP)@GrO, revealing that ZnO nanoparticles possessed a hexagonal structure and the particles are uniformly distributed across the GrO surface. The lattice fringes exhibit a d-spacing of 0.26 nm [Cf Figure 3.4 (c)], which corresponds to the (002) plane of hexagonal ZnO (Kandasamy et al., 2022). High-resolution TEM (HRTEM) images combined with selected area electron diffraction (SAED) patterns [Cf Figure 3.4 (e)] display distinct diffraction spots indexed to characteristic crystallographic planes of ZnO, consistent with the hexagonal wurtzite structure. These observations indicate that the ZnO nanoparticles incorporated onto the GrO matrix possess high crystallinity and well-ordered surface structure. Similarly, the TEM image of the CeONC@GrO composite [Cf Figure 3.4 (b)] shows that the CeONC particles exhibit a clear cubical morphology and are homogeneously anchored onto the GrO sheets. The measured lattice fringe spacing of 0.29 nm, as depicted in Figure 3.4 (d), corresponds to the (220) crystallographic plane of cerium oxide in its face-centered cubic (FCC) structure (Ralte et al., 2025). Additionally, Figure 3.4 (f) presents a TEM image of CeONC@GrO, characterized by selected area electron diffraction (SAED) patterns that demonstrated that the cerium oxide nanoclusters (CeONC) integrated into the GrO structure displayed unique diffraction spots associated with particular crystallographic planes. These spots signify the characteristic cubic fluorite structure of cerium oxide

nanoparticles. These discrete diffraction spots observed in the SAED pattern confirmed that the synthesized material exhibited well-defined cerium oxide nanocube (CeONC) with high crystallinity.

Therefore, the TEM investigations together indicate that both ZnO(NP)@GrO and CeONC@GrO nanocomposites display uniform nanoparticle distribution, distinct morphologies, and high crystallinity, showing the efficacy of the synthesis in generating ordered and stable nanostructures. ZnO(NP)@GrO has a hexagonal wurtzite structure, whereas CeONC@GrO is characterized by an FCC structure. The particle size distribution of ZnO(NP)@GrO and CeONC@GrO nanocomposites was carefully evaluated with TEM images. The investigation indicated that ZnO(NP)@GrO had an average particle size of around 18 nm [Cf Figure 3.4 (g)], whereas the CeONC@GrO nanocomposite had a smaller average size of about 9 nm [Cf Figure 3.4 (h)]. A prior study showed that the *Azadirachta indica* leaf extract synthesized the CeO₂ nanoparticles with a consistent particle size distribution (average particle size of 10-15 nm). The HRTEM images showed different morphological characteristics of synthesized CeONC, including mixed lattice fringe patterns. Agglomeration caused two crystals to overlap, partially obscuring lattice fringes with an average interplanar spacing of 0.31 nm for the (111) plane. Additionally, SAED patterns showed distinct concentric rings, validating the polycrystalline structure of CeO₂ nanoparticles (Sharma et al., 2017).



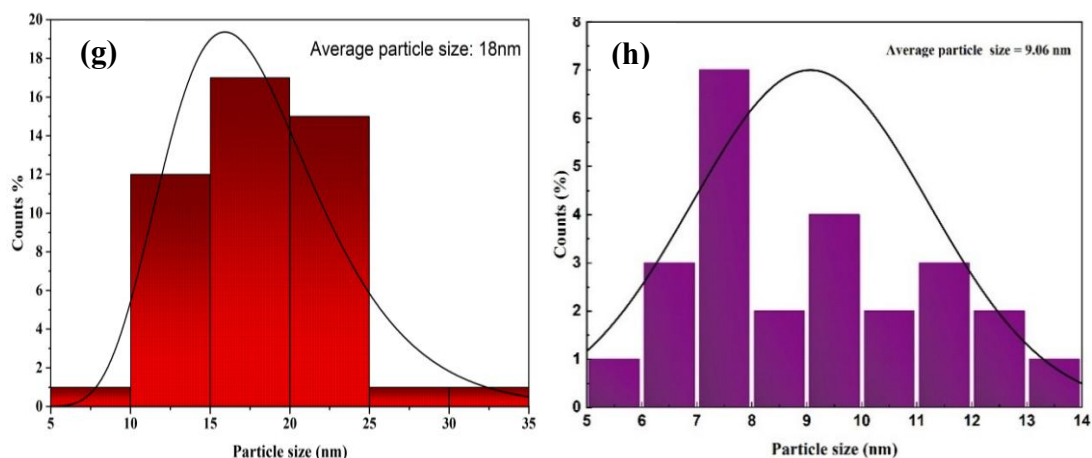


Figure 3.4. TEM image of (a) ZnO(NP)@GrO; (b) CeONC@GrO nanocomposite: d-spacings of (c) ZnO(NP)@GrO; (d) CeONC@GrO nanocomposite; and Electron diffraction pattern of (e) ZnO(NP)@GrO; (f) CeONC@GrO nanocomposite materials: Particle size distribution histogram of (g) ZnO(NP)@GrO; and (h) CeONC@GrO.

Additionally, the surface roughness of ZnO(NP)@GrO and CeONC@GrO-modified glassy carbon plates was examined using atomic force microscopy (AFM), and results are illustrated in Figure 3.5 (a & b). The three-dimensional AFM images demonstrated that both nanocomposite-coated surfaces have a markedly heterogeneous and disordered topography, indicating that nanoparticles were deposited onto the substrate surface. Moreover, higher-magnification 3D representations reveal the emergence of fine pillar-like structures on the electrode surface, attributable to the uniform distribution and anchoring of the nanocomposites. Additional quantitative analysis of the AFM data was conducted to assess the surface roughness of the nanocomposite-modified glassy carbon electrodes. The arithmetic average roughness (R_a), indicating the mean departure of the surface profile from the average height, and the root mean square roughness (R_q), reflecting the standard deviation of the surface heights, were computed for both samples. The ZnO(NP)@GrO coated carbon sheet exhibited R_a and R_q values of 9.65 nm and 15.23 nm, respectively, while the CeONC@GrO coated carbon sheet had markedly higher roughness values, with $R_a = 19.10$ nm and $R_q = 25.15$ nm. It was previously reported that the ZnO incorporated onto the reduced graphene oxide, i.e., ZnG, synthesized using ascorbic

acid, is densely distributed over the surface of rGO and further concluded that the surface roughness (R_q) along with the average roughness (R_a) were 6.75 and 4.85, respectively (Rai et al., 2021). CeO_2 thin films were synthesized via the spray pyrolysis technique, yielding surface roughness values between 24.70 nm and 19.36 nm, which significantly enhanced the surface-to-volume ratio and subsequently affected the optical, catalytic, and electrochemical properties of the CeO_2 films (Peláez et al., 2024).

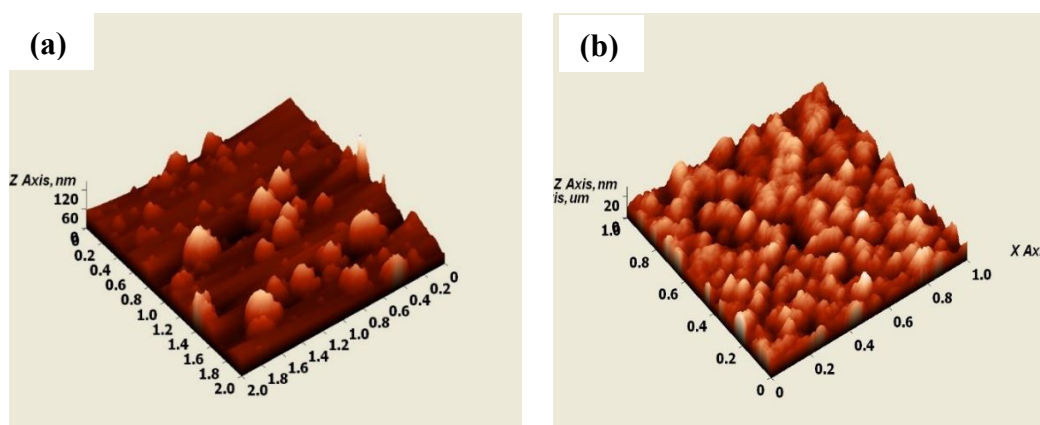


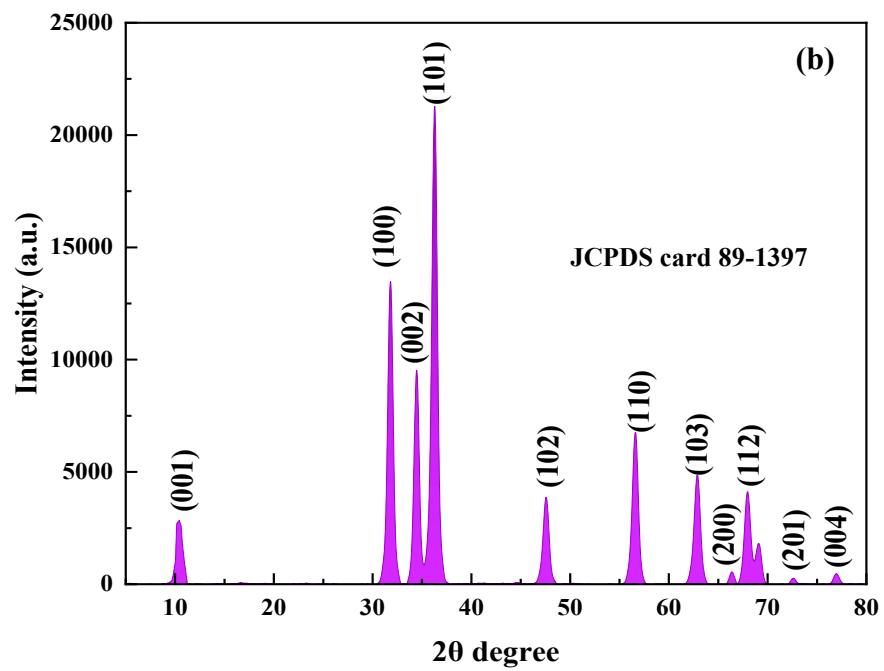
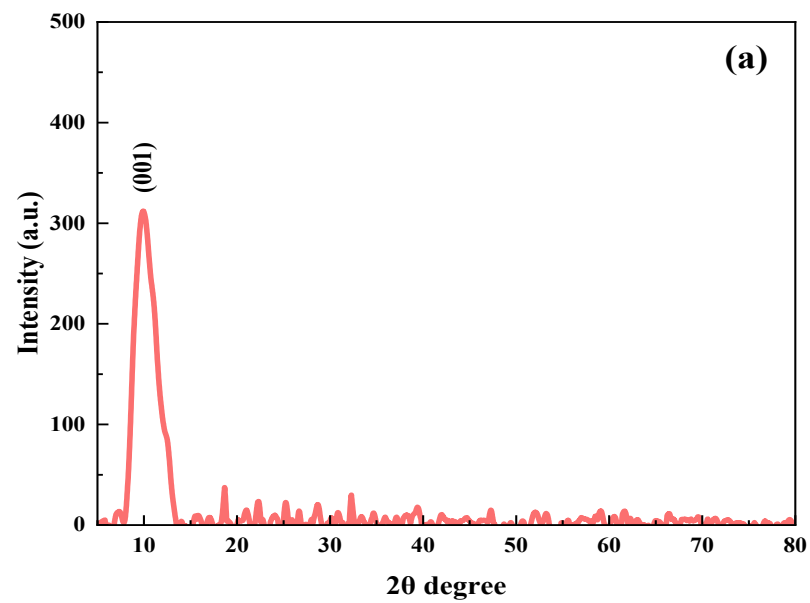
Figure 3.5. Atomic force micrographs of: (a) $\text{ZnO}(\text{NP})@\text{GrO}$; and (b) $\text{CeONC}@\text{GrO}$ nanocomposite materials.

3.1.4. Crystal phase identification and elemental analysis

The crystalline structures of GrO , $\text{ZnO}(\text{NP})@\text{GrO}$, and $\text{CeONC}@\text{GrO}$ were examined using X-ray diffraction (XRD) patterns of these solids, and the results are illustrated in Figure 3.6. Figure 3.6 (a) illustrates that the XRD pattern of graphene oxide (GrO) displays a distinctive peak at a 2θ value of 10.42° , which corresponds to the (001) plane of GrO . The peak, displaced from the conventional graphite (002) peak at around 26° , indicates an increased interlayer spacing due to the incorporation of oxygen-containing functional groups, including hydroxyl, epoxy, and carboxyl groups. The existence of this peak verifies that graphite has been completely oxidized to graphene oxide, yielding a well-exfoliated layered structure (Ahmadi et al., 2023). In the case of the $\text{ZnO}(\text{NP})@\text{GrO}$ nanocomposite [Cf Figure 3.6 (b)], the X-ray

diffraction (XRD) pattern exhibits multiple prominent peaks at 2θ values of 31.83° , 34.45° , 36.29° , 47.62° , 56.57° , 62.88° , 66.39° , 67.97° , 72.6° , and 76.94° , which correspond to the (100), (002), (101), (102), (110), (103), (200), (112), (201), and (004) crystallographic planes of ZnO, respectively, as indexed from the JCPDS card no. 89-1397 (Souza et al., 2019). The presence of these well-defined diffraction peaks confirmed the formation of a highly crystalline ZnO phase with a hexagonal wurtzite structure, which is the most thermodynamically stable form of ZnO.

Similarly, the CeONC@GrO nanocomposite is shown in Figure 3.6 (c). Figure 3.6(c) exhibits prominent peaks at 2θ values of 28.49° , 33.07° , 47.44° , 56.31° , 58.78° , 69.60° , 76.69° , and 78.77° , corresponding to the CeONC diffraction planes of (111), (200), (220), (331), (222), (400), (311), and (420) (JCPDS card no: 34-0394), indicating the characteristic face-centered cubic phase of CeO₂ nanoparticles (J. K. Sharma et al., 2017). Moreover, the observation of a diffraction peak at $2\theta = 10.42^\circ$ in both metal-oxide nanocomposites verifies the presence of graphene oxide in these two solids. This peak aligns with the (001) plane of graphene oxide, signifying that the oxidized graphene layers are preserved following the deposition of metal oxide nanoparticles. Comparable findings were documented in the literature, indicating that the intercalation of Zn, Al, Mn, and Cu oxides onto textured GrO multilayer films preserved the distinctive GO peak in the XRD pattern (P.-Y. Chen et al., 2016). The results demonstrate that the fabrication process retains the layered structure and interlayer spacing of graphene oxide while facilitating the uniform incorporation of metal oxide nanoparticles.



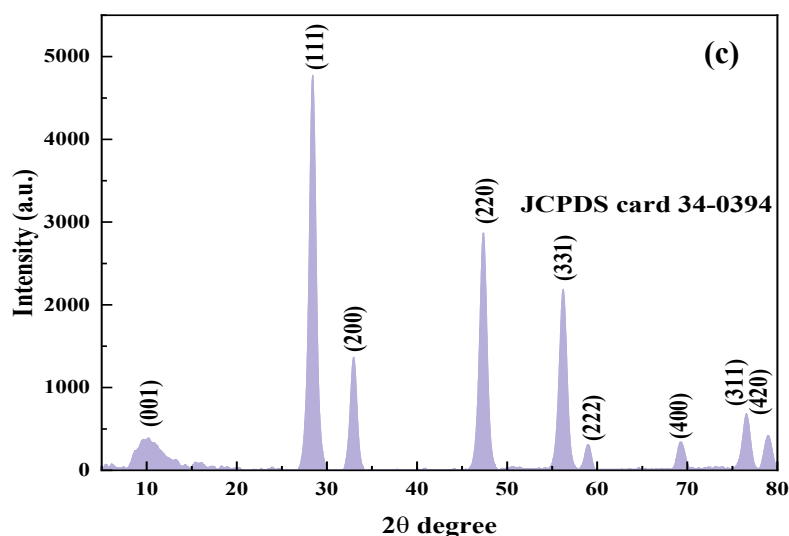
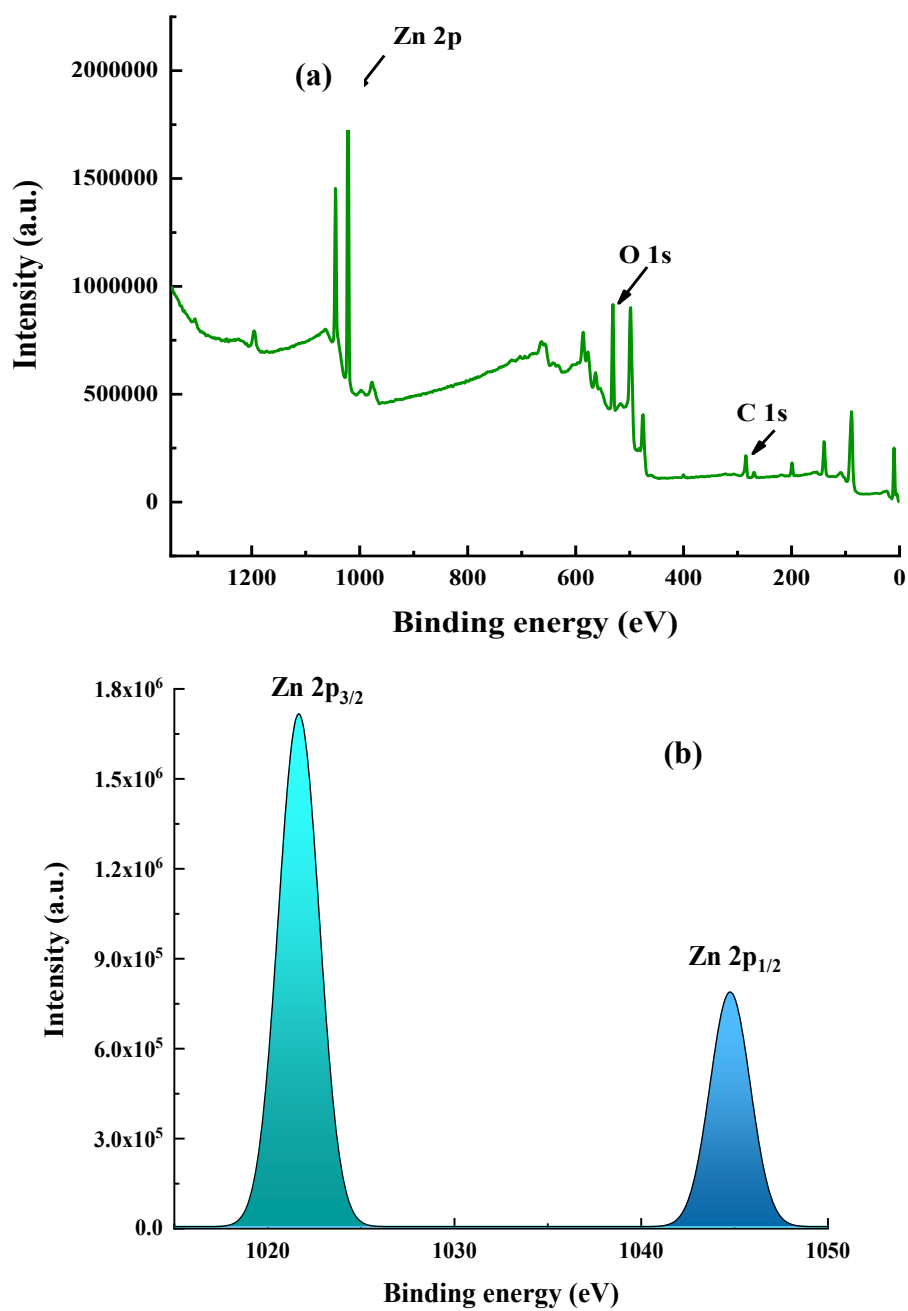


Figure 3.6. X-ray diffraction patterns of (a) GrO, (b) ZnO(NP)@GrO, and (c) CeONC@GrO nanocomposite materials.

XPS measurements were conducted to investigate the surface composition and electronic states of the ZnO(NP)@GrO and CeONC@GrO nanocomposites. The XPS spectrum of ZnO(NP)@GrO was displayed in Figure 3.7 (a-d), and the XPS survey [Cf Figure 3.7 (a)] affirms that nanocomposite material consists of elements *viz.*, Zn, O and C. Figure 3.7 (b) shows the Zn 2p XPS peaks occurred at binding energies of 1045.0 and 1021.8 eV, referring to Zn 2p_{1/2} and Zn2p_{3/2}, respectively, and indicating that zinc is presence to its +2 oxidation state, which confirms that ZnO is present in the synthesized material (Cabrera-German et al., 2017). Similarly, Figure 3.7 (c) presents the deconvoluted O 1s XPS peaks and shows three distinct XPS peaks. The peaks at 531.9 eV and 531.0 eV confirm the presence of chemisorbed oxygen species and lattice oxygen in the crystal structure of ZnO in its wurtzite form, respectively (Li et al., 2007). Further, a peak at 532.6 eV affirms the existence of the C=O bond in the ZnO(NP)@GrO (Qu et al., 2019). Moreover, Figure 3.7 (b) shows the deconvoluted C 1s XPS peaks at binding energies 284.2, 285.8, 287.4, and 290.9 eV, corresponding to different carbon species. The deconvolution analysis affirms the presence of sp²/sp³ (284.2 eV) carbon atoms involved in C–C or C=C, which are commonly present in the basal plane of graphene oxide (GrO), C-O-C (285.8 eV), where carbon is bonded to oxygen in a bridge-like structure, which is indicative of the epoxy functional group present on the graphene oxide. Moreover, the deconvoluted peaks at 287.4 and 290.9

eV are due to the C-OH hydroxyl groups and O=C-O-Zn bond, which indicates a robust interaction between ZnO(NP) and GrO, most likely via carboxylate groups (Fu et al., 2012; Wang et al., 2019).



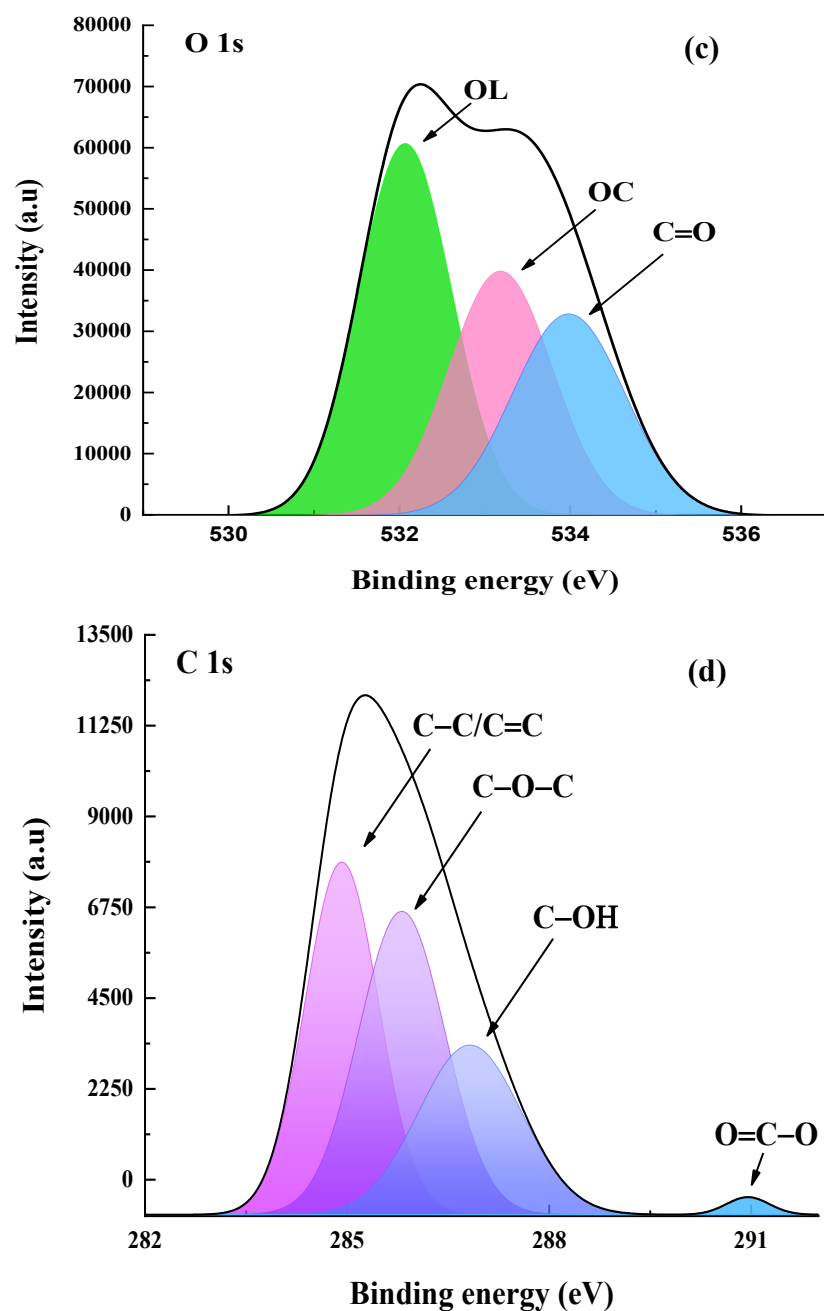
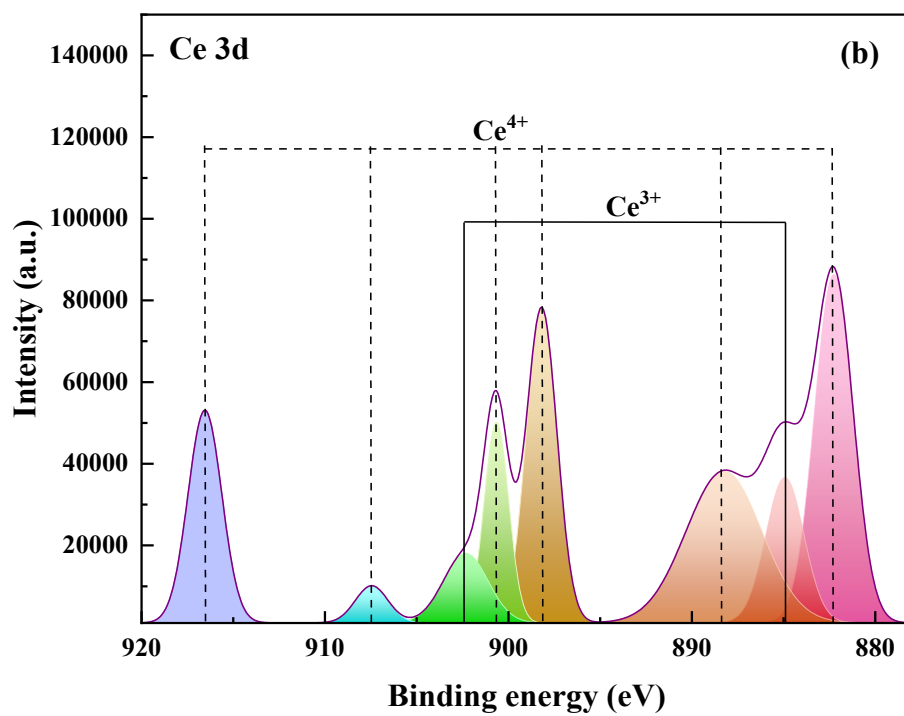
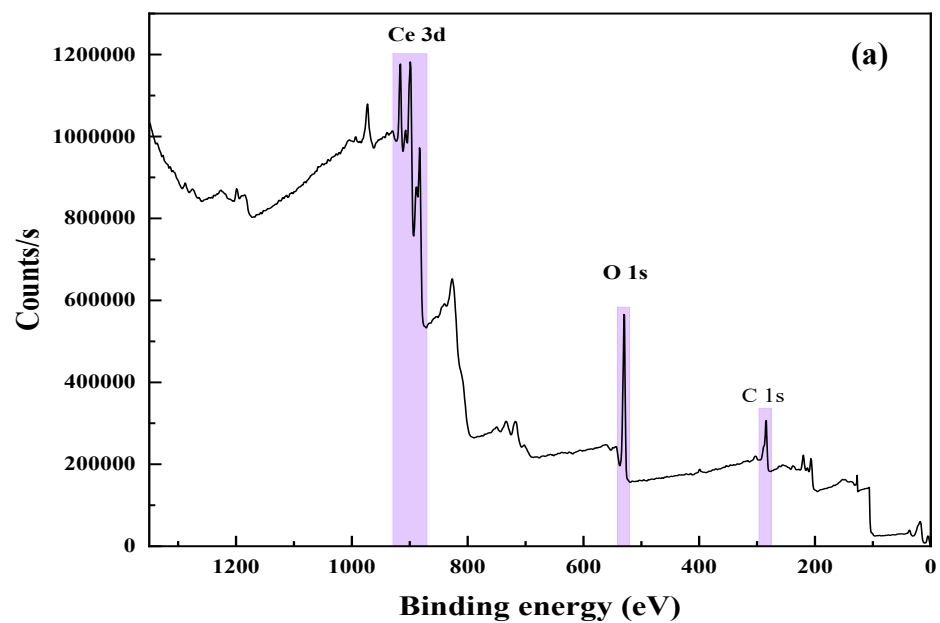


Figure 3.7. (a) XPS survey of ZnO(NP)@GrO; and XPS spectra of: (b) Zn 2p, (c) O 1s, (d) C 1s.

On the other hand, the XPS survey of CeONC@GrO is illustrated in Figure 3.8 (a), whereas the deconvoluted spectra for Ce, C, and O were displayed in Figure 3.8 (b-d). The results validate the existence of the Ce, C, and O elements in the solid. Figure 3.8 (b) shows the Ce 3d XPS peaks occurring at different binding energies. The principal peaks associated with the Ce^{4+} oxidation state, which are detected at binding

energies of 882.0, 888.6, 898.3 eV, 900.9, 907.4, and 916.6 eV, are attributed to the Ce 3d_{5/2} and Ce 3d_{3/2} spin–orbit components, respectively (Arul et al., 2015). The XPS spectrum, besides the notable Ce⁴⁺ peaks, also displayed distinct peaks at 885.4 eV and 903.04 eV, which correspond to the Ce³⁺ 3d_{5/2} and Ce 3d_{3/2}, respectively (Sharma et al., 2017). The presence of these characteristics peaks inferred that cerium is partially present in its +3 oxidized state, implying a partial reduction of Ce⁴⁺ to Ce³⁺ within the crystal lattice. Additionally, Figure 3.8 (c) presents the deconvoluted C1s XPS spectrum, highlighting specific peaks at binding energies 284.4, 285.8, and 288.5 eV, which correspond to various carbon bonding environments. The peaks identified at 284.4 eV are ascribed to non-oxygenated carbon (C–C), indicative of sp²-hybridized carbon atoms within the two-dimensional sheet of GrO. The second peak occurred at 285.3 eV, which belongs to carbon atoms bound to functional groups that consist of oxygen, such as hydroxyl (C–OH) and epoxide (C–O) moieties. The third peak, occurred at 288.5 eV, belongs to carbonyl groups (C=O). This part is usually found at the edges or defects in the GrO, where more highly oxidized carbon species like carboxylic acids or ketones are present (Jeevaraj & Muthuvinayagam, 2023). In addition, Figure 3.8 (d) displays the O 1s XPS spectrum and shows two individual peaks. A peak detected at 529.18 eV [denoted as O_a in Figure 3.8 (e)] is ascribed to lattice oxygen (O²⁻), which is linked with Ce⁴⁺ species (Siranjeevi et al., 2024). This binding energy is indicative of oxygen atoms that are firmly integrated within the CeO₂ crystal lattice, signifying a stoichiometric, well-ordered oxide phase predominantly composed of cerium in its completely oxidized form. The peak at 531.28 eV [denoted as O_b in Figure 3.8 (d)] is attributed to surface oxygen linked which are generally attached to surface defect sites or oxygen vacancies, and adsorbed oxygen species (O_c) that appeared at 533.5 eV (Machocki et al., 2004), representing surface hydroxyls, molecularly adsorbed water, and/or carbonates. This signifies the presence of oxygen vacancies or defects in the CeO₂ lattice, commonly arising from the partial reduction of Ce⁴⁺ to Ce³⁺ (Amaral et al., 2024; Dutta et al., 2006).



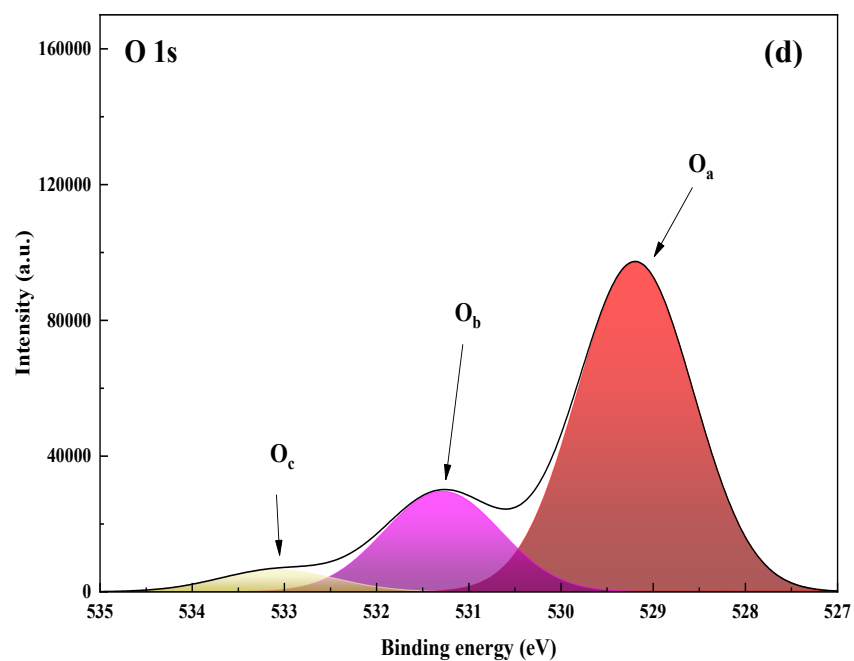
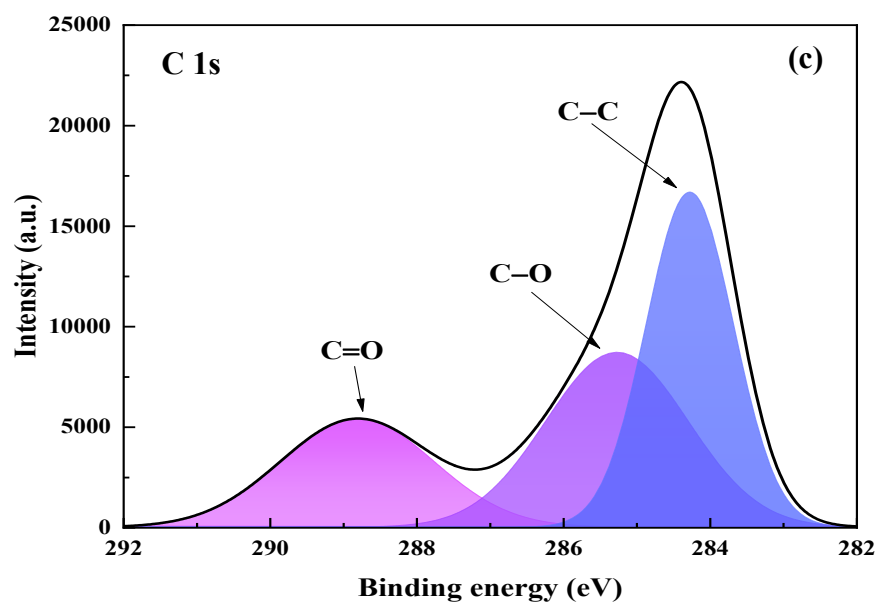


Figure 3.8. (a) XPS survey of CeONC@GrO; and XPS spectra of: (b) Ce 3d, (c) C 1s, (d) O 1s.

3.1.5. Ecotoxicity assessment of the ZnO(NP)@GrO and CeONC@GrO

The toxic impact of ZnO(NP)@GrO is illustrated in Figure 3.9 (a), showing an EC_{50} value of 115.7 mgL^{-1} for its acute toxicity toward *Daphnia magna* after 48 hours, with 95% confidence limits ranging from 103.3 to 129.6 mgL^{-1} . At elevated concentrations, ZnO(NP) induces immobilization and mortality in *D. magna*, primarily due to the release and dissolution of Zn^{2+} ions (Kim et al., 2009). However, the integration of ZnO(NP) into GrO markedly enhances stability, as the GrO acts as a stabilizing matrix for Zn, thereby reducing its toxicity. This stabilization leads to an increased EC_{50} value, indicating that a significantly higher concentration of ZnO(NP)@GrO is needed to produce toxic effects compared to the concentration present on the modified electrode (Xu & Wang, 2012). Consequently, *D. magna* experiences reduced stress, highlighting the modified electrode as a safe and environmentally sustainable material. Additionally, the acute toxicity of CeONC@GrO is presented in Figure 3.9 (b), showing an EC_{50} of 150.80 mgL^{-1} toward *D. magna* after 4 hours, with 95% confidence intervals of 158.0 mgL^{-1} and 180.2 mgL^{-1} for the lower and upper limits, respectively. The catalyst demonstrates low toxicity, as reflected by its relatively high EC_{50} value, indicating minimal adverse effects at environmentally relevant concentrations. In comparison, many conventional nanocatalysts, such as zinc oxide or copper oxide nanoparticles used for pollutant detection, typically exhibit much lower EC_{50} values, indicating higher toxicity to aquatic organisms (Lopes et al., 2014; Wu et al., 2017). The low toxicity of CeONC@GrO is attributed to the inherent biocompatibility of cerium and the stabilizing role of graphene oxide, which prevents nanoparticle aggregation and limits the uncontrolled release of toxic ions (Mushahary et al., 2024). This renders CeONC@GrO a more environmentally friendly option for sensing and degradation applications in aquatic ecosystems.

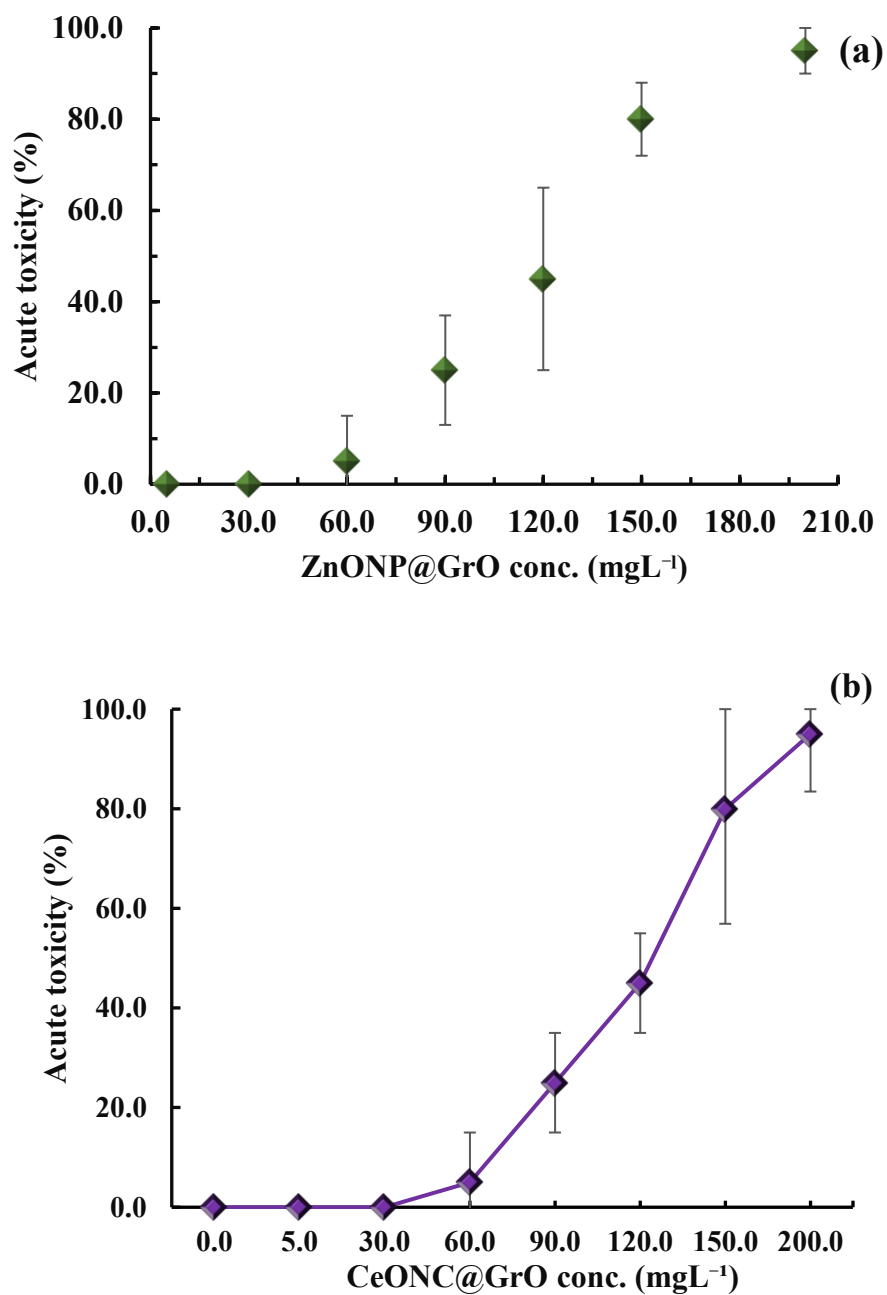
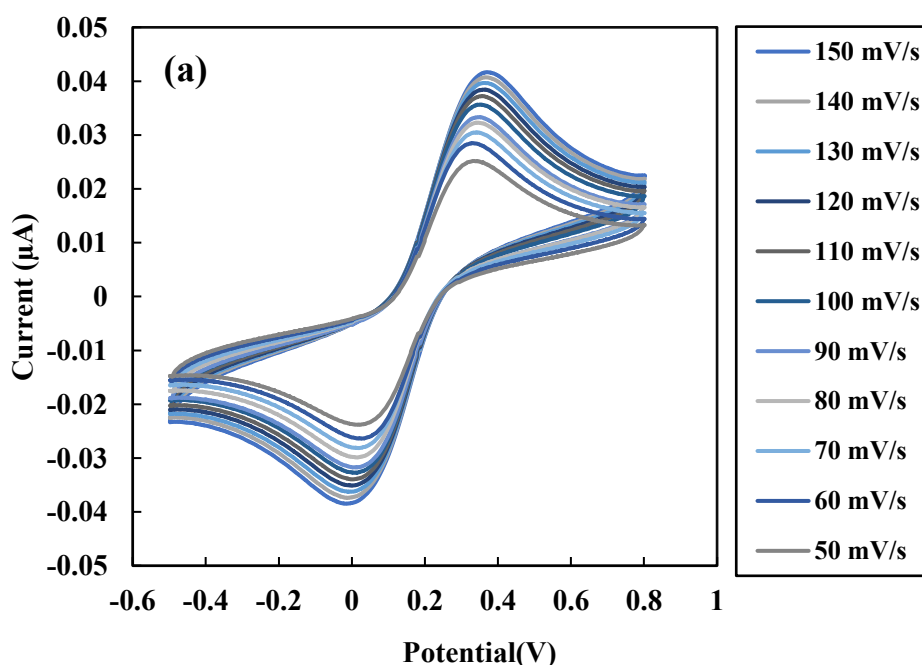


Figure 3.9. Acute toxicity of: (a) ZnO(NP)@GrO; (b) CeONC@GrO towards *D. magna*.

3.1.6. Electrochemical characterization of various fabricated electrodes

The electrochemical characterization of both bare and modified GCEs was conducted by scan rate studies using CV in a 0.001 molL⁻¹ [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ redox couple, employed in 0.1 molL⁻¹ sodium AcBS (pH 4.5). Cyclic voltammograms were obtained for each electrode within the potential range of -0.5 V to +1.0 V at scan

rates of 50 to 150 mVs⁻¹. Figure 3.10 (a–d) demonstrates that all electrodes displayed distinct and almost symmetrical anodic and cathodic peaks typical of the ferri/ferrocyanide redox system. The modified electrodes exhibited enhanced current responses compared to the bare GCE, signifying an increased electroactive surface area and enhanced charge transfer kinetics. At a scan rate of 100 mVs⁻¹, the anodic peak current was observed to increase progressively from 0.02 μ A for the bare GCE to 0.03 μ A for GrO GCE, 0.06 μ A for ZnO(NP)@GrO GCE, and 0.10 μ A for CeONC@GrO GCE. This clearly indicated that the nanocomposite materials significantly facilitated the electron transfer reactions at the electrode surface. Additionally, the peak-to-peak separation (ΔE_p) between the anodic and cathodic peaks was markedly lower for the GrO and nanocomposite-modified electrodes compared to the bare GCE, suggesting faster electron transfer kinetics and reduced resistance to charge transport. These findings confirm that the incorporation of GrO and nanocomposites not only increases the effective electroactive surface area but also enhances the reversibility of the ferri/ferrocyanide redox process, thereby favouring more efficient electrochemical performance.



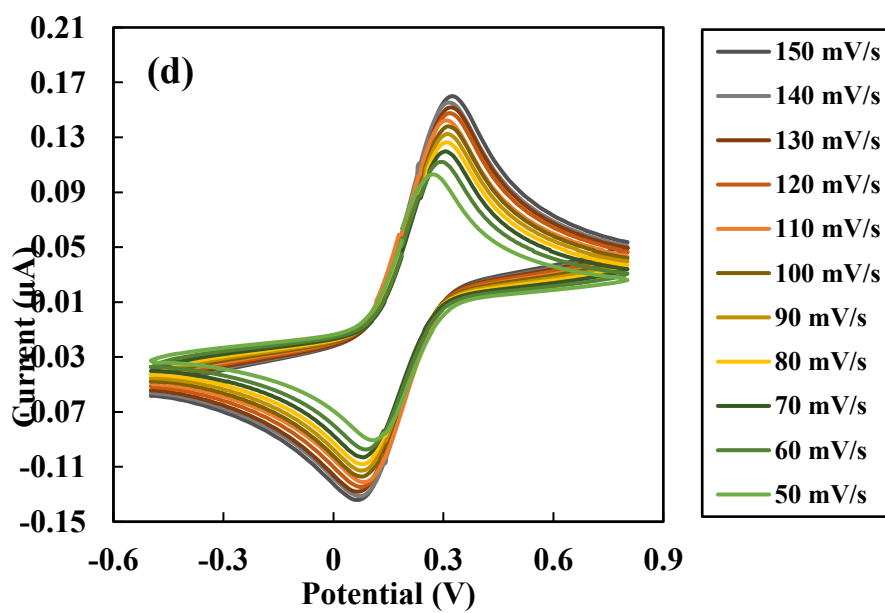
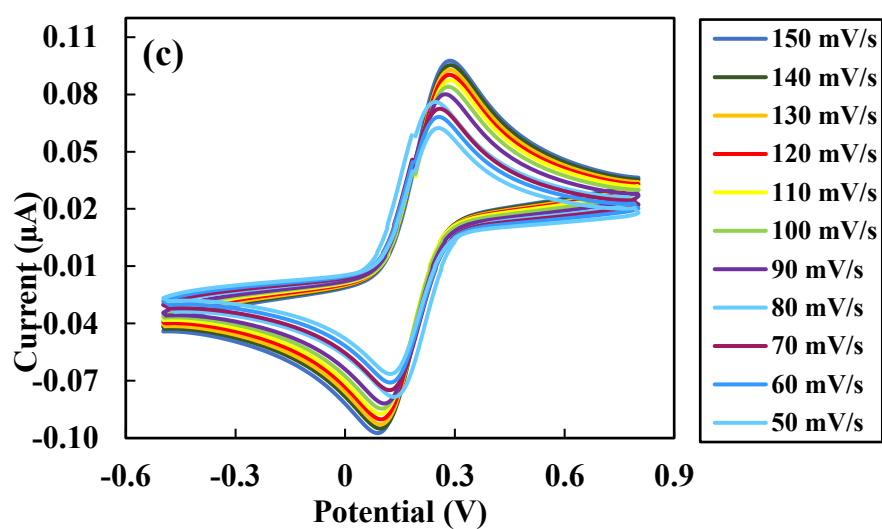
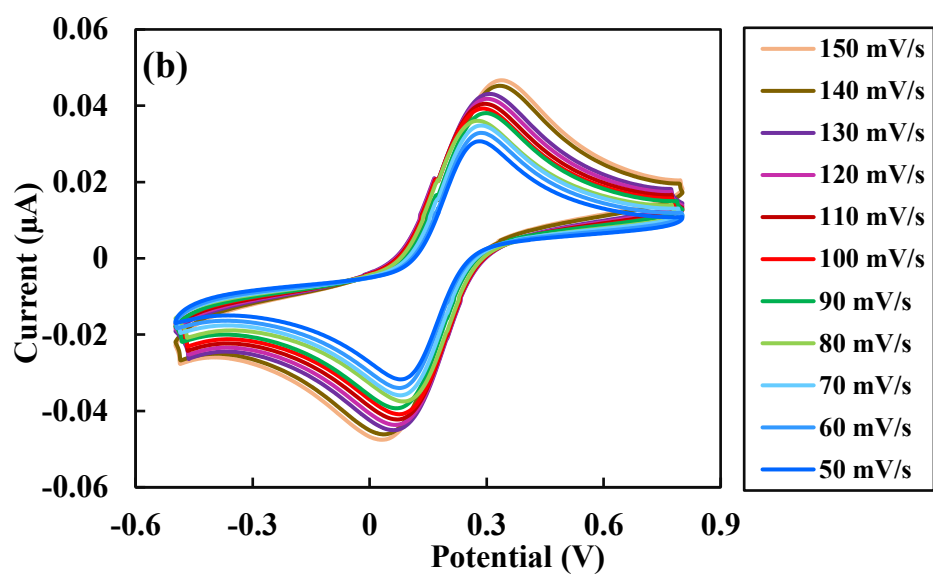


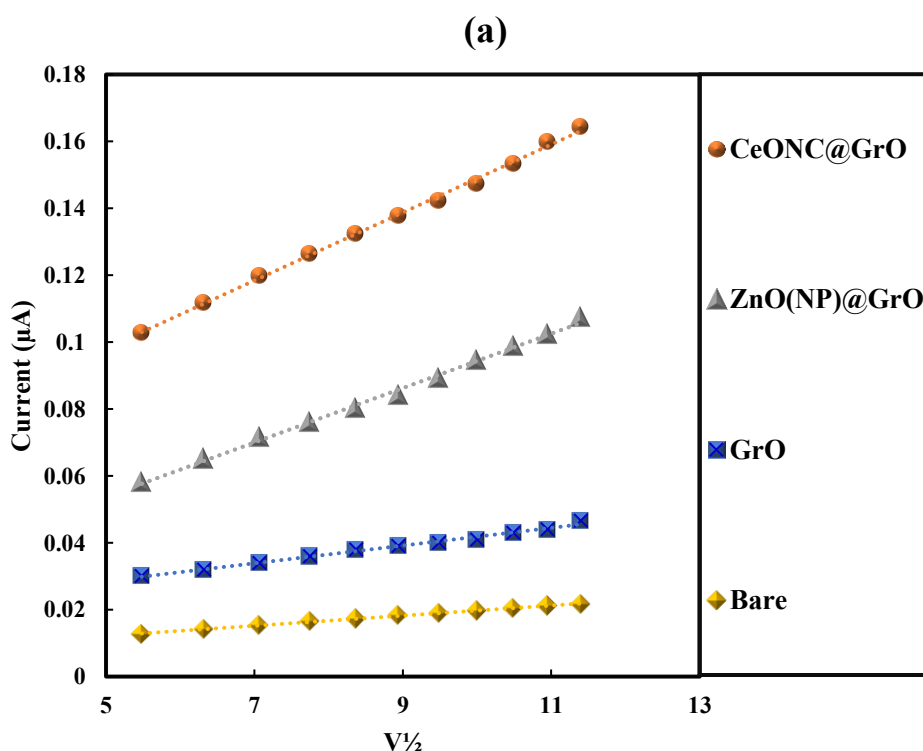
Figure 3.10. Effect of scan rate on cyclic voltammograms of 0.001 molL⁻¹ Fe³⁺/Fe²⁺ solution using: (a) Bare GCE; (b) GrO GCE; (c) ZnO(NP)@GrO GCE; and (d) CeONC@GrO GCE.

In addition, each electrode's electroactive surface area (ESA), *viz.*, GCE, GrO GCE, ZnO(NP)@GrO GCE, and CeONC@GrO GCE, was obtained in 0.001 molL⁻¹ ferric/ferrocyanide redox couple using cyclic voltammetry. Figure 3.11 (a–d) depicts the cyclic voltammograms of the corresponding electrodes at varying scan rates, highlighting the effect of scan rate on redox behaviour. The anodic and cathodic peak currents linked to the ferri/ferrocyanide redox process exhibited a linear rise with the square root of the scan rate, signifying that the electron transfer reaction at all electrodes was governed by diffusion control processes (Trachioti et al., 2023). Furthermore, to elucidate the mass transport mechanism, the scan rate dependence of the peak current was analysed, and according to the Randles-Ševčík equation, a diffusion-controlled process is indicated by a proportionality between the I_p and $v^{1/2}$ values. The plot of I_p/v (normalized current) versus v displays a gradual decreasing trend (*Cf* Figure 3.11 (b)). Therefore, Figure 3.11 (b) confirms that the redox reaction is predominantly a diffusion-controlled process (Bard et al., 2022; Moreno et al., 1991). The Randles-Ševčík equation for reversible systems was utilized to quantify the ESA. Typically, diffusion-controlled electrochemical processes exhibit a linear correlation between the peak oxidative or reductive current and the square root of the scan rates, as described by the Randles-Sevcik equation (3.1).

$$I_p = 2.69 \times 10^5 \times n^{2/3} \times v^{1/2} \times D^{1/2} \times C \times A \quad \text{..... (3.1)}$$

where I_p is the oxidative peak current (μA), ' n ' represents the number of electrons exchanged ($n = 1$ for the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ system), ' A ' denotes the electroactive surface area (cm^2), and ' D ' is the diffusion coefficient of the redox probe ($7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), ' C ' represents the concentration of the probe (mol cm^{-3}), and ' v ' denotes the scan rate (mVs^{-1}). The slope of the linear fit was derived from the plot of peak current (I_p) against the square root of the scan rate ($v^{1/2}$), which was then utilized in the aforementioned equation to compute the ESA for each electrode, and the results are given in Table 3.3. The calculated ESA values are 8.0×10^{-4} , 17.0×10^{-4} , 38.0×10^{-4} ,

and $66.0 \times 10^{-4} \text{ mm}^2$ for bare GCE, GrO GCE, ZnO(NP)@GrO GCE, and CeONC@GrO GCE, respectively, indicating a significant increase in the electroactive surface area following surface modification. The unmodified GCE exhibits a limited number of active sites because of its smooth surface; however, the incorporation of GrO approximately doubles the ESA by introducing a two-dimensional wrinkled shape and oxygenated functional groups that enhance electron transmission. The integration of ZnO nanoparticles enhances the ESA by increasing roughness, enlarging catalytic sites, and facilitating a synergistic interaction with GrO, producing a higher electroactive surface area and better electrochemical performance (X. Zhang et al., 2016). Moreover, the CeONC@GrO electrode demonstrates a relatively maximum electroactive surface area (ESA), almost eight times greater than that of bare GCE, due to the extensive surface area of CeONC nanostructures, their reversible $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox activity, and the conductive properties of graphene oxide (GrO) sheets.



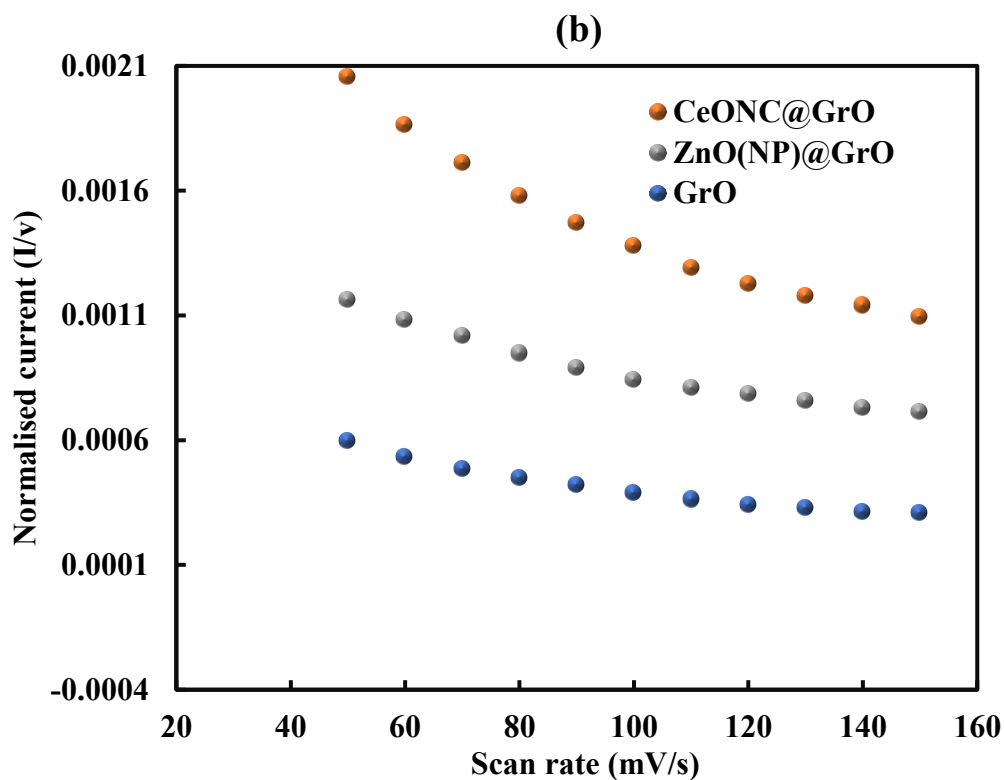


Figure 3.11. (a) Linear plots of oxidation peak current vs $v^{1/2}$; (b) Plot of normalized current (I/v) vs scan rate using various electrodes [0.001 M $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (0.1 M AcBS)]

Table 3.3. The calculated electroactive surface area of each working electrode using Randle's Sevcik equation.

Glassy carbon electrodes (GCE)	Electroactive surface area (mm^2)
Bare	8.0×10^{-4}
GrO	17.0×10^{-4}
ZnO(NP)@GrO	38.0×10^{-4}
CeONC@GrO	66.0×10^{-4}

Electrochemical impedance spectroscopy (EIS) measurements for the fabricated electrodes were also conducted using the standard redox probe system of $0.001 \text{ mol}\cdot\text{L}^{-1} \text{ Fe}^{2+}/\text{Fe}^{3+}$ obtained in $0.1 \text{ mol}\cdot\text{L}^{-1}$ sodium acetate buffer solutions (AcBS) (pH 4.5) at a frequency range of 80 kHz to 100 mHz, utilizing six data points per frequency decade and an AC amplitude of 10 mV. The imaginary impedance ($-Z_{\text{im}}$) was graphed against the real impedance (Z_{real}), and the findings are illustrated in the Nyquist plot (Figure 3.12). Additionally, the equivalent circuits for the various electrodes were constructed, and the experimental results were determined to coordinate most well with the Randles circuit, as seen in the inset of Figure 3.11. The obtained Nyquist plots were examined by fitting the experimental data to the corresponding Randles circuit expressed as $R_1 + Q_2/(R_2 + W_2)$. In this model, R_1 represents the solution resistance (R_s), Q_2 signifies the constant phase element linked to the double-layer capacitance (C_{dl}) at the electrode–electrolyte interface, R_2 indicates the charge transfer resistance (R_{ct}), and W_2 encompasses the Warburg impedance (W), which reflects diffusion-controlled processes. The R_{ct} is a crucial measurement that signifies the ease of electron flow at the electrode interface and the reactive analyte involved. The size of the semicircular region in Nyquist plots is directly proportional to R_{ct} , with a noticeable decrease in the semicircular region for the unmodified electrode compared to the modified electrodes, indicating improved charge transfer efficiency due to the presence of nanocomposite materials (Miao et al., 2020) (Cf Figure 3.10).

Table 3.4 shows the electron transfer resistance of $8.4 \times 10^3 \text{ Ohms}$ for the unmodified GCE. On the other hand, the modified electrodes exhibited significantly reduced R_{ct} values, measuring $2.6 \times 10^3 \text{ }\Omega$ for GrO GCE, $0.7 \times 10^3 \text{ }\Omega$ for ZnO(NP)@GrO GCE, and $0.3 \times 10^3 \text{ }\Omega$ for CeONC@GrO GCE. The decrease in R_{ct} for GrO GCE and ZnO(NP)@GrO GCE is mostly due to the higher electrical conductivity of GrO and ZnO(NP)@GrO, facilitating fast charge transfer reactions at the electrode–electrolyte interface. Moreover, nearly constant solution resistance (R_s) is obtained for all these electrodes, confirming a consistent electrochemical environment. The ZnO(NP)@GrO GCE demonstrated reduced resistance compared to the GrO GCE, suggesting that ZnO nanoparticles synergistically improved charge transfer processes by providing supplementary conductive channels and catalytic sites. The enhanced

conductivity and synergistic effect led to the better electrocatalytic activity of ZnO(NP)@GrO GCE. Among these modified electrodes, the CeONC@GrO GCE showed the lowest R_{ct} value ($0.3 \times 10^3 \Omega$), highlighting its superior charge transfer efficiency. This notable enhancement is attributed to the synergistic effect of cerium oxide nanoclusters and graphene oxide. Cerium oxide showed redox-active properties, facilitating efficient electron transport via the reversible Ce^{3+}/Ce^{4+} redox pair. Moreover, the partial reduction of Ce^{4+} to Ce^{3+} in cerium oxide produces oxygen vacancies that serve as active sites for the adsorption of reactive species (Pizúrová et al., 2022). The existence of these vacancies enhances the number of reactive centres, hence promoting more robust interactions between the electrode material and target analytes.

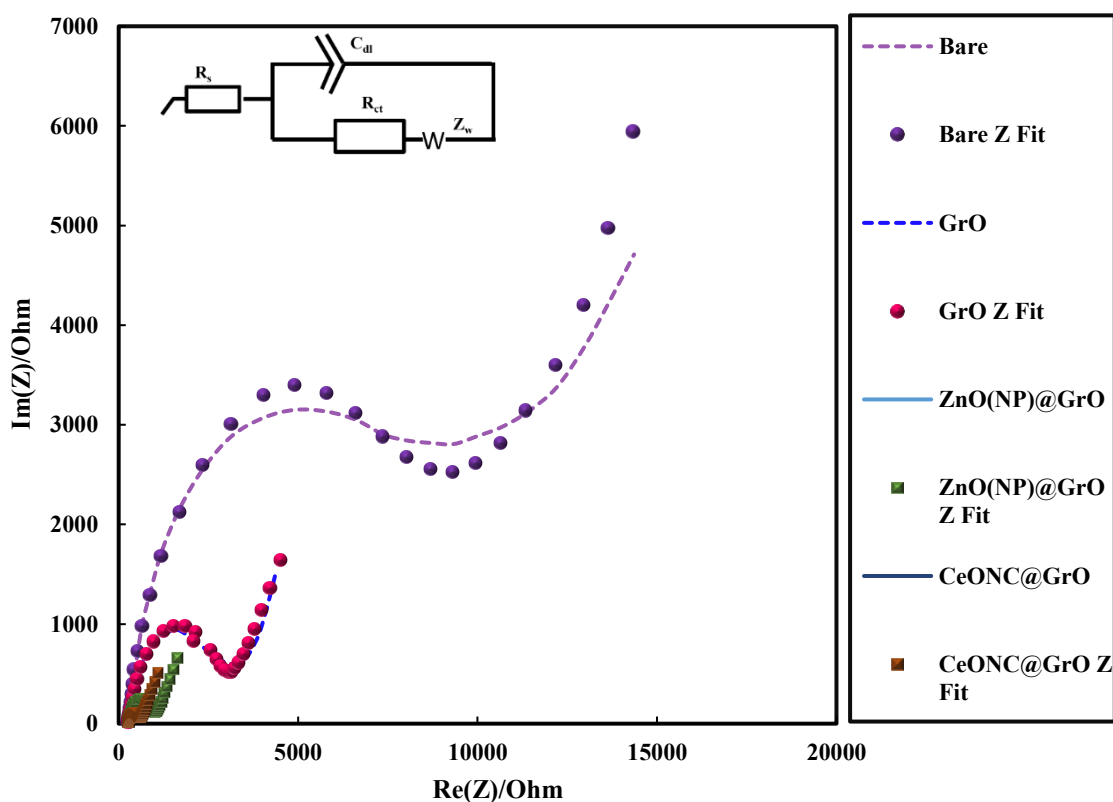


Figure 3.12. Nyquist fitting plots for different modified electrodes.

Table 3.4. EIS parameters estimated from the fitted equivalent electrical circuit for the Nyquist plots of various glassy carbon working electrodes.

Electrodes	R_s (Ω)	C_{dl} (μF)	R_{ct} (Ω)
Bare	280.3	0.95	8.4×10^3
GrO	280.6	0.86	2.6×10^3
ZnO(NP)@GrO	283.9	0.68	0.7×10^3
CeONC@GrO	280.6	0.59	0.3×10^3

3.2. SINGLE AND SIMULTANEOUS ELECTROCHEMICAL DETECTION OF Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+}

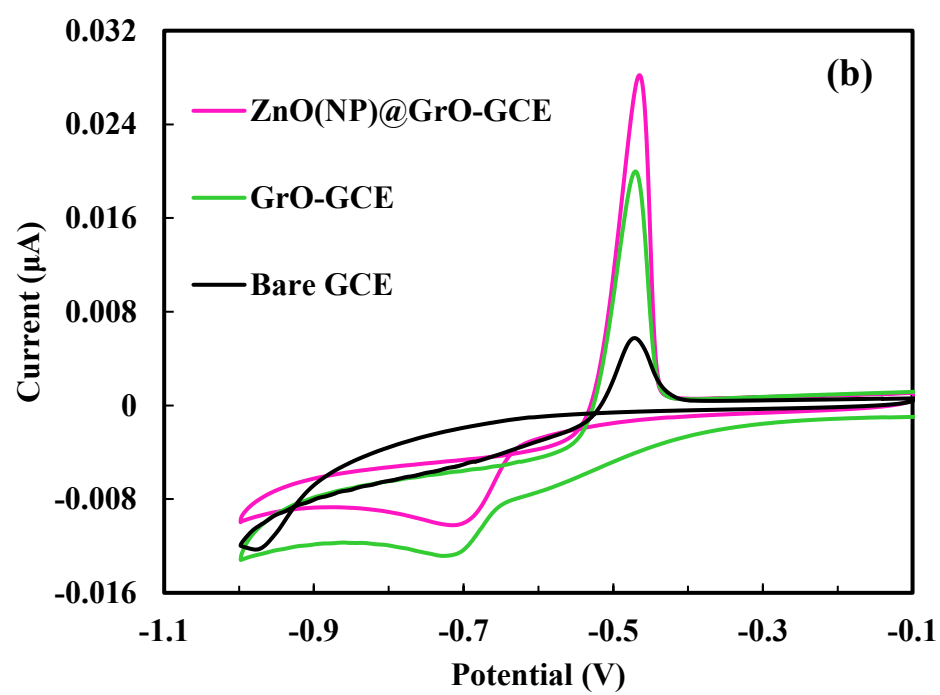
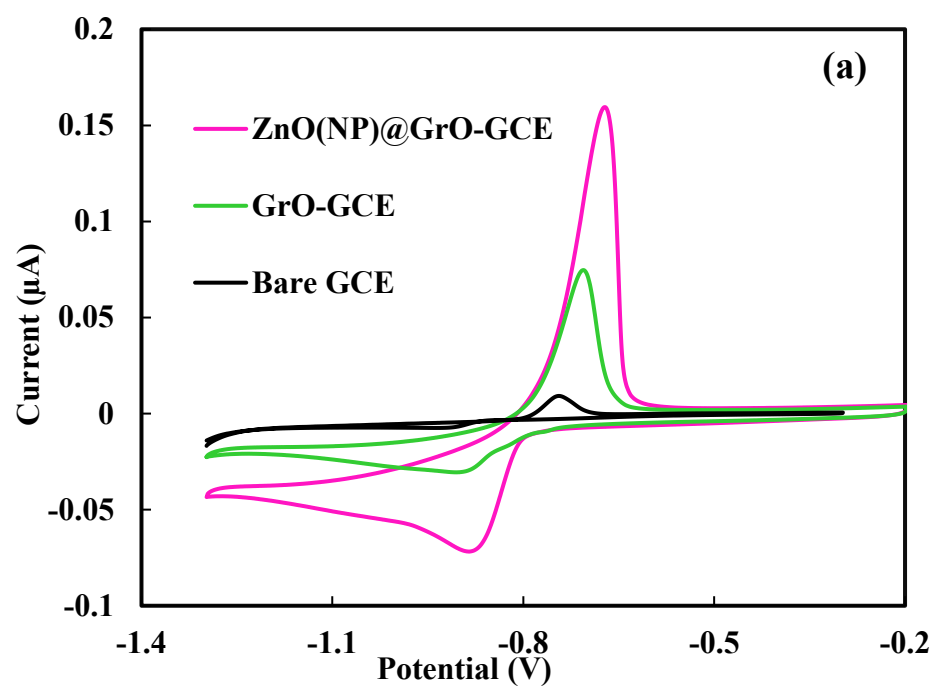
The electrochemical detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} was systematically conducted individually and simultaneously utilizing the nanocomposite-modified electrode (ZnO(NP)@GrO GCE). Differential pulse voltammetry (DPV) in conjunction with anodic stripping voltammetry (ASV) was utilized. The preconcentration-stripping processes of ASV provide better sensitivity and selectivity for the detection of several analytes. Before DPV analysis, the essential electrochemical characteristics of each metal ion were investigated by cyclic voltammetry (CV). The cyclic voltammograms of these metal ions were conducted utilizing the bare GCE, GrO modified GCE, and ZnO(NP)@GrO GCE to assess the impact of surface modification on electron transfer kinetics and electroactive surface area. Further, studies were performed for the efficient sensing and trace detection of the target analytes utilizing the ZnO(NP)@GrO GCE. All electrochemical investigations were conducted in a 0.1 molL^{-1} acetate buffer (pH 4.5) solution.

3.2.1. Cyclic voltammetric analysis of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+}

Figure 3.13 illustrates the cyclic voltammograms (CVs) of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} ions recorded using bare GCE, GrO GCE, and $\text{ZnO}(\text{NP})@\text{GrO}$ GCE electrodes, at a metal ion concentration of 1.0 mgL^{-1} in 0.1 molL^{-1} acetate buffer solution (pH 4.5). It is evident from the figures that the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE exhibits remarkably higher current responses compared to the bare GCE or GrO GCE, which indicates that the nanocomposite solid caused an enhanced electrocatalytic activity in the redox reactions of these metal ions at the electrode surface. Specifically, the cyclic voltammetric measurements for Cd^{2+} and Pb^{2+} were conducted within the optimized potential ranges of -1.2 to -0.3 V for Cd^{2+} and -0.9 to -0.1 V for Pb^{2+} at a scan rate of 100 mV/s . A distinct oxidation peak for Cd^{2+} was observed at -0.67 V , alongside a corresponding reduction peak at -0.87 V . The clearly defined anodic–cathodic pair confirms the direct electrochemical transformation between Cd^{2+} and metallic cadmium (Cd^0), which entails a two-electron transfer process, i.e., Cd^{2+} to Cd^0 . Similarly, Pb^{2+} exhibited a clear anodic peak at -0.46 V and a cathodic peak at -0.69 V , aligning with the equilibrium redox transformation of Pb^{2+} to Pb^0 (Shi et al., 2020). The presence of oxidation and reduction peaks for Cd^{2+} and Pb^{2+} indicates that these processes exhibit electrochemical reversibility within the examined potential range, since distinct redox peaks are observed in CV. Further, the electrochemical reversibility of the metal complexes was assessed using cyclic voltammetry. The peak potential separations (ΔE_p) for Cd^{2+} and Pb^{2+} were found to be 208 mV and 243 mV , respectively, which are significantly greater than the theoretical value of $59/n \text{ mV}$ expected for a reversible one-electron transfer process. This deviation indicates that the redox processes of both Cd^{2+} and Pb^{2+} at the modified electrode exhibit quasi-reversible electron transfer behaviour (Elgrishi et al., 2018). However, the observation of distinct and pronounced peaks clearly indicates the effective interaction between Cd^{2+} and Pb^{2+} ions with the $\text{ZnO}(\text{NP})@\text{GrO}$ modified electrode, facilitating efficient electron exchange and deposition/stripping processes.

In contrast, Hg^{2+} and Zn^{2+} display significantly different electrochemical behaviours when compared to Cd^{2+} and Pb^{2+} . A distinct oxidation peak is noted for

Hg^{2+} , while a corresponding reduction peak does not appear within the examined potential range, indicating an apparent irreversible oxidation process (*Cf* Figure 3.13(c)). The observed irreversibility is attributed to slow electron-transfer kinetics and the robust adsorption of oxidized mercury species on the electrode surface, hindering effective reduction in the reverse scan (Manivannan et al., 2002). The presence of stable intermediates, *viz.*, HgO species at the electrode surface, could hinder the reversibility of the $\text{Hg}^{2+}/\text{Hg}^0$ couple (H. Xu et al., 2021). Similarly, a significant oxidation peak is observed for zinc, while a reduction peak does not appear in the reverse scan (*Cf* Figure 3.13(d)). This is typically attributed to the development of a passivating oxide layer on the electrode surface during the oxidation process (Conway & Kannangara, 1987). Upon the formation of zinc oxide film on the electrode surface, it obstructs further the electron transfer reactions, thereby preventing the reduction of Zn^{2+} to its metallic form within the specified potential range. Nevertheless, significantly enhanced current responses were observed at $\text{ZnO}(\text{NP})@\text{GrO}$ GCE for all these metal ions compared to bare and GrO modified electrodes, indicating that the nanocomposite surface provides strong electrocatalytic activity and effective preconcentration capability, making it a promising platform for the multi-ion detection of these environmentally hazardous heavy metals. Therefore, $\text{ZnO}(\text{NP})@\text{GrO}$ GCE is utilized for further trace detection of these metal ions.



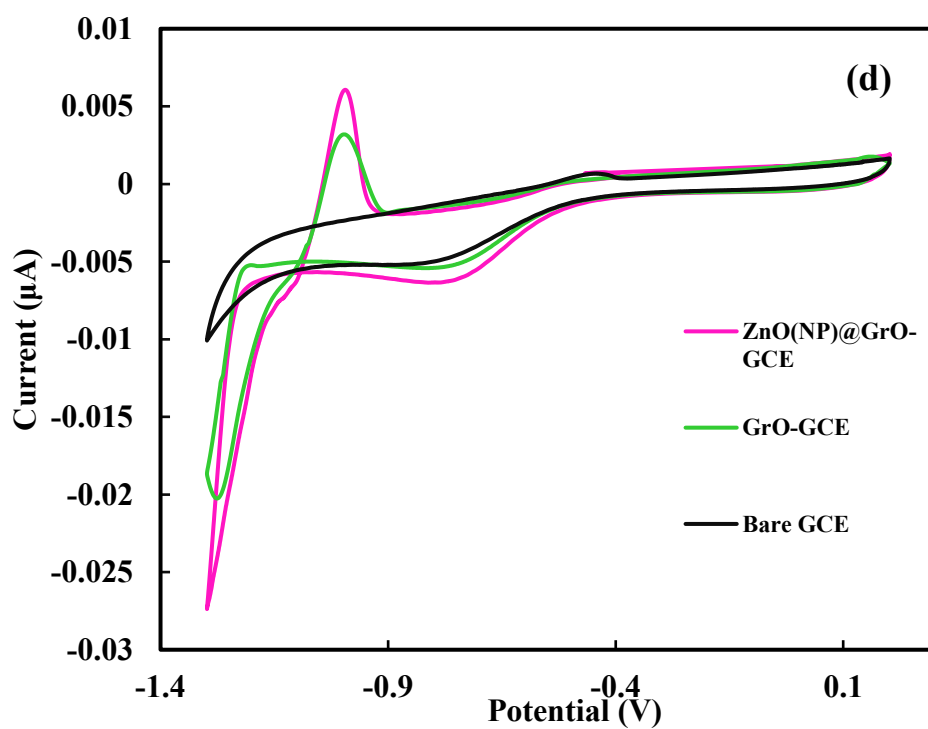
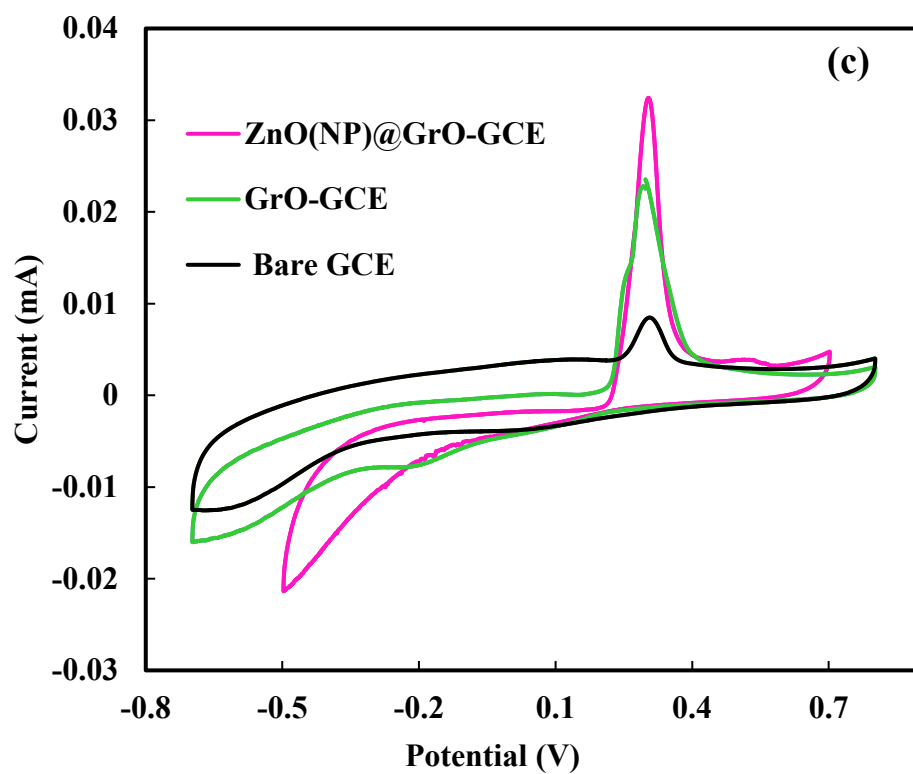


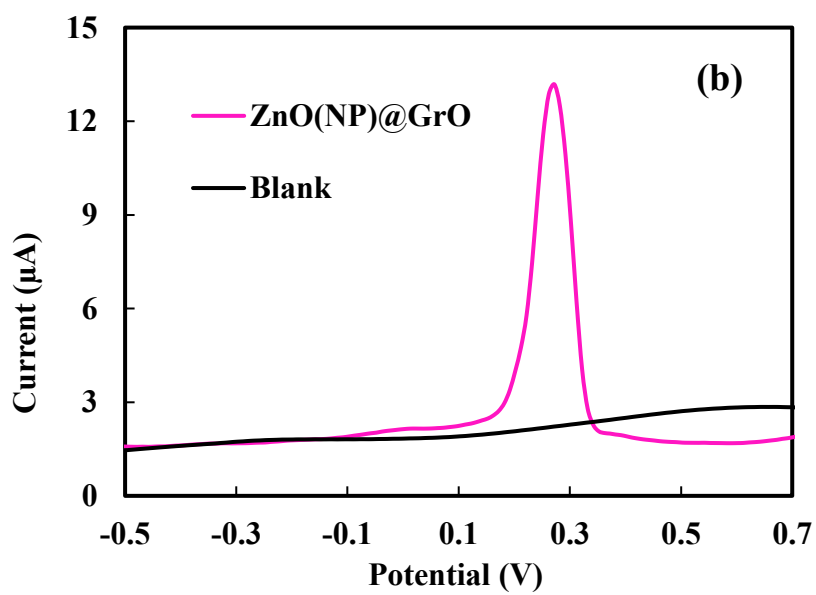
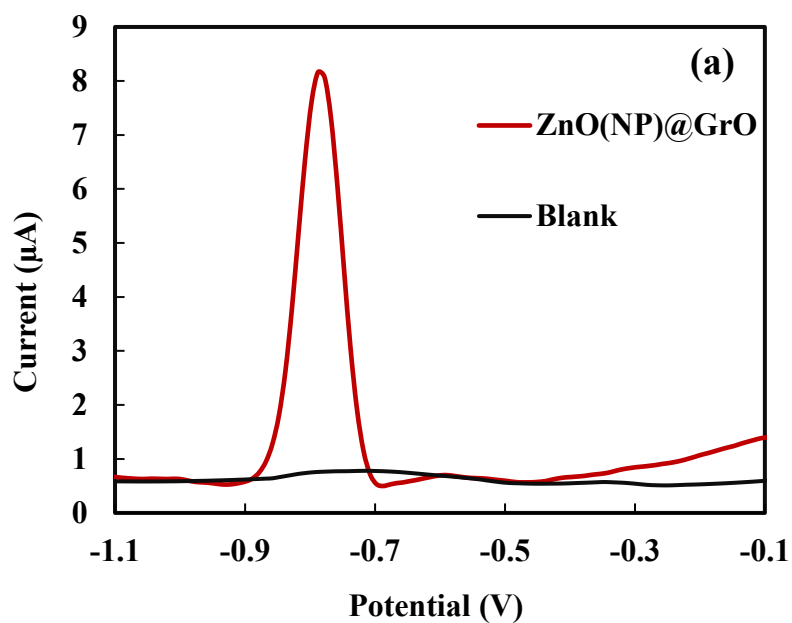
Figure 3.12. Cyclic voltammograms of 1.0 mgL⁻¹ of (a) Cd²⁺, (b) Pb²⁺, (c) Hg²⁺, and (d) Zn²⁺.

3.2.2. Low-level detection of Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ using DPASV techniques

The trace-level detection of Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ using ZnO(NP)@GrO-GCE was performed through differential pulse voltammetry (DPV) coupled with the anodic stripping technique. The working principle of DPASV involves three main stages: (i) accumulation (preconcentration), (ii) reduction (deposition), and (iii) stripping (oxidation). In the accumulation step, metal ions, *viz.*, Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺, migrate from the bulk solution toward the electrode surface, where they adsorb, form complexes, or interact with the nanostructured modifiers. During the reduction step, a potential more negative than the redox potential of the analytes is applied, promoting their electrochemical reduction into the corresponding metallic states. Finally, in the stripping step, the potential is scanned in the positive direction, leading to the oxidation of the deposited metals back into their ionic forms (e.g., Pb⁰ → Pb²⁺) (Shamsuddin & Sohn, 2023). This oxidation produces well-defined anodic peaks, each specific to a given metal ion. The peak current intensities are directly correlated with the concentrations of the respective ions, thereby enabling highly sensitive and selective quantification of Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ at trace levels.

Figure 3.14 (a-d) illustrates the DPASV responses of Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ obtained at the ZnO(NP)@GrO modified GCE surface, in both the absence and presence of 1.0 µgL⁻¹ of the respective analyte ions, utilizing 0.1 molL⁻¹ acetate buffer solution (AcBS) (pH 4.5). In the absence of metal ions (blank solution), the voltammogram displays no significant peaks within the applied potential window, confirming the stability of the modified electrode and the absence of interfering background signals. Upon the addition of 50 µgL⁻¹ of the target metal ions, numerous oxidative peaks appear. The observed peak potentials appear at *Ca.* -0.79 V for Cd²⁺ [Cf Figure 3.14 (a)], 0.27 V for Hg²⁺ [Cf Figure 3.14 (b)], -0.56 V for Pb²⁺ [Cf Figure 3.14 (c)], and -1.02 V for Zn²⁺ [Cf Figure 3.14 (d)], demonstrating well-defined separation among the signals. This distinction in oxidation potentials indicates that the

ZnO(NP)@GrO nanocomposite provides an excellent platform for the single and simultaneous detection of these environmentally significant heavy metal ions.



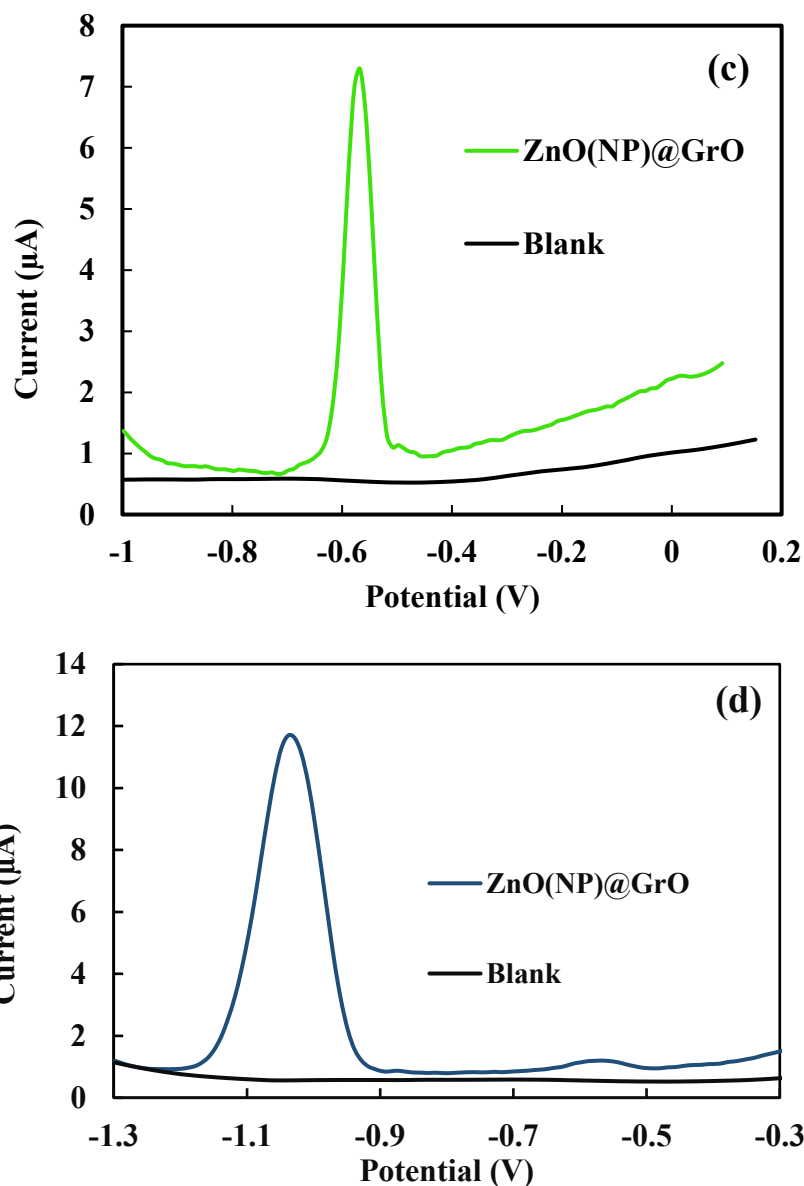


Figure 3.14 Differential pulse anodic stripping voltammograms of $50.0 \mu\text{g L}^{-1}$ of: (a) Cd^{2+} , (b) Hg^{2+} , (c) Pb^{2+} , and (d) Zn^{2+} using ZnO(NP)@GrO GCE.

3.2.3. Optimization of pH on detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+}

The pH of the solution is crucial for the electrochemical detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} ions, since it influences the ionic state of the analytes and the surface chemistry of the sensing material. Minor variation in pH can markedly affect the adsorption efficiency of metal ions at the electrode–electrolyte interface, thereby impacting the total redox reactions. The anodic peak currents of the target heavy metal

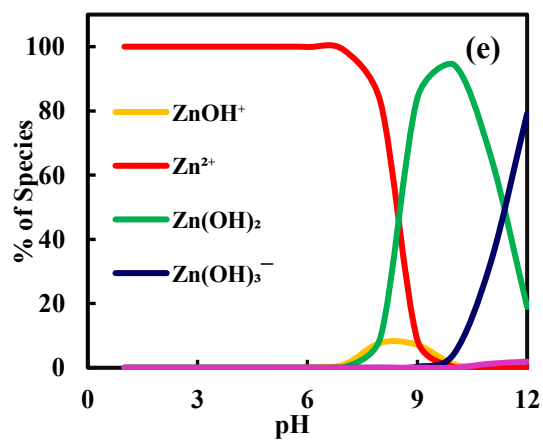
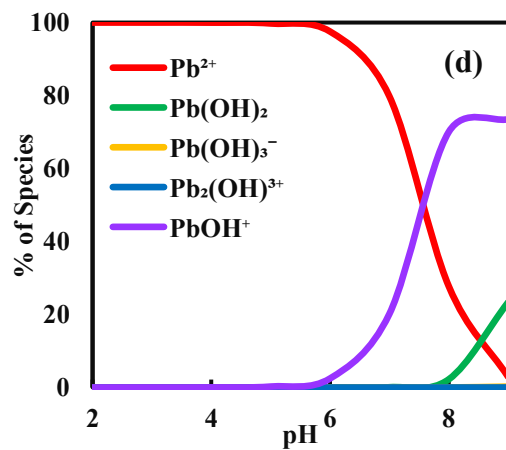
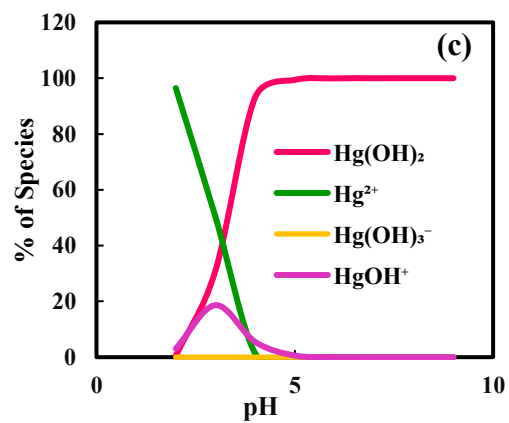
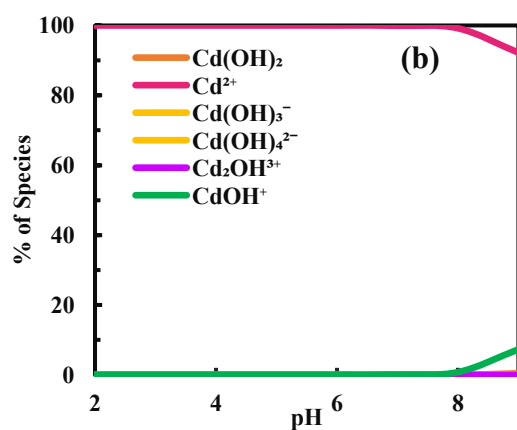
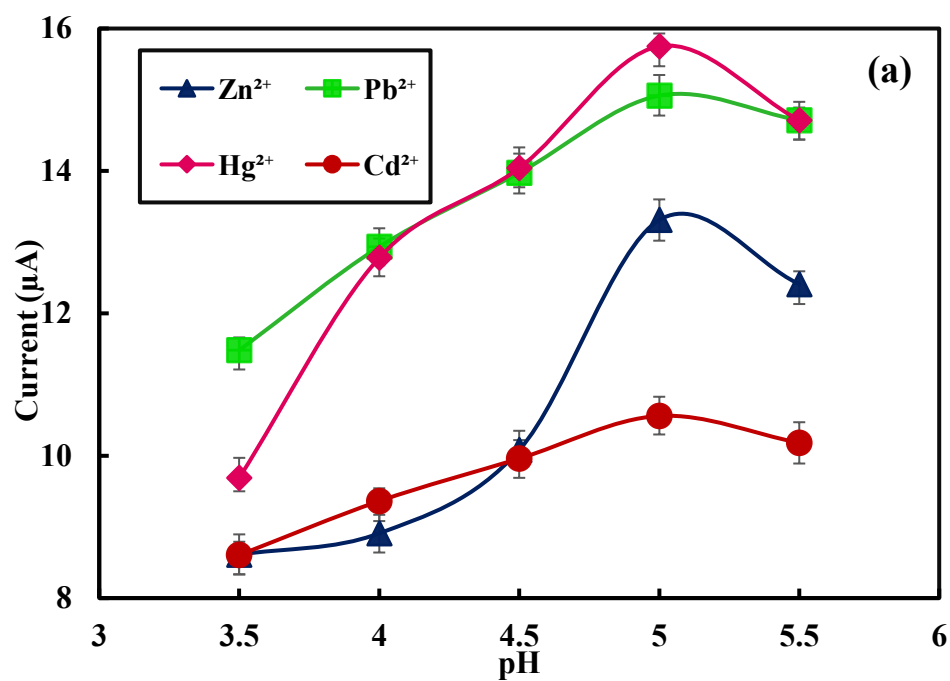
ions are measured within a pH range of 3.5 to 5.5 to investigate the pH impact on the detection of these metal ions. Figure 3.15 (a) demonstrates that the oxidation peak currents for Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} were increased with an increase in pH from 3.5 to 5.0. These results suggest that at mildly acidic conditions i.e., pH $\sim$ 5.0, the electrostatic attraction between positively charged metal ions and the dissociated functional groups on the electrode surface (such as $-\text{OH}$, $-\text{COOH}$, and oxygen vacancies) is predominant, leading to increased accumulation and elevated electron transfer rates (Y. Li et al., 2017; Szabó et al., 2006).

At lower pH values (around 3.5), the electrolyte solution contains a high concentration of protons (H^+). Under these conditions, the carboxylic functional groups ($-\text{COOH}$) present on the graphene oxide (GrO) surface become protonated. When protonated, these groups lose their negative charge and exist primarily in the neutral $-\text{COOH}$ form rather than the deprotonated $-\text{COO}^-$ form (Costentin et al., 2006). Because of this, the metal cations experience weak or negligible electrostatic attraction to the electrode surface, which in turn restricts their adsorption and preconcentration onto the electrode surface. Since effective adsorption is a prerequisite for sensitive electrochemical detection. Moreover, at low pH levels, an excess of H^+ ions competes with the target metal cations for active binding sites on the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE surface, thereby inhibiting their adsorption and resulting in a reduced current response. Figure 3.15(b-e) presents the speciation profiles of cadmium, lead, and zinc ions, indicating that cadmium (Cd^{2+}) is predominant in the pH region of 2.0-8.0 [Cf Figure 3.15 (b)], lead (Pb^{2+}) is within pH 2.0-5.5 [Cf Figure 3.15 (d)], zinc (Zn^{2+}) is within pH 3.0-7.0 [Cf Figure 3.15 (e)] while neutral species $\text{Hg}(\text{OH})_2$ dominated in the pH region of 5.0-9.0 [Cf Figure 3.15 (b)]. In contrast, the $\text{ZnO}(\text{NP})@\text{GrO}$ composite exhibits a point of zero charge (pH_{PZC}) of 6.2 as illustrated in Figure 3.15 (f). Notably, a higher electrochemical response is recorded at pH 5.0, where the peak current for these metal ions is comparatively higher. These metal ions are likely to be attracted to the surface with the electrostatic attraction, followed by specifically attaching to the surface and undergoing the ‘ion exchange’ process (Equation (3.2)) at the electrode surface.



At pH 5.0, the surface of graphene oxide (GrO) that is present in ZnO(NP)@GrO becomes favourable for heavy metal ion adsorption. In this moderately acidic environment, the oxygen-containing functional groups of GrO, particularly hydroxyl (–OH) and carboxyl (–COOH) groups, are deprotonated. Among these, the carboxylic groups are especially important, while they remain protonated (–COOH) under strongly acidic conditions, at slightly acidic it lose a proton and exist in their anionic form (–COO[–]) (Manzoor et al., 2024), attracting the positively charged metal ions to the electrode's surface. The increased adsorption increases the local concentration of metal ions at the electrode-solution interface, hence increasing their participation in electron transfer processes during the stripping step. As a result, the anodic peak current increases, indicating enhanced sensitivity and efficacy of electrochemical detection at this pH.

Further increase in pH, i.e., from 5.0 to 6.0, a gradual decline in the oxidation currents of the metal ions was observed. This decrease is attributed to the onset of partial hydrolysis of some cations, which leads to the formation of hydroxo complexes or precipitated hydroxide species. As a result, the concentration of free metal ions available for electrochemical oxidation is reduced, thereby lowering the stripping peak currents. These findings are in good agreement with earlier reports on the simultaneous detection of heavy metals such as Cd²⁺, Pb²⁺, and Hg²⁺, where an optimum response was achieved at pH 5.0 using amino-functionalized MXene and bimetallic MOF nanocomposites (Y. Shi et al., 2025). Further, it was noted that as the pH was increased from 5.0 to 7.0, the oxidation currents of Cd²⁺, Pb²⁺, and Hg²⁺ decreased significantly. This trend was explained by the greater tendency of these metal ions to undergo hydrolysis in a mildly alkaline medium, leading to the formation of insoluble hydroxides and thus reducing their electrochemical activity (Y. Shi et al., 2025).



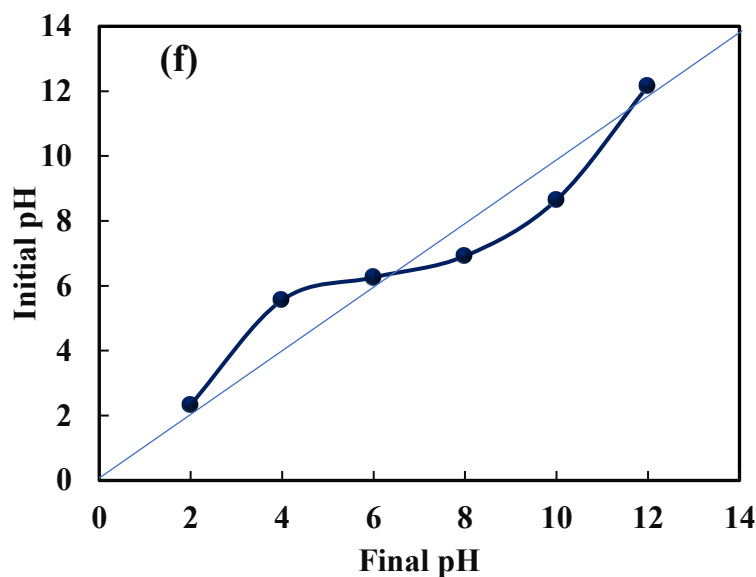
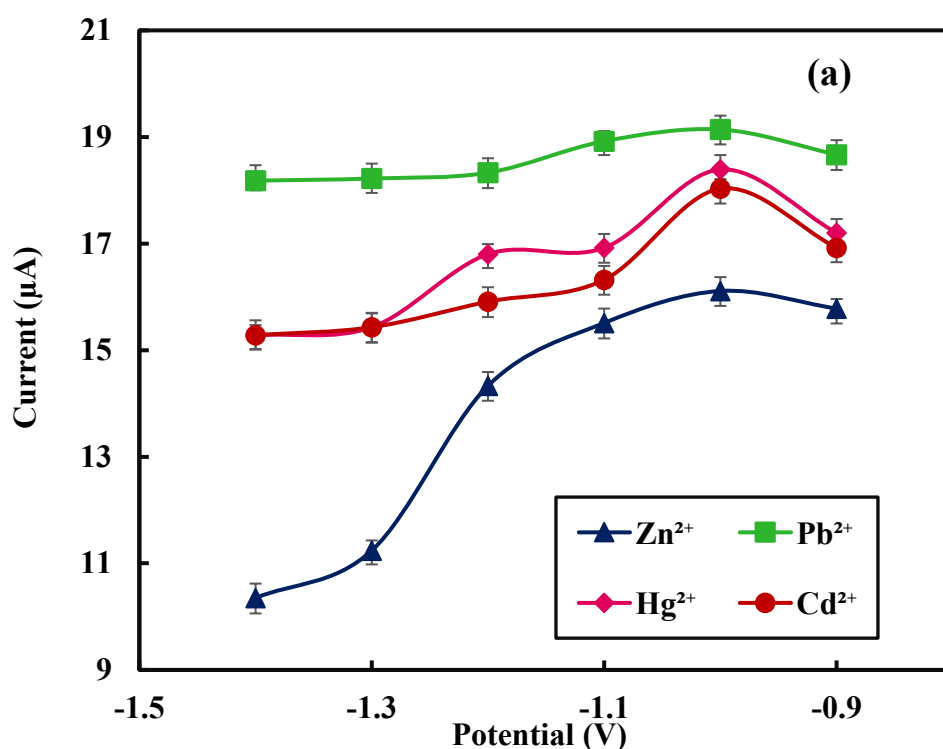


Figure 3.15. (a) Impacts on oxidation currents of Cd^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+} in a 0.1 molL^{-1} AcBS at varied pH values using $\text{ZnO}(\text{NP})@\text{GrO}$ GCE; Speciation studies of: (b) Cd^{2+} , (c) Hg^{2+} , (d) Pb^{2+} and (e) Zn^{2+} ; (f) pH_{PZC} determination of $\text{Zn}(\text{NP})@\text{GrO}$.

3.2.4. Optimization of deposition potential and time

The impact of accumulating potential upon the electrochemical response of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} in 0.1 molL^{-1} AcBS at pH 5.0 is examined within the potential range of -0.9 V to -1.4 V. Figure 3.16 (a) represents the oxidation peak current for these heavy metal ions against the accumulation potential. The maximum current is observed at an accumulation potential of -1.0 V for these metal ions. However, a noticeable decrease in the stripping currents is observed as the potential becomes more positive. This decline in the oxidation current is due to the incomplete reduction of these analyte ions at higher potentials (Borrill et al., 2019). The reduction process was suppressed at more negative accumulation potentials due to the interference of the H_2 evolution reaction. This reduces the availability of free electrons to reduce metal ions, lowering the overall electrochemical response and the stripping current. Consequently, the deposition potential of -1.0 V is an optimum stripping potential for an enhanced oxidative response of these metal ions.

Additionally, experiments are conducted at various time intervals ranging from 30 to 180 sec to assess the impact of accumulation time on the electrochemical response. Figure 3.16 (b) depicts that the oxidation currents for these metal ions were increased with an increase in deposition time, reaching a maximum value at 120 sec. This indicates that a longer accumulation time allows these ionic species to adsorb onto the electrode surface, enhancing the electrochemical response. However, above 120 sec, a further rise in the accumulation time results in a slight decline in the oxidation currents. This decline is attributed to the saturation of metal cations at the surface or the formation of side products that inhibit the electron transfer reactions. The optimal deposition time is 120 sec for lead and cadmium, producing the highest peak currents by achieving a balance between ion accumulation and stability of the electrode surface (Lieu et al., 2019).



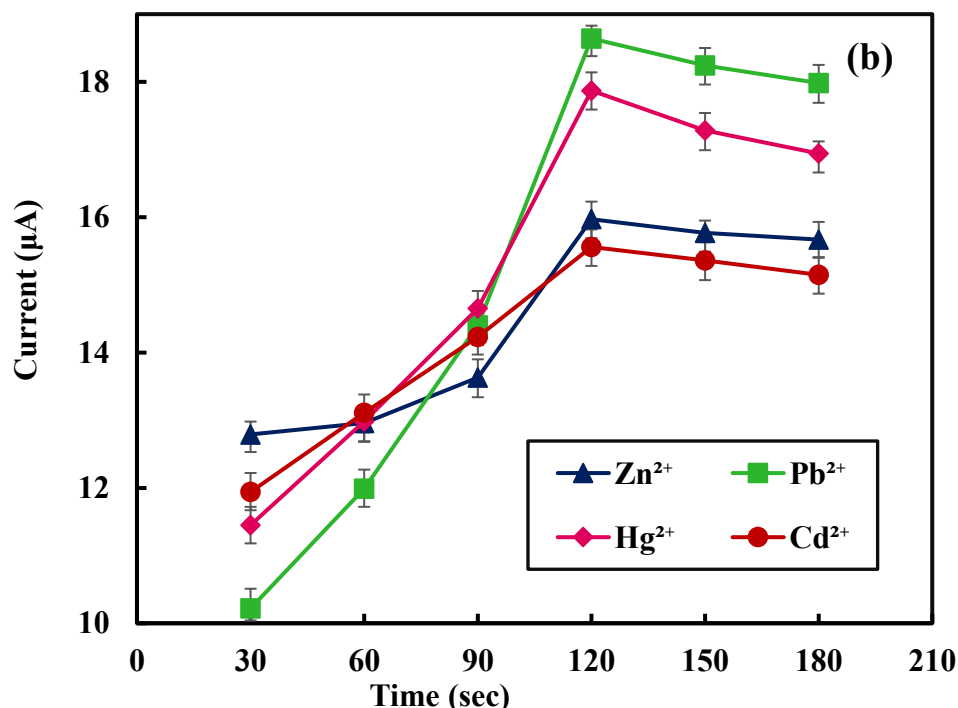
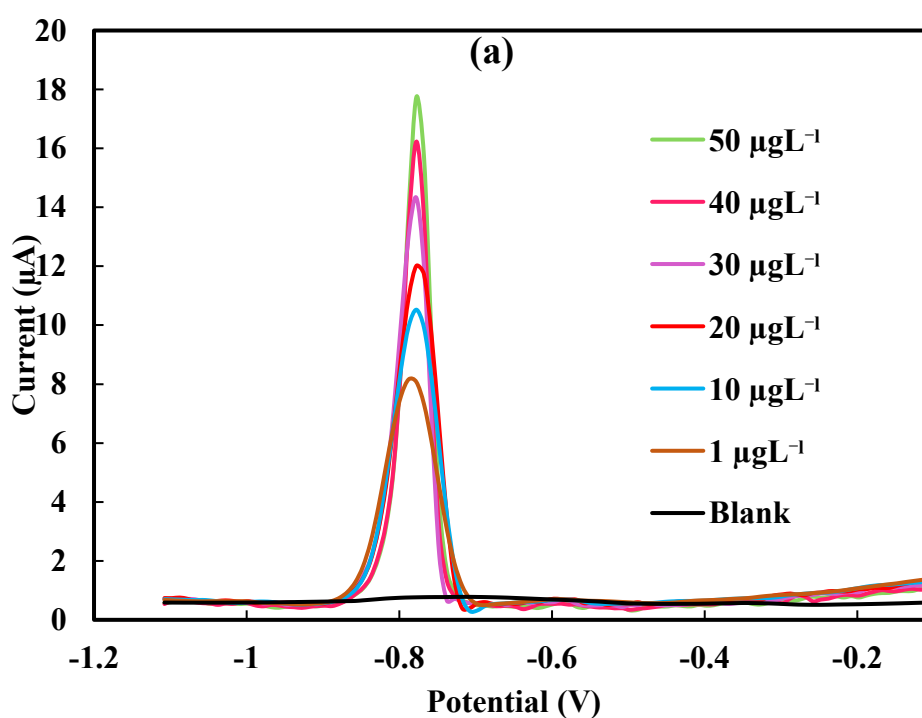


Figure 3.16. Impacts on oxidized current of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} in a 0.1 molL^{-1} AcBS (pH 5.0) of the following parameters: (a) Deposition potential; and (b) Deposition time

3.2.5. Concentration dependence studies and calibration plots for Cd^{2+}

The electrochemical detection of Cd^{2+} was extensively investigated at various Cd^{2+} concentrations under optimized DPASV conditions utilizing the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE. Figure 3.17 (a) displays the stripping voltammograms for different concentrations of Cd^{2+} , demonstrating a clear trend where the oxidative peak current rises as the Cd^{2+} concentration is increased from 0.1 to $50 \text{ } \mu\text{gL}^{-1}$. Increasing the Cd^{2+} concentration from 0.1 to $50.0 \text{ } \mu\text{gL}^{-1}$, a significant and proportional increase in the anodic peak current is recorded, demonstrating the remarkable sensitivity of the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE for detecting the Cd^{2+} . A calibration plot is drawn to assess the quantitative detection of Cd^{2+} . The line is drawn between the Cd^{2+} concentration against the corresponding oxidative peak current [Cf Figure 3.17 (b)]. The calibration curve showed a linear relationship within the Cd^{2+} concentration, represented by the equation $y (\mu\text{A}) = 0.1923x (\mu\text{gL}^{-1}) + 8.3614$. This demonstrates a good correlation, as

indicated by the correlation coefficient (R^2) of 0.996 [Cf Figure 3.17 (b)]. The increased linearity indicates the reliability of the electrode in measuring the Cd^{2+} in aqueous medium. Additionally, the performance of the electrode was assessed in terms of the limit of detection (LOD) and limit of quantification (LOQ). The determined LOD and LOQ values were $0.047 \mu\text{g L}^{-1}$ and $0.15 \mu\text{g L}^{-1}$, respectively, highlighting the exceptional sensitivity of the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE in detecting trace-level Cd^{2+} . Previously, it was reported that the thiol-modified screen-printed carbon electrode (SPCE) demonstrated a limit of detection (LOD) of $0.099 \mu\text{g L}^{-1}$ (0.882 nM) for Cd^{2+} (Tiwari & Kadu, 2024). The exceptionally low nanomolar detection capability underscores the importance of surface functionalization and electrode design in improving sensitivity.



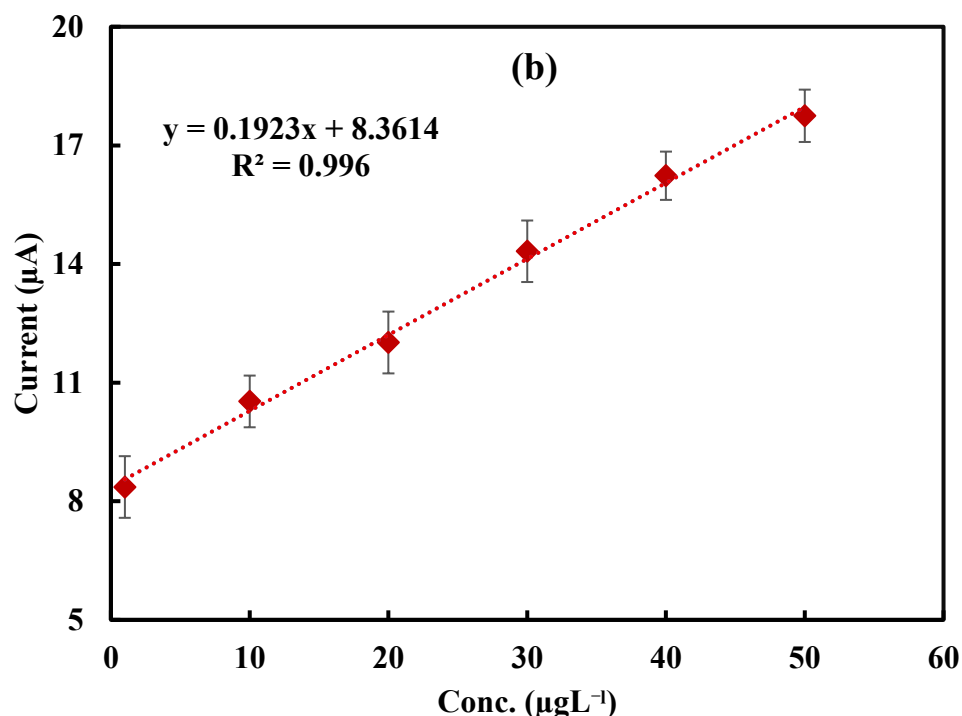
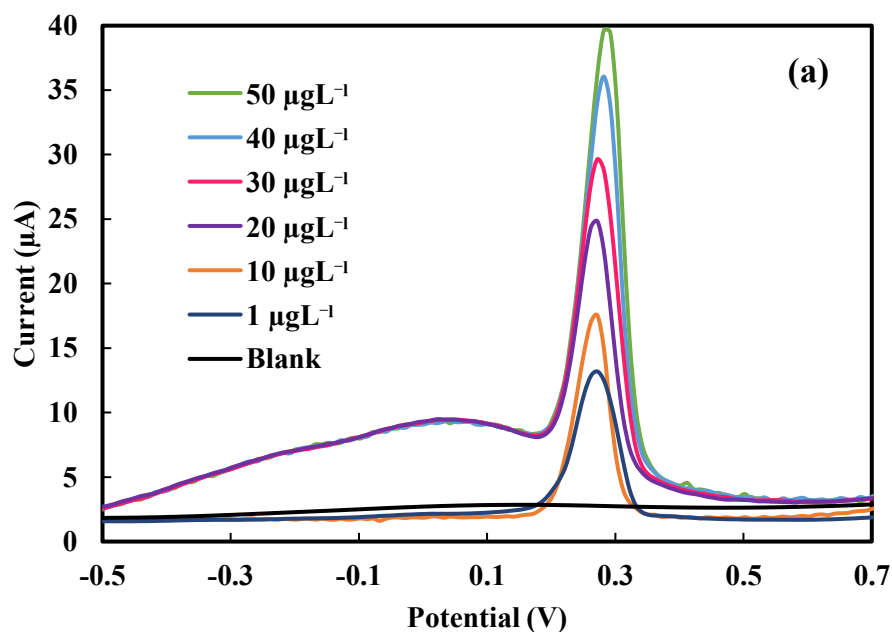


Figure 3.17. (a) The differential pulse anodic stripping voltammograms of Cd^{2+} at varied Cd^{2+} concentrations using $\text{ZnO}(\text{NP})@\text{GrO}$ (AsBS: 0.1 molL^{-1} ; pH: 5.0); (b) Calibration line obtained for the Cd^{2+} concentration against the oxidative peak currents.

3.2.6. Concentration dependence studies and calibration plots for Hg^{2+}

The electrochemical detection of Hg^{2+} was systematically examined at varied concentrations of Hg^{2+} under optimized DPASV conditions using the $\text{ZnO}(\text{NP})@\text{GrO}$ modified GCE. Figure 3.18 (a) presents the stripping voltammograms obtained for different Hg^{2+} concentrations, which reveal a distinct and gradual increase in the oxidative peak currents as a function of Hg^{2+} concentrations. Specifically, increasing the Hg^{2+} concentration from 1.0 to $50.0 \text{ }\mu\text{gL}^{-1}$ causes a gradual increase in the anodic peak current, demonstrating the high sensitivity of the $\text{ZnO}(\text{NP})@\text{GrO}$ -GCE towards Hg^{2+} detection. Further, a calibration plot is plotted between the Hg^{2+} concentrations

against the corresponding oxidative peak current values. The calibration curve exhibited excellent linearity over the tested range, and is expressed by the regression equation, $y \text{ (}\mu\text{A)} = 0.5653x \text{ (}\mu\text{gL}^{-1}\text{)} + 12.178$ with a correlation coefficient (R^2) of 0.997 [Cf Figure 3.18(b)]. A good linearity underscores the reliability of the sensor in quantifying Hg^{2+} . Furthermore, the limit of detection (LOD) of $0.016 \mu\text{gL}^{-1}$ and a limit of quantification (LOQ) of $0.53 \mu\text{gL}^{-1}$ are observed in the detection of Hg^{2+} . These values demonstrate the high sensitivity of the ZnO(NP)@GrO-GCE , enabling trace level detection of Hg^{2+} , which is much below the maximum allowable thresholds established by prominent environmental regulatory agencies, including the World Health Organization (WHO) recommendation of $1 \mu\text{gL}^{-1}$ (Alex, 2018).



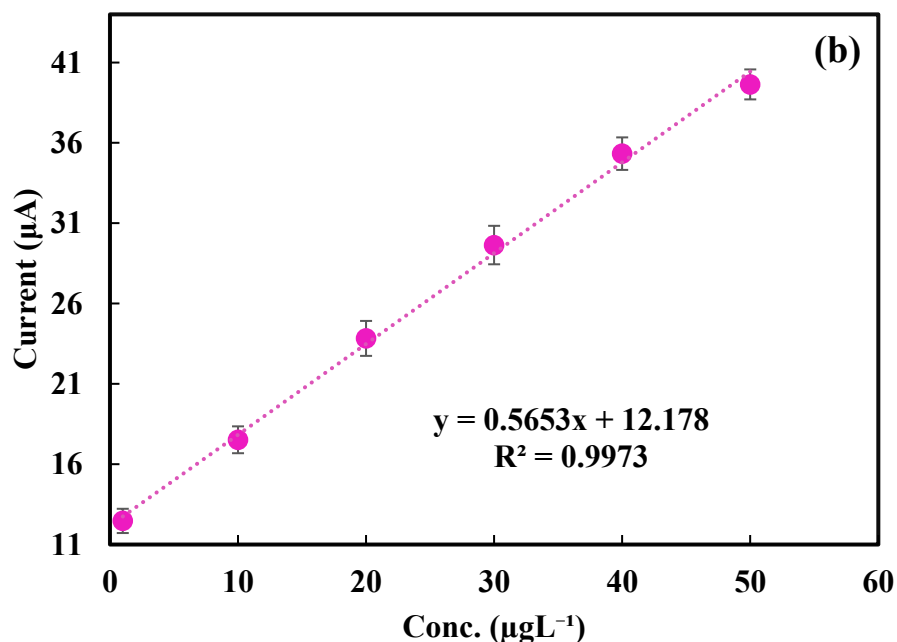


Figure 3.18. (a) The differential pulse anodic stripping voltammograms of Hg^{2+} and varied Hg^{2+} concentrations using $\text{ZnO}(\text{NP})@\text{GrO}$ (AsBS: 0.1 mol L^{-1} ; pH: 5.0); (b) Calibration plot of Hg^{2+} concentration versus anodic peak current.

3.2.7. Concentration dependence studies and calibration plots for Pb^{2+}

The electrochemical detection of Pb^{2+} ions was carried out under optimized DPASV conditions using the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE. Figure 3.19 (a) displays the stripping voltammograms of Pb^{2+} recorded at various concentrations, which clearly shows that as the Pb^{2+} concentration increased from 1.0 to $50.0 \text{ } \mu\text{g L}^{-1}$, the corresponding oxidative peak current is increased from $7.29 \text{ } \mu\text{A}$ to $18.64 \text{ } \mu\text{A}$ at an applied potential of -0.56 V . This showed the high sensitivity of the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE towards Pb^{2+} ion accumulation and oxidation processes. A calibration plot was then drawn between the Pb^{2+} concentrations and the corresponding oxidative peak current values. The calibration curve demonstrated a strong linear relationship over the tested concentration range, represented by the regression equation: $y \text{ (}\mu\text{A)} = 0.2356x \text{ (}\mu\text{g L}^{-1}\text{)} + 7.911$ with a correlation coefficient (R^2) of 0.998 as depicted in Figure 3.19 (b). In addition, the calculated LOD and LOQ are $0.03 \text{ } \mu\text{g L}^{-1}$ and $0.12 \text{ } \mu\text{g L}^{-1}$. Notably,

the LOD value obtained in this work is significantly lower than the $10.0 \mu\text{g L}^{-1}$ maximum permissible limit for Pb^{2+} in drinking water set by the World Health Organization (WHO) (Chowdhury et al., 2022), underscoring the practical applicability of the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE for trace-level Pb^{2+} monitoring in environmental water samples. In another study, Pb^{2+} in drinking water was detected via a screen-printed electrode enhanced with β -cyclodextrin-functionalized multiwalled carbon nanotubes (MWCNTs), which showed a low detection limit of $0.9 \mu\text{g L}^{-1}$ (Alam et al., 2019).

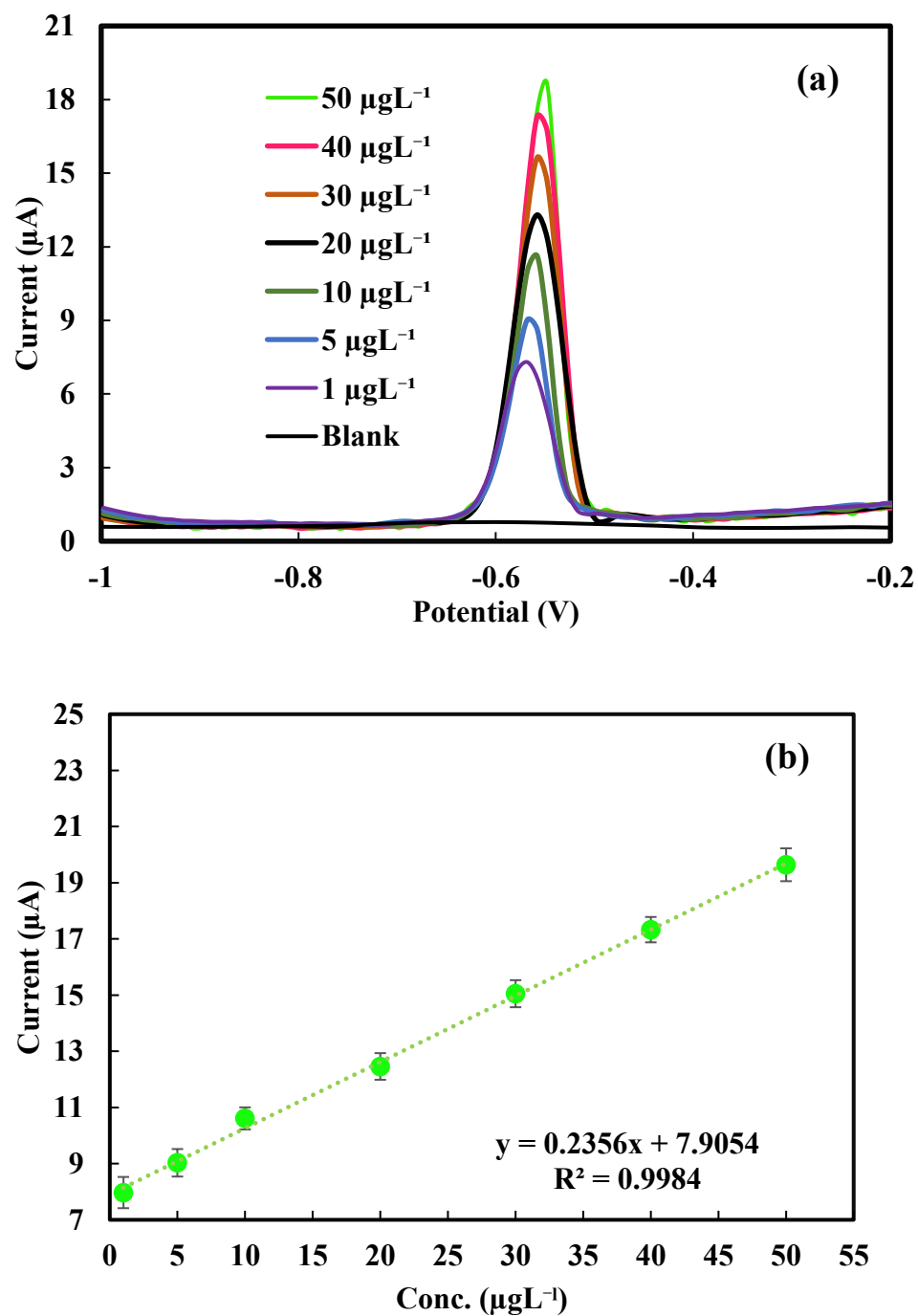


Figure 3.19. (a) The differential pulse anodic stripping voltammograms of Pb^{2+} at varied concentrations of Pb^{2+} using $ZnO(NP)@GrO$ (AsBS: 0.1 molL⁻¹; pH: 5.0); (b)

Calibration line obtained for the oxidative peak current of Pb^{2+} as a function of Pb^{2+} concentration.

3.2.8. Concentration dependence studies and calibration plots for Zn^{2+}

The electrochemical detection of Zn^{2+} was performed using $\text{ZnO}(\text{NP})@\text{GrO}$ GCE under the optimized DPASV parameters within a concentration range of 1.0 to 30.0 μgL^{-1} in 0.1 molL^{-1} AcBS (pH 5.0). Figure 3.20 (a) displays the voltammograms of Zn^{2+} , which shows that the oxidation current increased with an increase in Zn^{2+} concentrations. Further, the calibration line is drawn between the Zn^{2+} concentration and the corresponding oxidative peak current, as shown in Figure 3.20 (b). Relatively, a good linear relationship is obtained, having the linear equation of $y (\mu\text{A}) = 0.4185 x (\mu\text{gL}^{-1}) + 9.5976$ (R^2 of 0.999). Using these linear regression data, the LOD and LOQ are calculated as 0.021 μgL^{-1} and 0.072 μgL^{-1} , respectively. The results from the single detection of Zn^{2+} ions demonstrate that the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE offers a highly accurate low-level detection of Zn^{2+} . Similarly, earlier studies have reported enhanced electrochemical activity towards target heavy metal ions using electrochemically reduced graphene oxide (ERGO), where the high surface area and abundant defect sites of ERGO facilitated improved electron transfer and adsorption of analytes (Kudr et al., 2016). In particular, ERGO-based electrodes achieved sensitive detection of Zn^{2+} with a detection limit as low as 5 ngmL^{-1} .

Further, Table 3.5 compares the LOD for Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} using the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE with other advanced materials. The results indicate that $\text{ZnO}(\text{NP})@\text{GrO}$ GCE exhibits a relatively lower detection limit for detecting these heavy metal ions in an aqueous medium.

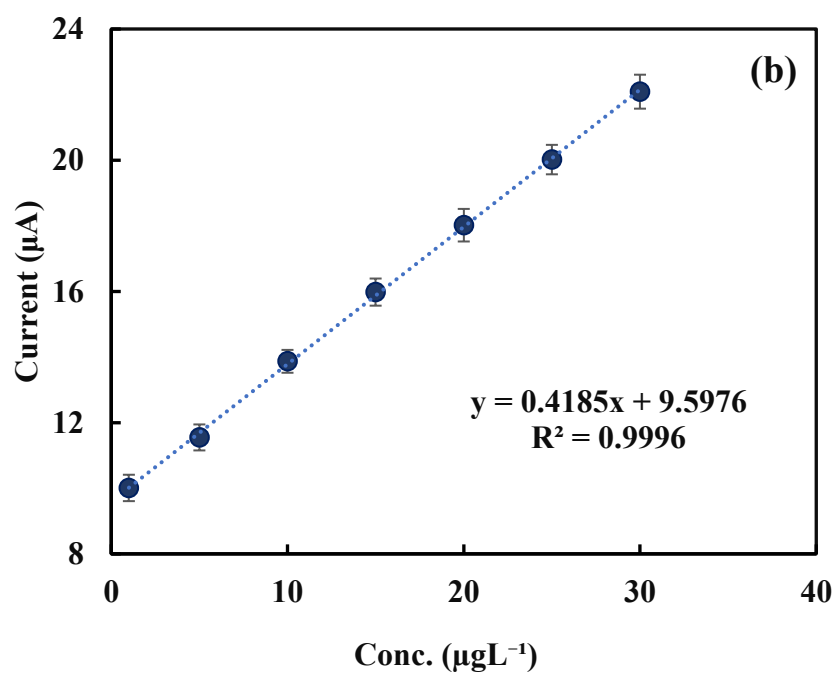
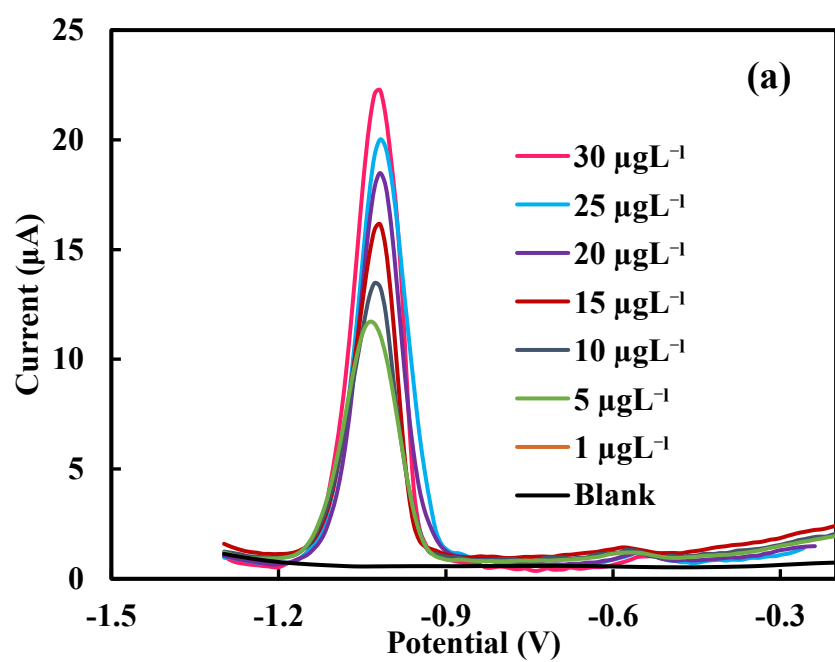


Figure 3.20. (a)The differential pulse anodic stripping voltammograms of Zn^{2+} at varied concentrations of Zn^{2+} using $\text{ZnO}(\text{NP})@\text{GrO}$ (AsBS: 0.1 molL^{-1} ; pH: 5.0); (b) Calibration plot of anodic peak current versus as a function of Zn^{2+} concentration.

Table 3.5 Comparison of the $\text{ZnO}(\text{NP})@\text{GrO}$ material with other materials for electrochemical detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} .

Material	Heavy metals	Concentration range (μgL^{-1})	LOD (μgL^{-1})	References
Bi@ZIF-8/CMWCNTs	Pb^{2+} Cd^{2+}	2–50	0.76 0.87	(S. Hu et al., 2024)
ZIF-67/rGO	Pb^{2+} Cd^{2+}	5-100	5 2.93	(Garg et al., 2023b)
MPCE/Biochar	Zn^{2+}	5-300	1.72	(Oliveira et al., 2015)
3-D printed carbon electrode	Zn^{2+}	12-450	8.60	(Honeychurch et al., 2018)
Gold nanoparticles	Hg^{2+}	1-100	200	(Ratner & Mandler, 2015b)
ZnO quantum dots	Hg^{2+}	5-50000	5	(Bhanjana et al., 2015)
ErGO	Pb^{2+} Cd^{2+}	10-100000	2.52 1.02	(Vasanthi Sridharan & Mandal, 2022)
rGO/Bi	Zn^{2+} Cd^{2+} Pb^{2+}	20-1000	17 2.81 0.55	(Sahoo et al., 2013)
Hg/CMWCNTs@ZIF-8	Zn^{2+}	5-100	5.23	(Qin et al., 2023)
CNTs	Hg^{2+}	2-200	2	(Kim et al., 2009)
$\text{ZnO}(\text{NP})@\text{GrO}$	Cd^{2+} Hg^{2+} Pb^{2+} Zn^{2+}	1-50 1-50 1-50 1-30	0.02 0.03 0.01 0.02	This work

Bi@ZIF-8/CMWCNTs -bismuth complex and carboxylated multi-walled carbon nanotubes, ZIF-67/rGO -Zeolite Imidazole Framework and Reduced Graphene Oxide, MPCE/Biochar- modified carbon paste electrode biochar, ZnO-Zinc oxide, ErGO- EDTA reduced graphene oxide, rGO/Bi- reduced graphene oxide/Bi nanocomposites,

Hg/CMWCNTs@ZIF-8- functionalized MOF composite—a carboxylated multi-walled carbon nanotube-zeolitic imidazolate framework material (CMWCNTs@ZIF-8) composite with mercury film, CNTs- carbon nanotubes.

3.2.9. Concentration studies and calibration for simultaneous detection

The simultaneous detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} is carried out by varying the concentration of the mixed analytes from 1.0 to 40.0 $\mu\text{g L}^{-1}$ under the optimized conditions. The voltammetric response for simultaneously detecting these metal ions is shown in Figure 3.21 (a), where distinct oxidized peak currents appear at potentials of -0.78 V, 0.24 V, -0.57 V, and -1.14 V for Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} , respectively. These results align with the peaks observed in the individual detection system. However, the concentration studies display straight lines with varying analyte concentrations, and the straight line equation for the Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} is represented as: $y (\mu\text{A}) = 0.3474 x (\mu\text{g L}^{-1}) + 10.417$ (R^2 of 0.997), $y (\mu\text{A}) = 0.3039 x (\mu\text{g L}^{-1}) + 9.4908$ (R^2 of 0.993), $y (\mu\text{A}) = 0.6766 x (\mu\text{g L}^{-1}) + 18.979$ (R^2 of 0.995), and $y (\mu\text{A}) = 0.4501 x (\mu\text{g L}^{-1}) + 18.551$ (R^2 of 0.971), respectively [Cf Figure 3.21 (b)]. Further, the LOD values of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} employing $\text{ZnO}(\text{NP})@\text{GrO}$ GCE are 0.026, 0.03, 0.010, and 0.020 $\mu\text{g L}^{-1}$, respectively. A recently reported electrochemical sensor employing a platinum electrode modified with poly(3,4-ethylenedioxythiophene) and *N*α, *N*α-bis(carboxymethyl)-l-lysine hydrate (PEDOT/NTA) demonstrated effective detection of Hg^{2+} , Pb^{2+} , and Zn^{2+} ions using square wave voltammetry (SWV) (Alshawhi et al., 2022). The sensor exhibited linear responses for these ions over the concentration range of 5–100 $\mu\text{g L}^{-1}$, with the detection limits of 1.73 $\mu\text{g L}^{-1}$ for Hg^{2+} , 2.33 $\mu\text{g L}^{-1}$ for Pb^{2+} , and 1.99 $\mu\text{g L}^{-1}$ for Zn^{2+} , respectively. However, these values are comparatively higher than the limits of detection obtained in the present work, where the $\text{ZnO}(\text{NP})@\text{GrO}$ modified electrode demonstrated LODs in the range of 0.010-0.030 $\mu\text{g L}^{-1}$. The device demonstrates higher sensitivity and efficiency in detecting these metal ions simultaneously at concentrations far below the maximum permissible levels. The excellent analytical performance of the $\text{ZnO}(\text{NP})@\text{GrO}$ glassy carbon electrode (GCE) is attributed to the factors viz., i) zinc oxide (ZnO) is a versatile semiconductor having high excitation binding energy and wide band gap making it an excellent material for electrochemical

sensing applications, and ii) the high electron mobility of ZnO, coupled with the conductive nature and porous structure of GrO, ensures efficient electron transfer during electrochemical reactions (Beitollahi et al., 2020; Junaid et al., 2023).

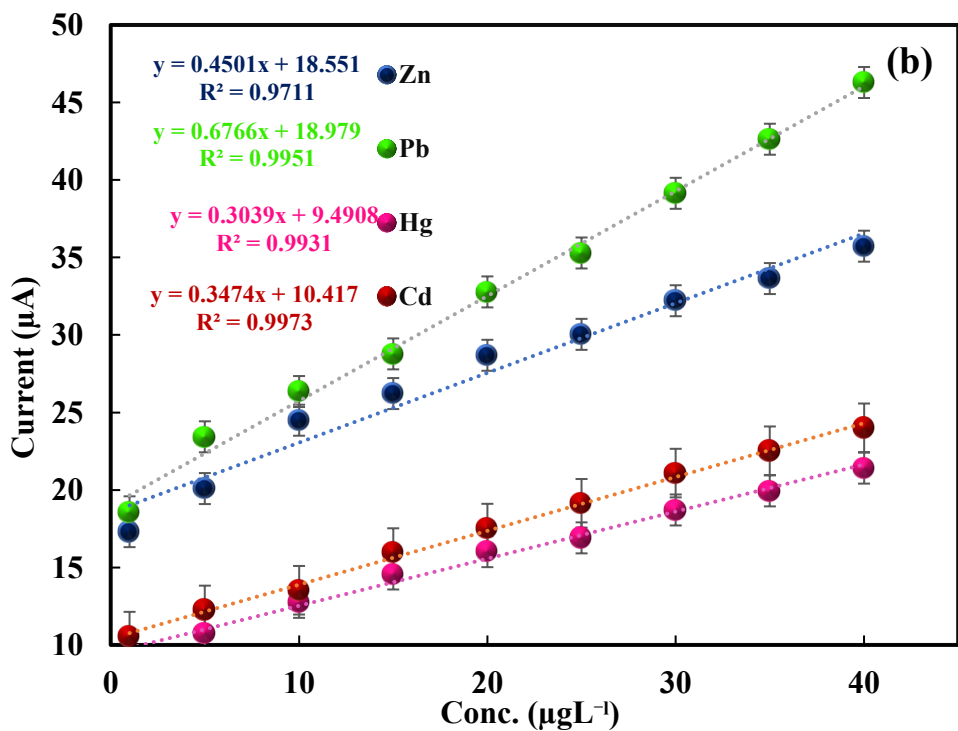
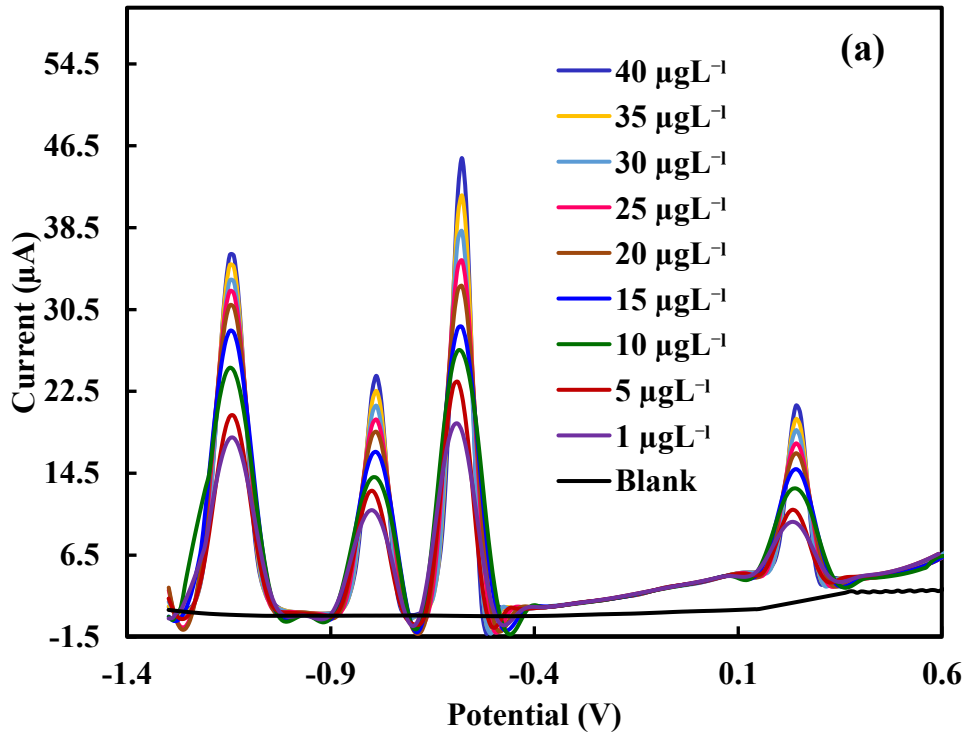


Figure 3.21. (a) Differential pulse anodic stripping voltammograms for simultaneous detection of Cd^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+} at varied concentrations of these ions (1.0 to 40.0 μgL^{-1}); (b) Calibration plots of Cd^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+} .

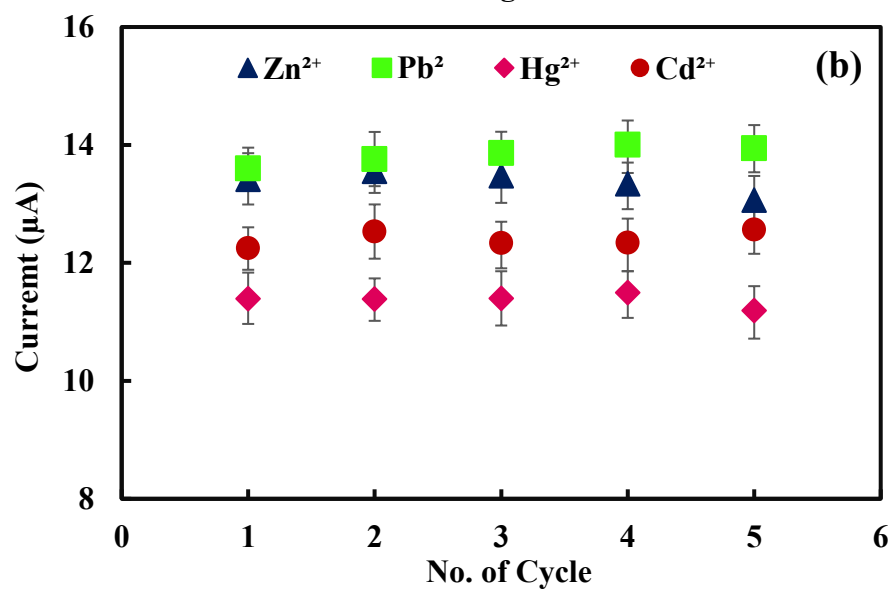
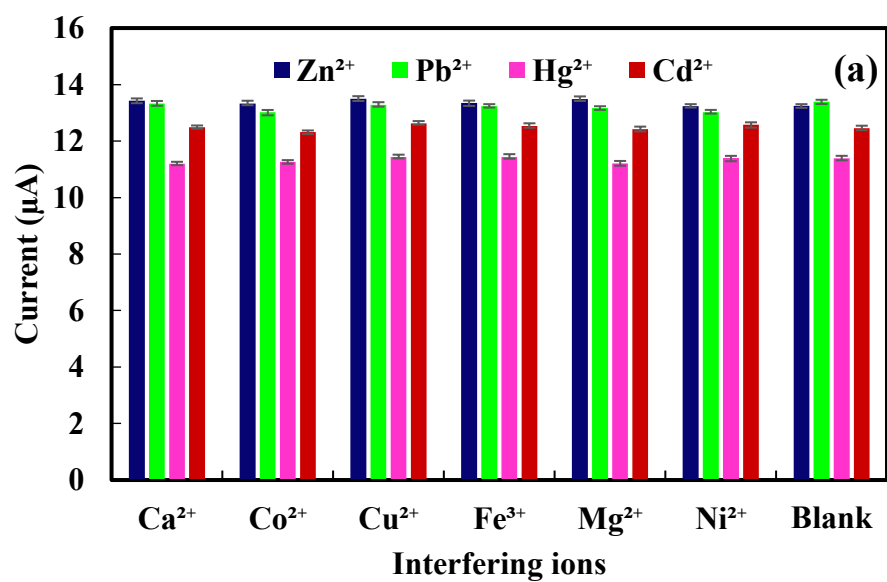
3.2.10. Study of interfering ions

The selectivity of the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE for simultaneous detection of Cd^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+} is obtained in the presence of several potential interfering ions *viz.*, Ca^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Mg^{2+} , and Ni^{2+} at concentrations ten times higher than the concentrations of the analytes (i.e., 50.0 μgL^{-1} for the interfering ions compared to 5.0 μgL^{-1} for the analytes). The study simulates conditions for interference of common ions, and the experimental data are presented in Figure 3.21 (a). Figure 3.22(a) shows that these interfering ions are not significantly influencing the anodic peak current of these cations, which indicates that the $\text{ZnO}(\text{NP})@\text{GrO}$ modified electrode exhibits excellent selectivity, as the coexistence of these ions does not notably impede the detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} simultaneously. The higher selectivity of the $\text{ZnO}(\text{NP})@\text{GrO}$ sensor towards these heavy metals is attributed due to the synergistic interaction between zinc oxide nanoparticles ($\text{ZnO}(\text{NP})$) and graphene oxide (GrO), which enhances the preferential adsorption and complexation of target heavy metal ions (Cd^{2+} , Hg^{2+} , Pb^{2+} , Zn^{2+}) at the electrode surface, whereas the common interferents such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} possesses lower affinity at the surface (Peinelt & Apell, 2002). Alkali and alkaline earth metal ions serve as hard Lewis acids and exhibit little interaction with oxygen-containing sites, whereas the target heavy metal ions demonstrate increased coordination binding owing to their higher charge density and softer acid properties (Zeng et al., 2024). Transition metal ions, including Cu^{2+} and Fe^{3+} , are less competitive, either due to reduced diffusion to the surface. Therefore, the electrochemical sensor is a reliable and robust platform for simultaneously detecting these metal ions in complex samples, having minimal interference from common environmental ions. Previously it was reported that the $\text{ZnO}@\text{graphene}$ -modified electrode showed less influence of coexisting ions (1000-fold excess of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Cl^- , and SO_4^{2-} , a 300-fold excess of Co^{2+} , Fe^{3+} , and NO_3^- , and a 200-fold excess of Mn^{2+}) in the detection of Cd^{2+} and Pb^{2+} due to the strong surface affinity of

the nanocomposite for Cd^{2+} and Pb^{2+} and its efficient electron transfer kinetics (Yukird et al., 2018).

3.2.11. Stability and repeatability of simultaneous detection

The fundamental characteristic of a sensor is its stability, which guarantees consistent and reliable data during repeated detection processes and indicates the longevity of the manufactured electrode. This study assessed the performance of the $\text{ZnO}(\text{NP})@\text{GrO}$ modified GCE through prolonged and repeated measurements for the detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} ions at a concentration of $5.0 \mu\text{gL}^{-1}$. The repeatability test was conducted five times at varying time intervals, with the electrode meticulously cleaned and air-dried between each trial. Table 3.6 demonstrates that the percentage relative standard deviation (%RSD) for all four metal ions was below 2%, hence affirming the exceptional repeatability of the electrode. Moreover, Figure 3.22(b) demonstrates that the anodic peak current of each analyte remained rather stable throughout five successive cycles, signifying no surface fouling and substantial operational stability. Moreover, the electrode's long-term usability was assessed over 48 hours at different time intervals. After each measurement, the electrode was meticulously cleaned and dried at room temperature before reuse. Figure 3.22(c) illustrates that the anodic peak current responses were approximately 98% for Cd^{2+} and Hg^{2+} , 97% for Pb^{2+} , and 99.9% for Zn^{2+} in comparison to the baseline values, even after 48 hours of operation. The results indicate that the $\text{ZnO}(\text{NP})@\text{GrO}$ modified electrode displays exceptional durability and structural integrity, preserving its electrochemical activity after several uses. Prior recent research indicated that a new origami microfluidic paper-based electrochemical device ($\text{E}\mu\text{PAD}$) engineered for the concurrent detection of Cd^{2+} , Pb^{2+} , and Hg^{2+} exhibited remarkable reproducibility and stability, with RSD values of 3.76%, 3.31%, and 2.30%, with current retention surpassing 94% after 14 days of storage (Wei et al., 2025). The $\text{ZnO}(\text{NP})@\text{GrO}$ GCE in the current study demonstrated comparable reproducibility and retained over 97% of its initial current response after 48 hrs, underscoring its dependable and stable performance for the simultaneous detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} in aqueous media.



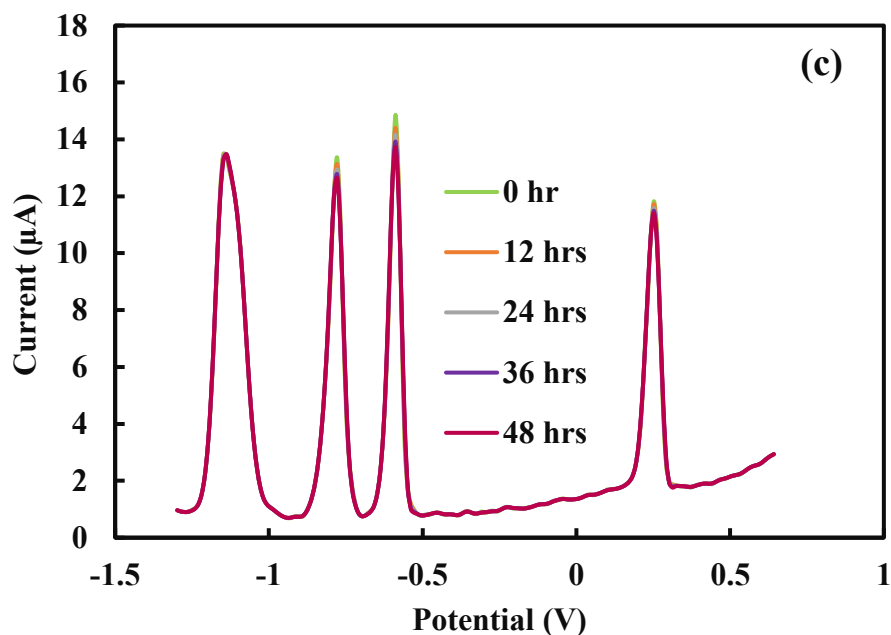


Figure 3.22. (a) Effect of each interfering ion on simultaneous detection of $5.0 \mu\text{gL}^{-1}$ of Cd^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+} , (b) The anodic peak current change of these ions using $\text{ZnO}(\text{NP})@\text{GrO}$ GCE for 5 repetitive measurements, (c) Simultaneous detection of Cd^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+} at different time intervals.

Table 3.6 Stability tests for $\text{ZnO}(\text{NP})@\text{GrO}$ electrode in the simultaneous detection of Cd^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+} .

Time	Repetition (times)	RSD (%)			
		Cd^{2+}	Hg^{2+}	Pb^{2+}	Zn^{2+}
0 hr	5	0.84	0.96	0.722	1.41
12 hrs	5	0.93	1.06	0.78	1.48
24 hrs	5	0.92	1.23	0.94	0.58
36 hrs	5	0.71	1.15	1.04	1.17
48 hrs	5	0.73	0.99	1.14	1.28
60 hrs	5	0.94	1.11	1.29	1.08
1 week	5	1.27	0.84	1.34	1.32

3.2.12. Real water studies

The water sample is collected from Ebenezer Hospital wastewater near Tuikual Lui, Aizawl (India). The water sample is filtered with filter paper (11 μm) and subjected to various physicochemical parametric studies using a pH meter, multiparameter photometer, TOC analyzer, and AAS (Atomic Absorption Spectrometer). Table 3.7 includes various parametric screening of a real water sample, indicating high inorganic carbon levels, possibly due to carbonates or bicarbonates. The samples also showed significant amounts of organic compounds, as evidenced by NPOC values of 88.67 ppm. In contrast, the sulphate, phosphate, fluoride, and aluminium concentrations are relatively low, with trace amounts of Ni, Pb, Mn, and Fe. The water sample is spiked with known concentrations (5.0 to 30.0 μgL^{-1}) of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} using 0.1 molL^{-1} AcBS (pH 5.0). The other optimal conditions are maintained as deposition potential = -1.4 V, deposition time = 120 s, pulse amplitude = 50 mV, frequency = 10 Hz, pulse increment = 10 mV)

Figure 3.23(a) presents the DPASV results obtained for real water using the $\text{ZnO}(\text{NP})@\text{GrO}$ electrode, where four distinct oxidation peaks are observed at potentials of -0.78 V, 0.24 V, -0.57 V, and -1.14 V, referring to the Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} . Further, increasing the concentration of these metal ions caused a gradual increase in the oxidation peak current values. Moreover, a reasonably linear relationship is obtained between the concentration of these metal ions and the oxidation peak current values as depicted in Figure 3.23 (b). Table 3.8 compares the actual and spiked amounts of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} , along with their recovery from the spiked value. The results demonstrate that the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE electrode achieves a high recovery rate of 91.6% to 101.2% for Cd^{2+} , 89.9% to 99.92% for Hg^{2+} , 99.42% to 104.6% for Pb^{2+} , and 90.9% to 106.4% for Zn^{2+} in real water samples. The results align with previous studies, wherein a graphene–polyaniline (G/PANI)-based electrochemical sensor was utilized for the concurrent detection of Zn^{2+} , Cd^{2+} , and Pb^{2+} in human serum samples at pH 4.5 with the recovery rates ranging from 93.8% to 109.7% (RSD 9.0%) (Ruecha et al., 2015). The analogous recovery performance of the $\text{ZnO}(\text{NP})@\text{GrO}$ sensor underscores its analytical efficacy and appropriateness for concurrent detection of several metal ions at trace concentrations. These findings infer

the potential use of ZnO(NP)@GrO in device development to simultaneously detect Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} at trace levels.

Table 3.7. Various physicochemical parametric analyses of hospital wastewater

Parameter	Hospital wastewater
pH	7.71
Oxidation Reduction Potential (Mv)	149.3
Conductivity EC ($\mu\text{S}/\text{cm}$)	956
Resistivity ($\text{M}\Omega\text{cm}$)	0.001
Total Dissolved Solid (ppm)	478
Salinity (PSU)	0.52
NO_3^-	85.9 mgL^{-1}
SO_4^{2-}	31.0 mgL^{-1}
PO_4^{3-}	2.12 mgL^{-1}
F^-	0.28 mgL^{-1}
Al^{3+}	0.14 mgL^{-1}
Ni^{2+}	0.172 mgL^{-1}
Mg^{2+}	17.0 mgL^{-1}
Ca^{2+}	130.0 mgL^{-1}
Pb	0.034 mgL^{-1}
Mn	0.744 mgL^{-1}
Fe	0.845 mgL^{-1}
IC	42.5 mgL^{-1}
NPOC	88.67 mgL^{-1}

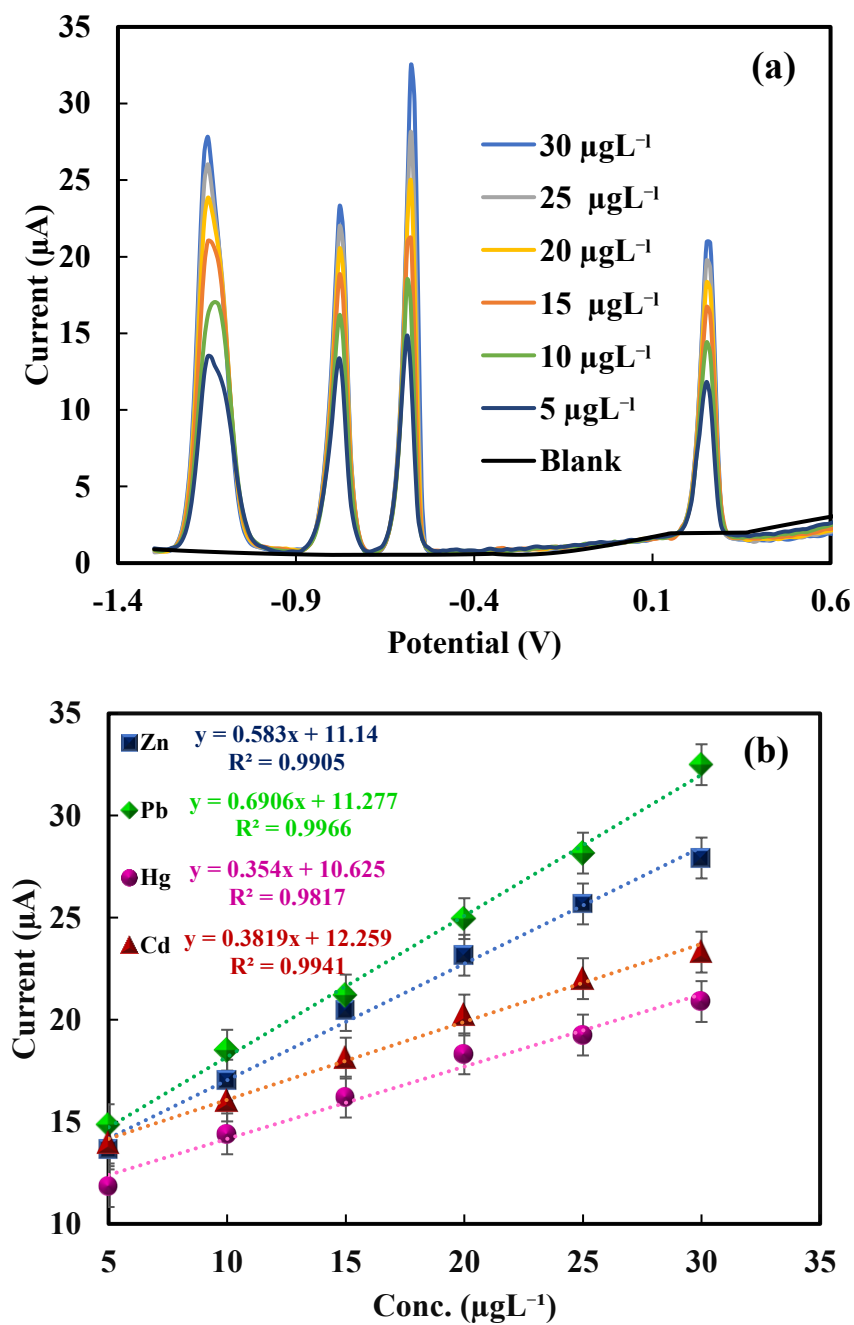


Figure 3.23. (a) Differential pulse anodic stripping voltammograms for simultaneous detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} at varied concentrations of these ions (5.0 – $30 \mu\text{g/L}^{-1}$) in hospital wastewater samples, (b) Calibration plots of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} .

Table 3.8. Recovery percentage of Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ in hospital wastewater.

Spiked amount of analyte (μg L ⁻¹)	Found (μg L ⁻¹) ± 3σ				Recovery (%)			
	Cd ²⁺	Hg ²⁺	Pb ²⁺	Zn ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Zn ²⁺
5.0	4.58± 0.42	4.47± 0.53	5.58± 0.58	4.54± 0.46	91.6	89.5	103.7	90.9
10.0	9.84±0.16	9.87±0.13	10.46±0.4	10.12±0.1	98.4	98.7	104.6	101.2
15.0	14.98±0.0	14.92±0.0	15.25±0.2	15.96±0.9	99.92	99.9	101.6	106.4
20.0	20.25±0.2	19.42±0.5	19.88±0.1	20.61±0.6	101.2	97.1	99.42	103.0
25.0	25.01±0.0	24.3±0.7	25.22±0.2	24.9±0.1	100.0	97.4	100.9	99.69
30.0	28.93±1.0	28.9±1.1	30.71±0.7	28.78±1.2	96.45	96.6	102.3	95.94

3.2.13. Conclusion

The detection of Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ ions was investigated using the ZnO(NP)@GrO GCE through the cyclic voltammetry and differential pulse anodic stripping voltammetry techniques. Comparative studies revealed that the ZnO(NP)@GrO GCE exhibited significantly enhanced electrochemical responses compared to the bare GCE and even the pristine GrO modified GCE. Experimental parameters, including solution pH, preconcentration time, and deposition potential, were systematically optimized to enhance the sensitivity and detection efficiency of the heavy metal ions. The optimal conditions were determined to be pH 5.0, a preconcentration time of 210 s, and a deposition potential of −1.2 V (Provide values). The Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ were detected using the ZnO(NP)@GrO-GCE both individually and simultaneously at a wide range of analyte concentrations varied from 1.0 μg L⁻¹ to 50.0 μg L⁻¹. Calibration curves were obtained for individual detection of Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ and the linear equations obtained were: Cd²⁺ → y (μA) = 0.1923x (μg L⁻¹) + 8.3614 (R² = 0.996), Hg²⁺ → y (μA) = 0.3039x (μg L⁻¹) + 9.4908 (R² = 0.993), Pb²⁺ → y (μA) = 0.6766x (μg L⁻¹) + 18.979 (R² = 0.995), and Zn²⁺ → y (μA) = 0.4501x (μg L⁻¹) + 18.551 (R² = 0.971). Additionally, the material was able to

detect simultaneously with detection limits of 0.026, 0.030, 0.010, and 0.020 $\mu\text{g L}^{-1}$ for Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} , respectively. Further, the limits of quantification were 0.08, 0.1, 0.04, and 0.06 $\mu\text{g L}^{-1}$ for Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} , respectively. The detection limits obtained under individual ion detection showed no significant deviation from the simultaneous detection of these ions, demonstrating the reliability and wider applicability of the detection method utilizing the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE. Furthermore, real matrix analysis of hospital effluent water taken from Ebenezer hospital, Aizawl spiked with Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} , yielding high recovery rates in the range of 91.6–101.2% for Cd^{2+} , 89.9–99.92% for Hg^{2+} , 99.42–104.6% for Pb^{2+} , and 90.9–106.4% for Zn^{2+} , thereby reaffirming the accuracy and efficiency of the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE in trace detection of these ions. The presence of common interfering ions such as Ca^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Mg^{2+} , and Ni^{2+} did not significantly affect the detection of these metal ions. In addition, the $\text{ZnO}(\text{NP})@\text{GrO}$ thin-film electrode exhibited excellent reproducibility and long-term stability after 5 repeated applications with RSD (%) less than 2. Moreover, long-term stability of the fabricated electrode was observed with high detection reproducibility, i.e., 98% for Cd^{2+} and Hg^{2+} , 97% for Pb^{2+} , and 99.9% for Zn^{2+} , even after 48 hours of operation, indicating an extended operational lifetime. These findings suggest that the thin-film electrode is a promising, efficient, and robust sensing material, useful to devise the miniaturized devices for simultaneous trace detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} in an aqueous environment.

3.3. ELECTROCHEMICAL DETECTION OF IBUPROFEN

3.3.1. Electrochemical studies of ibuprofen using cyclic voltammetry

The electrochemical behaviour of ibuprofen (IBP) was carefully investigated by cyclic voltammetry (CV), with voltammograms recorded using bare GCE, GrO GCE, and $\text{CeONC}@\text{GrO}$ modified GCE. The measurements were conducted in an aqueous solution of IBP (1.0 mg L^{-1}) in 0.1 mol L^{-1} acetate buffer solution (pH 5.0) within a potential window of -0.2 V to $+0.7$ V and at a scan rate of 100 mV s^{-1} . The results are shown in Figure 3.24. The recorded voltammograms demonstrate that both the GrO and $\text{CeONC}@\text{GrO}$ glassy carbon electrodes showed distinct anodic and

cathodic peak currents, whereas the bare GCE displayed negligible anodic or cathodic peak currents. The bare GCE has a relatively low electroactive surface area and poor electron-transfer capability, which limits the adsorption of IBP molecules and hinders the redox reactions of IBP. The sharp anodic and cathodic peaks observed for the modified electrodes clearly demonstrate that the oxidation and reduction processes of IBP occur effectively at their surfaces. The anodic peak was seen at roughly +0.76 V, indicating the oxidation of IBP, whereas the cathodic peak was noted at around +0.46 V, linked to the reduction process. Moreover, the large ΔE_p value (300 mV), which is much greater than 59 mV, confirms that the reaction is electrochemically quasi-reversible (Mann & Bottomley, 2015). The GrO and CeONC@GrO modified electrodes possessed the nitrogen- and oxygen-containing functional groups present in graphene oxide (GrO) are seemingly interacting with the IBP molecule by the and possibly forming the with the $-\text{COOH}$ group of the IBP molecule by the $\pi-\pi$ interactions or even the hydrogen bonding (Mekassa et al., 2018). Moreover, the presence of ceria provides enhanced electrical conductivity, hence, synergizes with the electrical response of IBP at the CeONC@GrO electrode. Previously, it was reported that the oxidation and reduction processes of ibuprofen on multi-walled carbon nanotubes (MWCNTs) occurred at relatively low potentials, around +0.315 V (oxidation) and +0.065 V (reduction), which results from the $\pi-\pi$ interactions between the aromatic ring of IBP and the sp^2 -hybridized carbon structure of MWCNTs, thereby promoting the adsorption and electron transfer reactions (Motoc et al., 2013).

Interesting to observe that despite the alteration in redox cycles, the CeONC@GrO electrode exhibits remarkable electrocatalytic activity owing to the synergistic actions of graphene oxide and cerium oxide nanocomposite. Graphene oxide provides a substantial surface area and functional groups that enhance IBP adsorption, whereas CeO_2 , characterized by its mixed $\text{Ce}^{3+}/\text{Ce}^{4+}$ states and oxygen vacancies, facilitates charge transfer and stabilizes intermediate species. Moreover, to affirm that the detected redox peaks are attributable to IBP rather than the supporting electrolyte, control CVs were recorded in a blank AcBS (*Cf* Figure 3.23). The results showed that no redox peaks occurred in the blank scans, indicating that the electrochemical signals recorded in the test solution are due to the oxidation-reduction of IBP. Moreover, the electro-catalyzed oxidation process was significantly enhanced

at the CeONC@GrO nanocomposite surface. Therefore, the CeONC@GrO modified GCE was employed in subsequent investigations for the sensitive and efficient detection of IBP at trace levels.

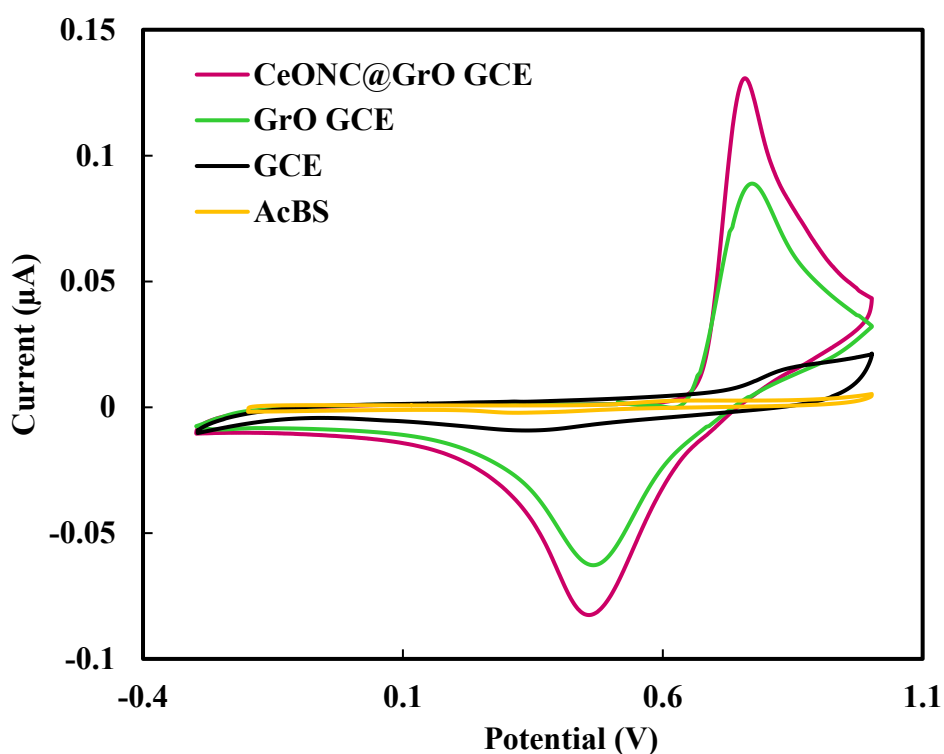
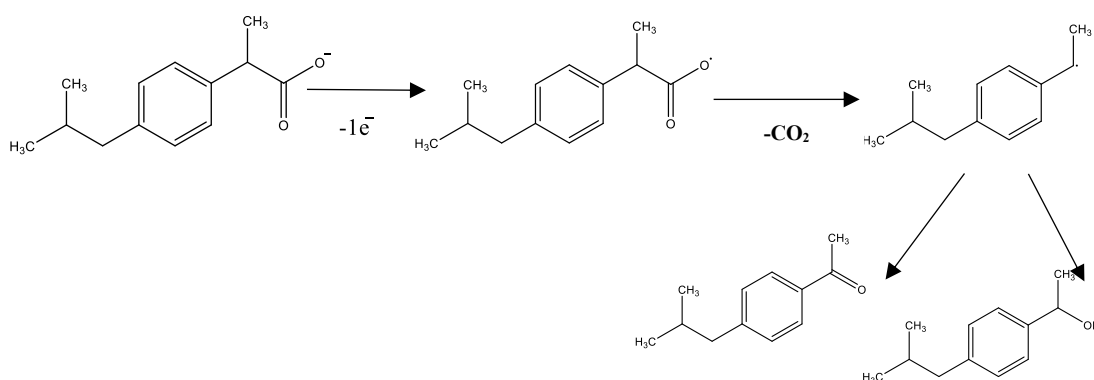


Figure 3.24. Cyclic voltammograms of IBP (1.0 mgL^{-1}) using the bare glassy carbon electrode and various fabricated glassy carbon electrodes.

3.3.2. Electroanalytical performance of modified electrodes for ibuprofen

Differential pulse anodic stripping voltammetry (DPASV) was found to be more suitable for the efficient and low-level detection of ibuprofen (IBP). This is attributed to the enhanced signal-to-background ratio in DPASV, where the charging current is significantly smaller relative to the faradaic current, resulting in a clearer and more defined response. Consequently, DPASV was selected for further electroanalytical studies for IBP. All parameter optimizations and subsequent investigations with real water samples were performed using nanocomposite CeONC@GrO GCE. The detection of IBP at these modified electrodes was carried out using the anodic stripping method, wherein the anodic peak current arising from the

electrochemical oxidation process was employed for the quantification of IBP in aqueous samples. Figure 3.25 shows the DPASV responses of IBP at the CeONC@GrO modified GCE, recorded in the absence and presence of $50.0 \mu\text{g L}^{-1}$ IBP using 0.1 mol L^{-1} acetate buffer solution. In the blank solution, no significant peaks were obtained within the applied potential window, indicating the stability of the modified electrode and minimal background interference. However, the addition of $50.0 \mu\text{g L}^{-1}$ IBP, a well-defined oxidation peak appeared at 0.74 V. This peak was due to the electrochemical oxidation of IBP. The electrochemical oxidation of IBP proceeded through one electron transfer that generates a radical intermediate, which subsequently undergoes decarboxylation to produce two primary products: 4-isobutylacetophenone and 1-(1-hydroxyethyl)-4-isobutylbenzene (Lima et al., 2021; Stoytcheva et al., 2022). The possible reaction was demonstrated as in Scheme 1. The anodic peak current that occurred during the electrochemical procedure was utilized for the quantitative analysis of IBP in aqueous samples.



Scheme 3.1. Proposed mechanism for electrochemical oxidation of ibuprofen (IBP)

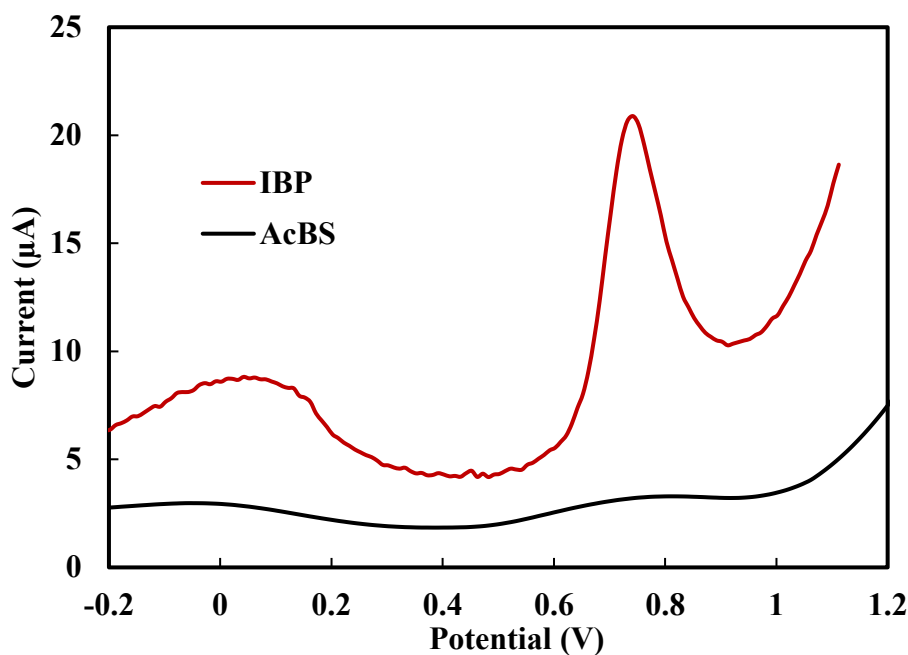


Figure 3.25. Differential pulse anodic stripping voltammogram of ibuprofen (50.0 μgL^{-1}) using CeONC@GrO GCE.

3.3.3. Optimization of pH on trace detection of IBP

The effect of pH on the oxidative peak current of IBP was investigated throughout a pH range from 3.0 to 6.0. The speciation of IBP at varied pH was investigated using its acid dissociation constant ($\text{pK}_a = 4.9$) (Zhang, 2016). The speciation studies are depicted in Figure 3.26. The IBP is predominantly present in its neutral species until $\text{pH} \sim 4.0$. However, further increase in pH caused a gradual increase in anionic species of IBP, and at pH around 6.5 it turned to its anionic species. Within pH 4.0~6.5, the IBP coexists as a mixture of both neutral and ionic species (Oh et al., 2016).

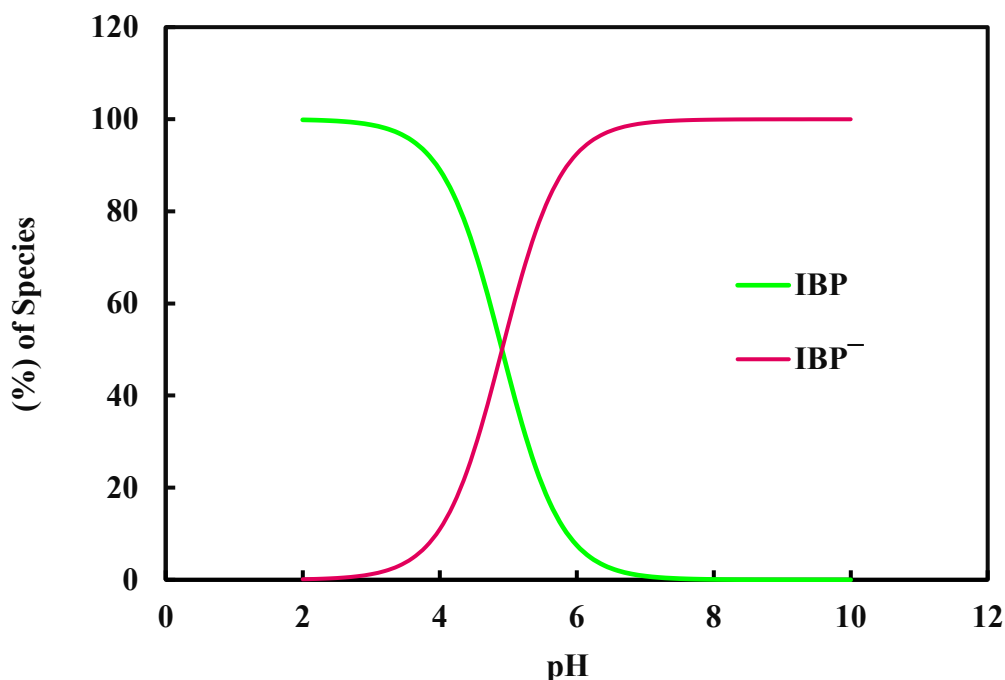
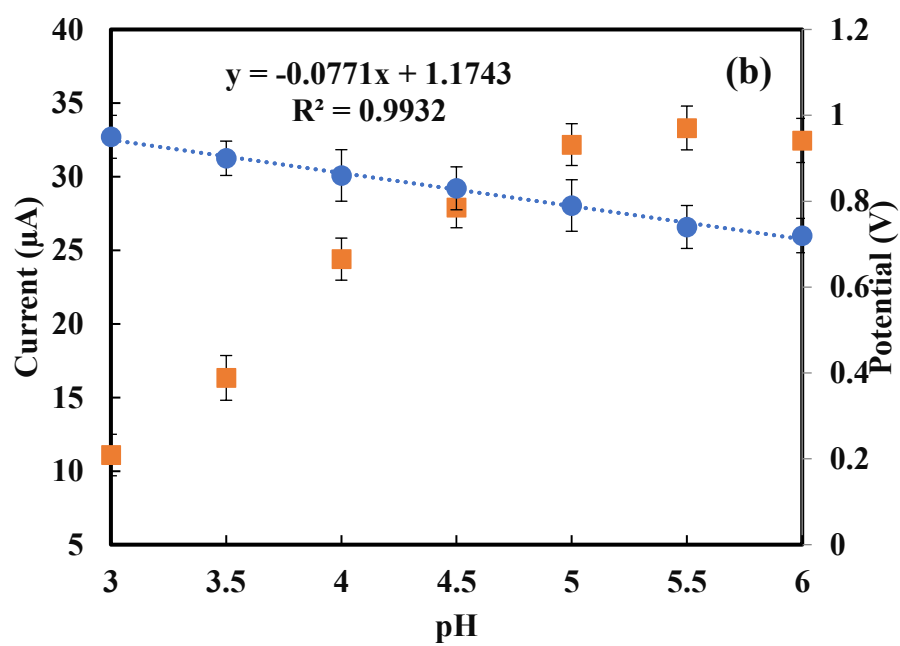
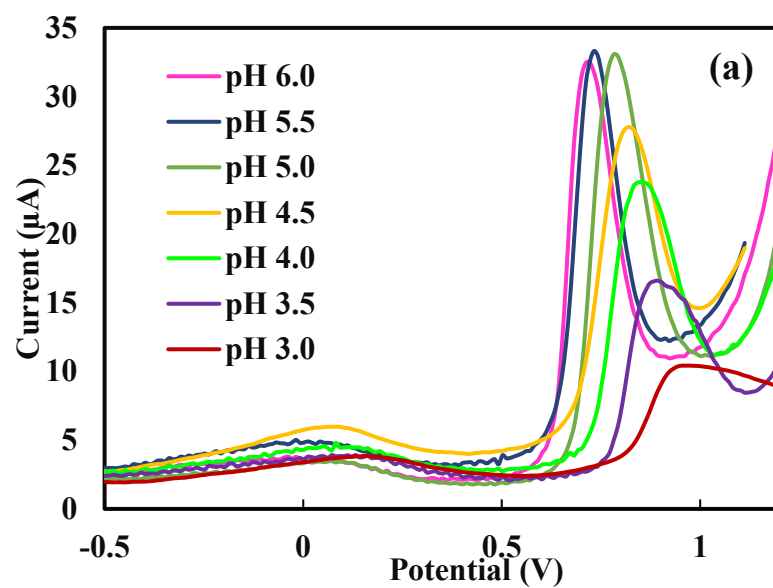


Figure 3.26. Speciation distribution of various species of IBP as a function of pH.

Figure 3.27 (a) displays the DPASV of IBP obtained at different pH levels. The findings indicate that both the peak current and peak potentials are significantly affected by the solution pH. Moreover, the influence of pH on the anodic current response of IBP was investigated over the pH range of 3.0–6.0, and the results are shown in Figure 3.27(b). These results reveal that under mildly acidic conditions (pH 5.0–6.0), the anodic peak current reached its maximum value at pH 5.5, indicating that this pH range favours the efficient electron transfer and oxidation of IBP. At this pH range (6.0 to 10.0), IBP predominantly exists as partially or fully negatively charged species, while the CeONC@GrO electrode, having a point of zero charge (pH_{PZC}) of 6.4 (*Cf* Figure 3.27(c)), possesses a slightly positive surface charge. The positive surface charge facilitates the electrostatic attraction of the negatively charged IBP species, enhancing the aggregation of IBP molecules onto the electrode surface. Enhanced sorption allows closer interaction between IBP and the electrode surface, thereby improving electron transfer reactions and resulting in relatively higher oxidation current. Further, $\text{pH} < 5.0$, either IBP remains mostly neutral at lower pH values and the electrode surface possesses predominantly the positive charges,

therefore, reducing the electrostatic attraction between the solid surface and the IBP molecules, leading to the limited electron transfer reactions and relatively lesser anodic current response

Additionally, Figure 3.27 (b) illustrates the variation of anodic peak potential (E_{pa}) of IBP with pH in the region of 3.0–6.0 (AcBS buffer). A clear trend is observed where the E_{pa} values gradually shift toward more negative potentials as the solution pH is increased. These results indicate that the electrochemical oxidation of IBP at the CeONC@GrO GCE surface is strongly coupled with proton transfer reactions. Additionally, the oxidation potential exhibited a linear relationship described by equations: $E_{pa} \text{ (IBP) (V)} = -0.0771 \text{ pH} + 1.1743$ ($R^2 = 0.993$). The robust linear correlation confirmed the direct influence of proton concentration in the redox mechanism of IBP. The slope of -0.0771 V/pH is close to the predicted Nernstian value of -59 mV/pH anticipated for a 1:1 proton-to-electron transfer ratio at 25°C . The somewhat steeper slope implies that the oxidation of IBP may include a more intricate proton-electron coupling, potentially signifying a non-ideal process or supplementary surface interactions with the CeONC@GrO nanocomposite. Similar behaviour was shown in the electro-oxidation of ibuprofen using electropolymerization of L-aspartic acid (L-Asp) modified GCE (P(L-Asp/GCE)), demonstrating a linear relationship between the oxidation peak potential and solution pH, represented by the regression equation $E \text{ (V)} = -0.062 \text{ pH} + 1.5$, $R^2 = 0.9932$ (Mekassa et al., 2018). They further reported that the slope of -0.062 V/pH closely aligned with the predicted Nernstian value (-59 mV/pH), suggesting that the electrode reaction occurs via a proton-coupled electron transfer mechanism involving an equivalent amount of protons and electrons (Mekassa et al., 2018). This result was consistent with the proposed mechanism, where the electrochemical oxidation of IBP involves a single electron transfer through radical formation.



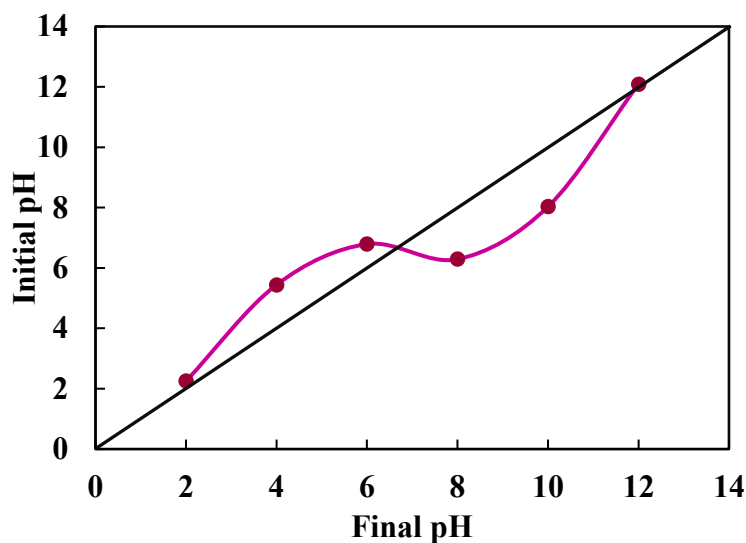


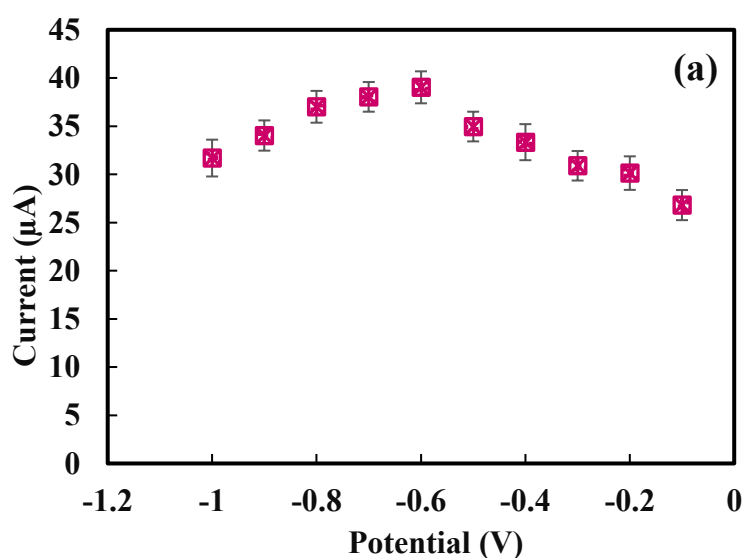
Figure 3.27. (a) Differential pulse anodic stripping voltammogram of $30.0 \mu\text{g L}^{-1}$ IBP at different pH values using the CeONC@GrO GCE; (b) Impacts on oxidation current and E_{pa} vs pH; (c) pH_{PZC} determination of CeONC@GrO.

3.3.4. Optimization of accumulation potential and time

The influence of accumulation potential and accumulation time on the anodic peak current response of IBP at the CeONC@GrO modified glassy carbon electrode (GCE) was systematically examined using a standard solution of $50.0 \mu\text{g L}^{-1}$ IBP prepared in 0.1 M acetate buffer solution (pH 5.5). The electrochemical behaviour was investigated within an excitation potential window ranging from -1.0 V to -0.1 V . The results indicated that the peak current values gradually increased with increasingly negative accumulation potentials, which is due to the enhanced driving force for IBP reduction and improved adsorption of the analyte onto the nanocomposite electrode surface. This linear increase was continued until a maximum current response occurred at -0.6 V . However, further negative increase in potential, a noticeable decrease in current intensity was obtained for both the bare and nanostructured electrodes (Figure 3.28(a)) The decline at more negative potentials is most likely due to competing hydrogen evolution reactions, which interfere with the preconcentration processes and partially block the active sites of the electrode, thereby reducing the effective accumulation of IBP. Based on these observations, -0.6 V was selected as an optimum

deposition potential, since it provides sufficient analyte accumulation and minimization of background interference.

In addition to accumulation potential, the influence of accumulation time was also assessed, as longer accumulation periods generally enhance the number of analyte molecules adsorbed at the electrode surface, thereby amplifying the stripping peak current. The effect of accumulation time on the anodic peak current response of IBP was also studied in the accumulation time range 30–210 s, while maintaining the optimized accumulation potential of -0.6 V and at pH 5.5. The stripping peak current was increased gradually with an increase in accumulation times, reflecting enhanced accumulation of IBP molecules onto the CeONC@GrO modified electrode surface. A nearly linear rise in current was observed up to 180 s, indicating that within this period, additional accumulation sites remained available and the preconcentration process was governed primarily by adsorption kinetics (Figure 3.28 (b)). Beyond 180 s, however, the peak current either slightly decreased or reached a constant value, suggesting that the electrode surface had reached its saturation. At this stage, most of the available adsorption sites on the nanostructured electrode were occupied, and further increase of deposition time did not significantly affect the oxidative peak current. These findings clearly indicate that 180 s was an optimum preconcentration of IBP onto the CeONC@GrO GCE and was selected as the optimum accumulation time for subsequent electroanalytical experiments.



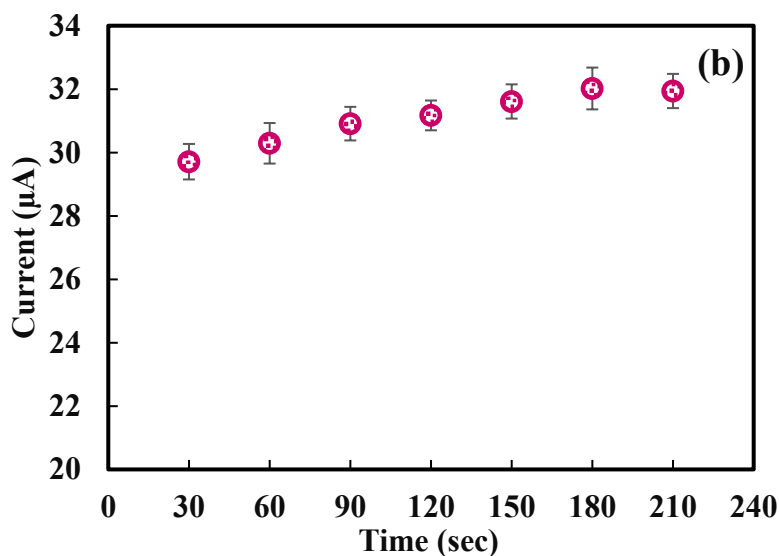
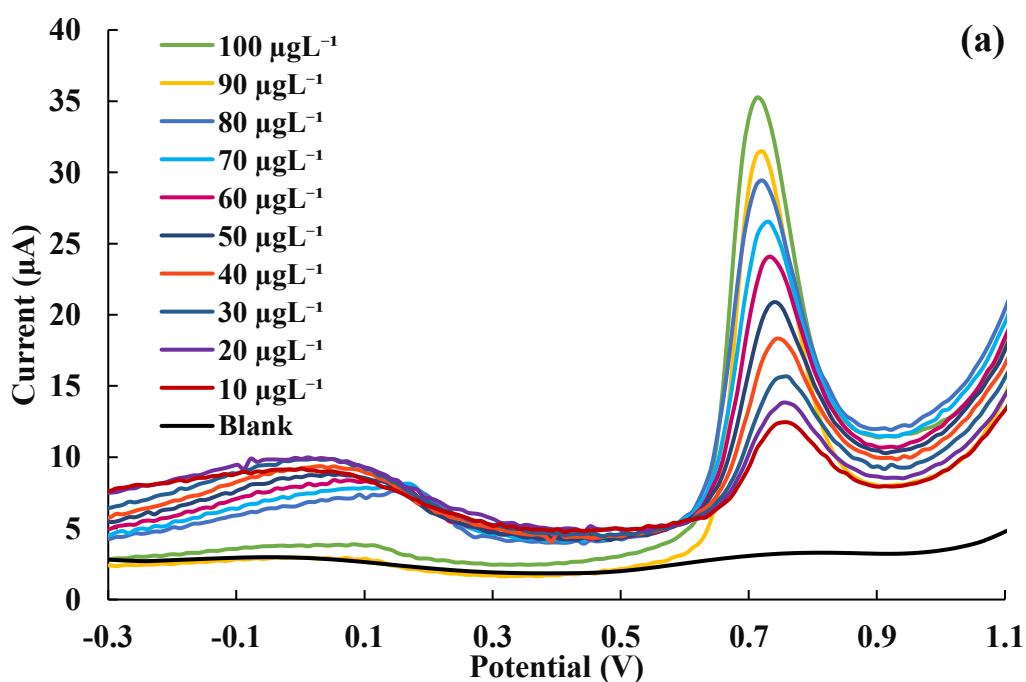


Figure 3.28. Oxidative peak current values of IBP ($50.0 \mu\text{g L}^{-1}$) as a function of: (a) Accumulation potentials (V); (b) Accumulation time (sec) using the CeONC@GrO modified GCE.

3.3.5. Concentration dependence and calibration studies

To evaluate the analytical performance of the CeONC@GrO modified GCE toward ibuprofen detection, the influence of analyte concentrations on the oxidative peak current response was systematically examined. DPASV measurements were carried out over a concentration range of $10.0\text{--}100.0 \mu\text{g L}^{-1}$ of IBP under the optimized experimental parameters (deposition potential: -0.9 V , deposition time: 180 sec, pulse amplitude: 50 mV, pulse increment: 10 mV, and pulse width: 50 ms). Figure 3.29(a) shows the voltammograms of IBP as a function of IBP concentrations. It is evident from the figure that an increase in IBP concentration caused a gradual increase in anodic peak current. This trend is observed because, within the linear response range, a higher bulk concentration increases the mass transport of IBP molecules to the electrode surface during the preconcentration period (Langhus, 2001) leading to an enhanced surface coverage, which yields a larger oxidation current during the subsequent stripping step as the peak current is directly proportional to the surface concentration of the adsorbed analyte (Holze, 2009). Further, the anodic peak current

values were plotted against the corresponding IBP concentrations, and a well-defined linear calibration line was achieved (*Cf* Figure 3.29(b)). The linear regression line between the anodic peak current (I_p) and the IBP concentration is obtained as: y (μA) = $0.2533 x$ (μgL^{-1}) + 8.678 with $R^2 = 0.992$. Where y represents the anodic peak current and x corresponds to the IBP concentration. The high correlation coefficient (R^2 close to unity) indicates that an excellent calibration line is obtained for the trace detection of IBP using the CeONC@GrO GCE. The results suggest that the electrode surface interactions with IBP molecules were highly reproducible and consistent for a wide range of IBP concentrations. Further, the calculated LOD and LOQ values are 0.30 and 1.02 μgL^{-1} , respectively. These low detection limits highlight the higher sensitivity of the CeONC@GrO modified GCE for IBP detection, making it suitable for trace-level monitoring of IBP in environmental and pharmaceutical samples. The combination of high linearity, wide dynamic range, and low LOD/LOQ values demonstrates the potential of the sensor for practical applications in electrochemical sensing of emerging pharmaceuticals.



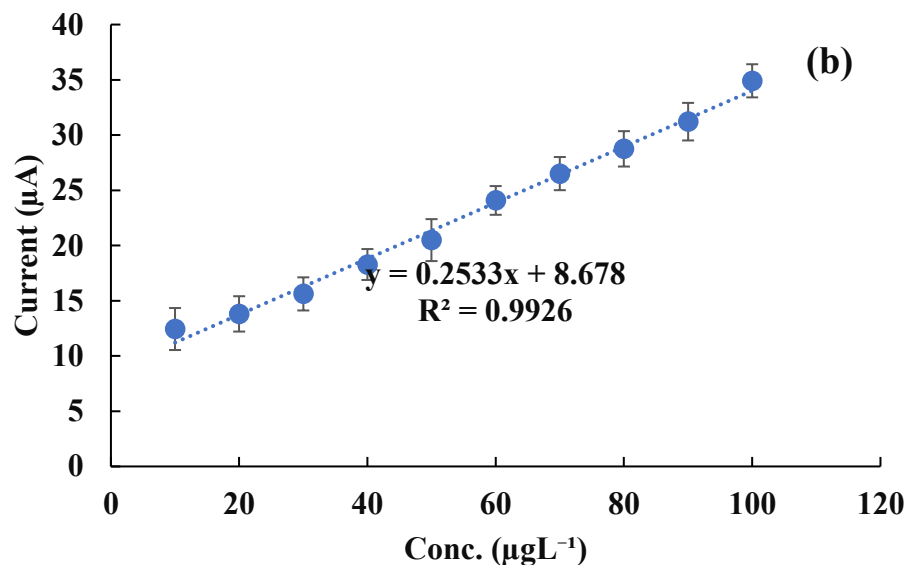


Figure 3.29. (a) Differential pulse anodic stripping voltammograms of IBP at varied concentrations of IBP (10.0 to 100.0 μgL^{-1}) using CeONC@GrO GCE; (b) Calibration line obtained for IBP against the oxidative peak current of IBP.

Further, Table 3.9 includes the LOD values obtained for IBP detection utilizing various materials and different electrochemical platforms. The present study showed that the results are quite comparable or even significantly lower than many other studies. The results showed the promise of CeONC@GrO GCE for trace and efficient detection of IBP in aqueous medium.

Table 3.9. Comparison of CeONC@GrO modified electrodes with other materials for IBP determination.

Electrode	Linear range (μmolL^{-1})	pH	LOD (μmolL^{-1})	Reference
AgNPs@Af-GO-MIP GCE	1–100	4.5	8.7×10^{-3}	(Nair & Sooraj, 2020)
polyaniline nanofiber/GCE	0.96–1.94	1.0	0.48	(E. L. Hayat et al., 2022)
MWCNT–CPE	2.36–242	7.02	9.1	(Rivera-Hernández et al., 2016)
CPE–Clay/ Al_2O_3	1–1000	6.0	19.5×10^{-3}	(E. L. Hayat et al., 2022)
P(L-Asp)/GCE	1–150	4.0	0.22	(Mekassa et al., 2018)
Cu_3TeO_6 /GCE	0.02–5, 9–246	5.0	1.7×10^{-2}	(Mutharani et al., 2020)
CeONC@GrO-GCE	0.0485– $0.485 \mu\text{molL}^{-1}$	5.5	1.45×10^{-3}	This work

AgNPs@Af-GO-MIP- molecular imprinted polymer-wrapped silver nanoparticles decorated acid-functionalized graphene oxide modified glassy carbon electrode

MWCNT–CPE: multiwalled carbon nanotube composite modified carbon paste electrode

CPE–Clay/ Al_2O_3 : aluminum oxide particles supported on clay-modified carbon paste electrode

P(L-Asp)/GCE: electropolymerization of L-aspartic acid

Cu_3TeO_6 /GCE: 3D stone-like copper tellurate modified glassy carbon electrode

3.3.6. Co-existing ion study on IBP detection

Interference investigations on the detection of IBP using CeONC@GrO were conducted by adding a tenfold excess of common ions, including Ca^{2+} , Mg^{2+} , NO_3^- , and SO_4^{2-} , as well as several pharmaceuticals such as paracetamol (PRT), diclofenac (DFN), and tetracycline (TTC). These ions are introduced at tenfold higher concentrations ($500.0 \mu\text{g L}^{-1}$) than IBP concentration ($50.0 \mu\text{g L}^{-1}$), and the results are shown in Figure 3.30. The results of the interference studies indicated that the anodic peak current of IBP was not significantly affected in the presence of these cations/anions, *viz.*, Ca^{2+} , Mg^{2+} , NO_3^- , and SO_4^{2-} . These ions do not interfere with the detection of IBP, hence, CeONC@GrO GCE showed greater selectivity towards the detection of IBP in aqueous medium. Similarly, the interference was investigated with the pharmaceuticals such as PRT, DFN and TTC. These drugs are of particular concern because they are electroactive and can potentially undergo oxidation within a comparable potential range. Nevertheless, the results showed that the anodic peak current of IBP was not significantly affected in the presence of these pharmaceutical compounds, except for a slight change that was recorded in the presence of DFN. The percentage change in peak current was less than 5% in the presence of DFN. Such minimal deviations indicate that the CeONC@GrO electrode surface has a stronger affinity and fair affinity towards IBP. The results reaffirm the fair selectivity and reliability of the CeONC@GrO modified electrode for IBP detection, even amid elevated concentrations of coexisting ions and other pharmaceuticals, thereby showing it to be a formidable sensing platform for IBP detection. Prior investigations assessed the impact of probable interferents by adding a 20-fold excess of common substances, including ascorbic acid (AA), naproxen (NPX), glucose (GLU), and chlorpromazine (CPZ) at the 3D stone-like copper tellurate (Cu_3TeO_6) glassy carbon electrode (GCE). The findings demonstrated that these species caused relatively negligible changes in the current response ($<5\%$), affirming that they did not substantially influence the electrochemical detection of IBP (Mutharani et al., 2020).

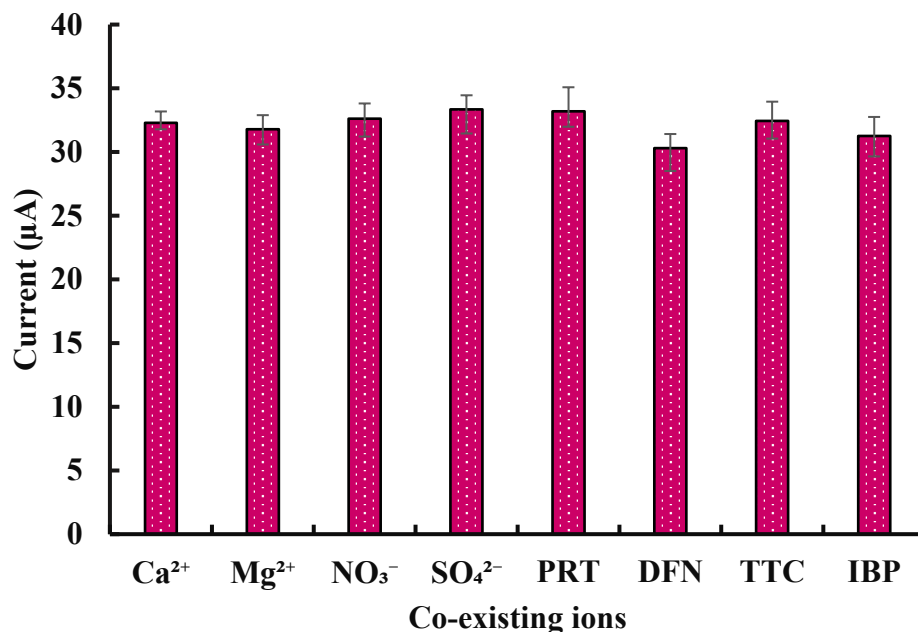


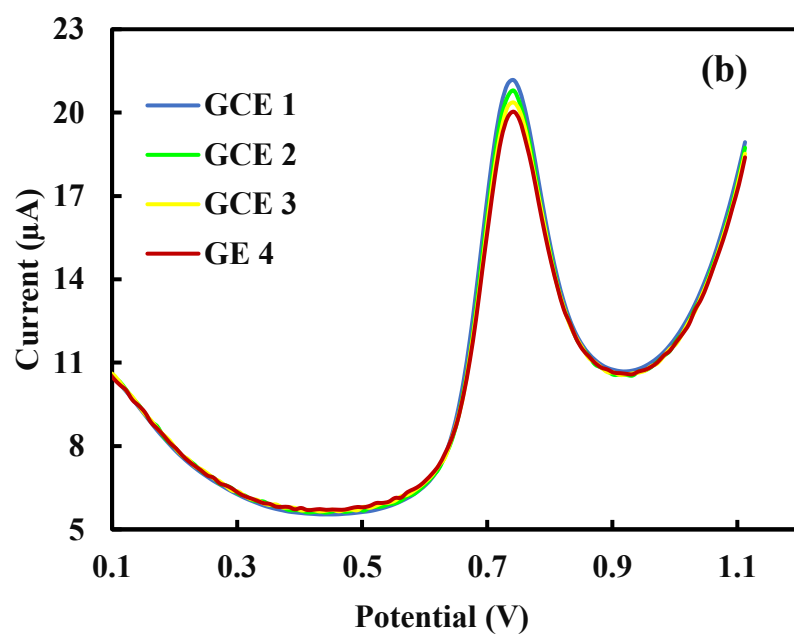
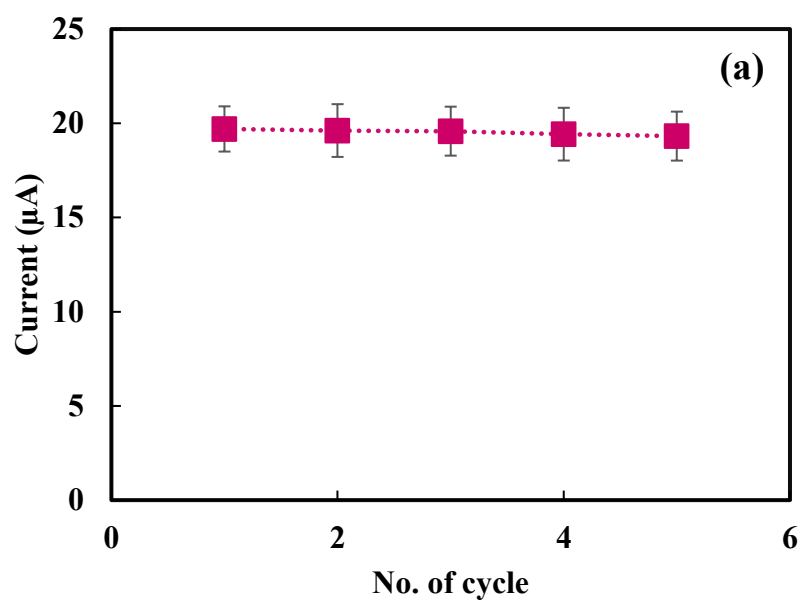
Figure 3.30. Effect of co-existing ions in the detection of IBP using the CeONC@GrO GCE.

3.3.7. Repeatability, stability, and reproducibility of modified electrodes

The repeatability of the CeONC@GrO GCE toward IBP detection was evaluated to assess the stability of the fabricated electrode for repeated detection systems. Therefore, five consecutive DPASV measurements were performed using a freshly prepared IBP ($50.0 \mu\text{gL}^{-1}$) solution in 0.1 molL^{-1} acetate buffer (pH 5.5), employing the same CeONC@GrO GCE under optimized experimental conditions. Figure 3.31 (a) shows the anodic peak currents recorded for the five successive cycles, which exhibited only negligible variation in peak current values. Moreover, it was observed that the peak shapes and peak positions remained unaffected for successive cycles of detection. The calculated relative standard deviation (%RSD) of the peak current values was found to be less than 1%, demonstrating excellent repeatability of the CeONC@GrO GCE.

Similarly, the reproducibility of the CeONC@GrO GCE was evaluated by comparing the anodic peak current responses obtained from independently prepared electrodes. Three glassy carbon electrodes modified with CeONC@GrO (designated

as GCE 1, 2, and 3) were fabricated following the same procedure to assess the uniformity of the electrode modification process. In addition, one gold electrode modified with CeONC@GrO (designated as electrode GE 4) was also tested to further confirm the applicability of the nanocomposite to different electrode substrates. Figure 3.31 (b) illustrates that the peak current responses for IBP ($50.0 \mu\text{gL}^{-1}$) using all four electrodes displayed only slight variations in intensity, with no notable changes in peak position or shape. The observed consistency indicates that the electrode fabrication protocol is dependable and yields consistent sensing interfaces. The stability of the modified electrode was further examined by recording the current response for IBP at the CeONC@GrO GCE over a period of 96 consecutive hrs under identical experimental conditions. Table 3.9 presents the percentage relative standard deviation RSD (%) for five consecutive measurements, conducted at 24-hour intervals, which was found to be less than 2% after 96 hrs. Moreover, the electrode maintained a nearly consistent performance throughout the test duration, retaining about 97% of its initial current response after 96 hrs of continuous use (*Cf* Figure 3.31 (c)). The results demonstrate the excellent stability and durability of the fabricated electrode material. The minimal loss in activity indicates that the surface of the electrode remains largely unaffected by fouling, degradation, or passivation during repeated measurements.



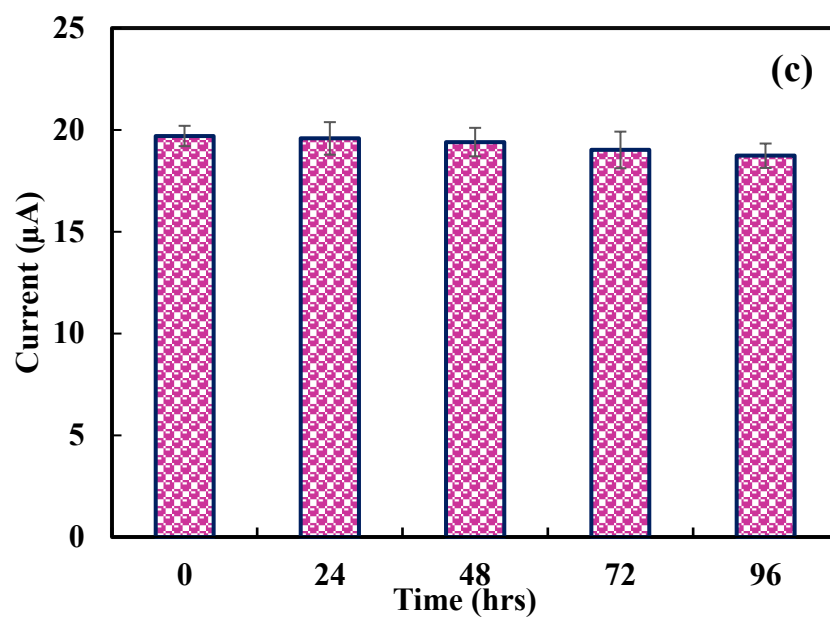


Figure 3.31. (a) Anodic peak current change of IBP using CeONC@GrO GCE for 5 repetitive measurements; (b) Reproducibility measurements of CeONC@GrO GCE using four different electrodes [GCE 1, GCE 2, GCE 3, GE 4]; (c) Anodic current change of IBP at different time intervals using CeONC@GrO GCE.

Table 3.10. Stability of CeONC@GrO GCE in the detection of IBP at varied time intervals using the same fabricated electrode.

Time (hrs)	Repetition	RSD (%)
0	5	0.78
24	5	0.75
48	5	0.84
72	5	1.32
96	5	1.39

3.3.8. Studies in real water samples

A water sample was collected from hospital effluents (Ebenezer Hospital) near Tuikual Lui, Aizawl (India). The collected sample was first filtered using a filter paper (11 μm) and subsequently analysed for various physicochemical parameters by the pH meter, multiparameter photometer, TOC analyser, and atomic absorption spectrometer (AAS). The results are summarized in Table 3.7, which indicates elevated levels of inorganic carbon, likely originating from carbonates or bicarbonates. In addition, the samples contained a considerable amount of organic matter, as reflected by the NPOC value of 88.67. Conversely, the concentrations of sulphate, phosphate, fluoride, and aluminium were comparatively low, while only trace levels of heavy metals such as Ni, Pb, Mn, and Fe were detected.

Further, the practical applicability of the CeONC@GrO modified GCE in the IBP detection in the real water sample was conducted by spiking the known concentrations of IBP. The detection was conducted utilizing the differential pulse anodic stripping voltammetry (DPASV) under the previously optimized experimental conditions (*Cf* Figure 3.32 (a)). The results revealed that the peak potential position of IBP remained unchanged, suggesting that the complex matrix of the effluent sample did not interfere with the electrochemical response of the IBP. This observation highlights the robustness and reliability of the sensing platform for the selective detection of IBP in a real water environment. Moreover, the IBP detection was conducted at a concentration range of 10.0 $\mu\text{g L}^{-1}$ to 50.0 $\mu\text{g L}^{-1}$. A good linear correlation was established between the oxidative peak current and the IBP concentrations, with an R^2 value of 0.991 (Figure 3.32(b)), highlighting the sensor's repeatability and accuracy in real-sample analysis. Further, Table 3.11 exhibited very high recovery values lying between 90.43% and 104.8%, with RSD% less than 1.32% for IBP detection; hence, validating the accuracy and dependability of the modified electrode for assessing IBP in actual matrices. These findings affirm that the CeONC@GrO GCE offers a very efficient and selective electroanalytical platform for the detection of IBP, exhibiting low interference from competing species in complicated water samples. The electrochemical quantification of ibuprofen (IBU) in actual wastewater (Northern Wastewater Treatment Plant in Gauteng, South Africa)

utilizing manganese oxide nanoparticles (MnO₂NPs/SPCE) screen-printed carbon electrode, and the recovery values were ranged within 105–110% with RSD of 0.151% (Lizzy Mokaba et al., 2024).

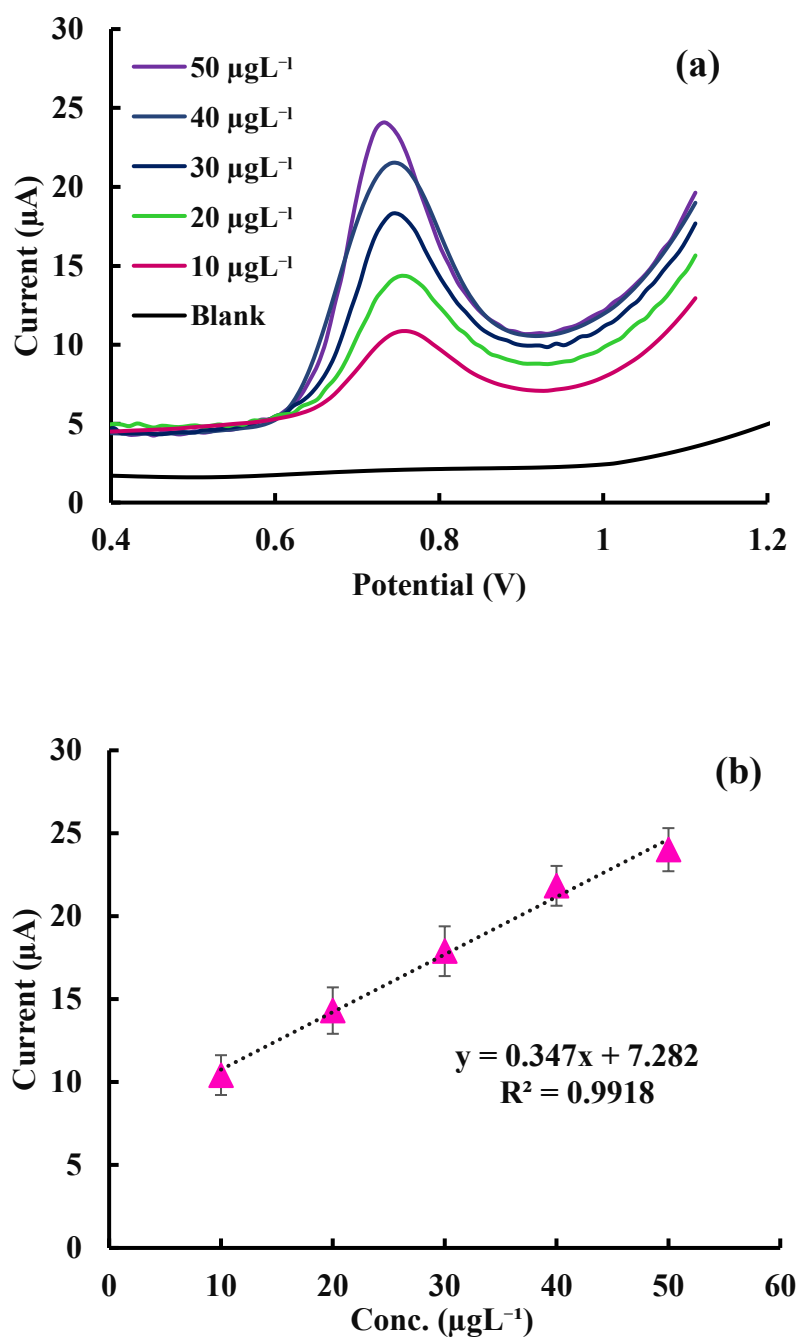


Figure 3.32. (a) Differential pulse anodic stripping voltammograms of IBP at varied concentrations (10.0 to 50.0 µg/L) using CeONC@GrO GCE in hospital wastewater;

(b) Calibration line obtained between the oxidative peak current of IBP and IBP concentrations.

Table 3.11. Recovery percentage of IBP in hospital wastewater samples using the CeONC@GrO GCE

Spiked amount of analyte (μgL^{-1})	Found (μgL^{-1}) $\pm 3\sigma$	Recovery (%)	RSD (%)
10	9.04 ± 0.11	90.43	0.98
20	20.25 ± 0.05	101.26	0.86
30	29.18 ± 0.23	97.29	1.35
40	40.11 ± 0.14	104.81	0.32
50	50.71 ± 0.11	96.41	0.21

3.3.9. Conclusion

The CeONC@GrO nanocomposite-modified GCE was employed for the low-level electrochemical detection of ibuprofen (IBP). Cyclic voltammetry measurements exhibited a single anodic peak at approximately +0.76 V and a corresponding cathodic peak at +0.46 V, indicating a single-electron transfer process for IBP. The large peak separation ($\Delta E_p = 0.30$ V) suggests that the oxidation of IBP at the CeONC@GrO GCE is quasi-irreversible. The incorporation of CeONC@GrO significantly enhanced the electrochemical response compared to the bare GCE, demonstrating the catalytic and signal-amplifying properties of the nanomaterial. The DPASV was optimized with an optimal pH, accumulation potential, and accumulation time of 5.5, -0.6 V, and 180 s, respectively. Under these optimized conditions, the linear regression line between the anodic peak current (I_p) and the IBP concentration is obtained as: y (μA) = $0.2533 x$ (μgL^{-1}) + 8.678 with $R^2 = 0.992$. The calculated LOD and LOQ for IBP were found to be $0.30 \mu\text{gL}^{-1}$ and $1.02 \mu\text{gL}^{-1}$, respectively. Interference studies revealed that the most common co-ions, even at ten-fold excess, did not significantly affect the IBP detection, except for diclofenac (DFN), which caused minor interference. The negligible variation in anodic peak currents among independently prepared electrodes confirmed the uniformity and reliability of the fabrication process for these different electrodes.

Furthermore, the electrode retained approximately 97% of its initial current response after 96 hours of continuous operation, with an RSD value below 2%, indicating exceptional operational stability. Furthermore, the detection of IBP in the hospital effluent showed high recovery, ranging from 90.43% to 104.8%, with RSD values below 1.32%, highlighting the real implication of the fabricated electrode. These results collectively indicate that the CeONC@GrO-modified electrode possesses high affinity and selectivity for IBP, making it highly suitable for trace-level detection of IBP in aqueous medium.

3.4. ELECTROCHEMICAL DETECTION OF CHLORAMPHENICOL AND SULFAMETHOXAZOLE

3.4.1 Cyclic voltammetric studies in electrochemical detection of chloramphenicol (CRP) and sulfamethoxazole (SFX)

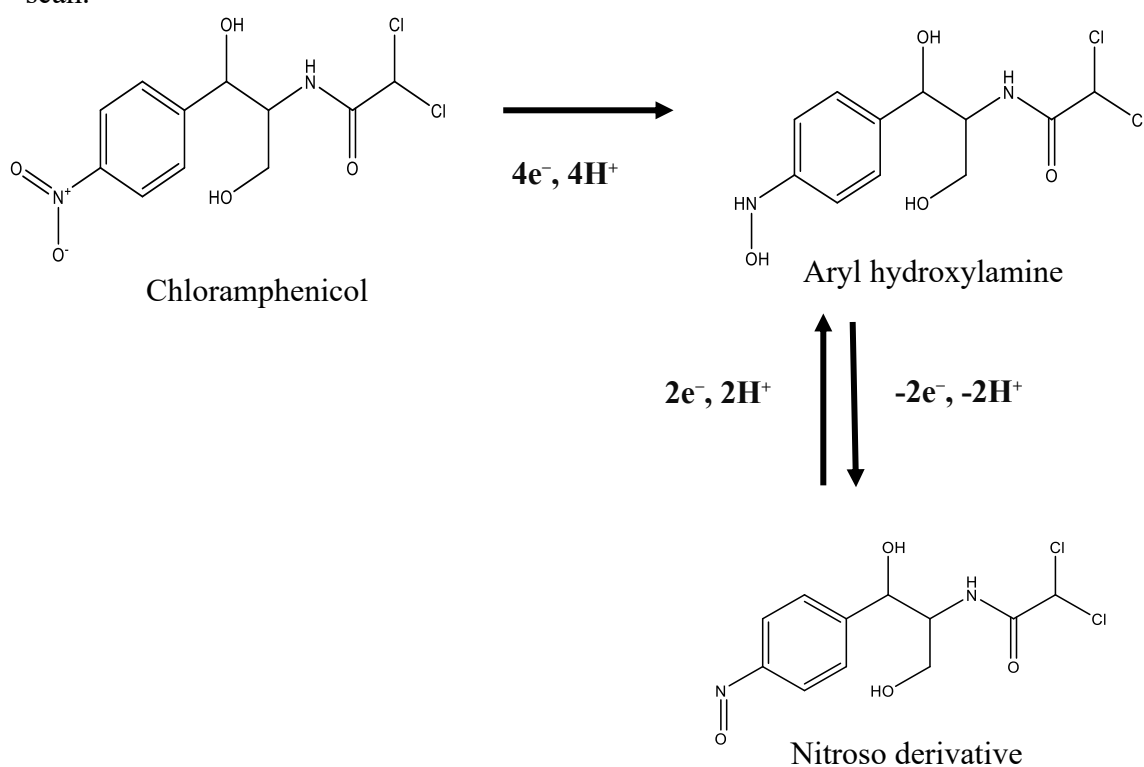
The electrochemical behaviour of chloramphenicol (CRP) and sulfamethoxazole (SFX) was examined by the cyclic voltametric studies utilizing the various modified GCEs along with the bare GCE. The studies provide an impetus for these electrodes in electrocatalytic performance and sensing efficacy. Figure 3.33 (a) displays the comparative voltammograms of CRP and SFX obtained at the bare GCE, the graphene oxide-modified electrode, and the CeONC@GrO nanocomposite-modified GCE under uniform experimental conditions. All measurements were conducted in a phosphate buffer (0.1 molL^{-1}) (pH 6.0) containing 1.0 mgL^{-1} CRP and SFX. The CV response of the CeONC@GrO-modified GCE was also recorded without CRP and SFX, revealing no prominent redox peaks, which confirms that the observed peaks are attributable to the analyte molecules rather than the electrode material or buffer solution.

Figure 3.33 (a) illustrates the CV profile of CRP, with a prominent oxidation peak around +0.05 V and a corresponding reduction peak at *Ca.* -0.07 V. The observed peaks at 0.05 V and -0.07 V indicate a reversible redox couple, reflecting the transformation between the hydroxylamine and nitroso derivatives of CRP (Yang & Zhao, 2015). The possible reaction mechanisms are given in Scheme 2. Previous studies have reported the appearance of two distinct peaks at -0.85 V and 0.44 V during

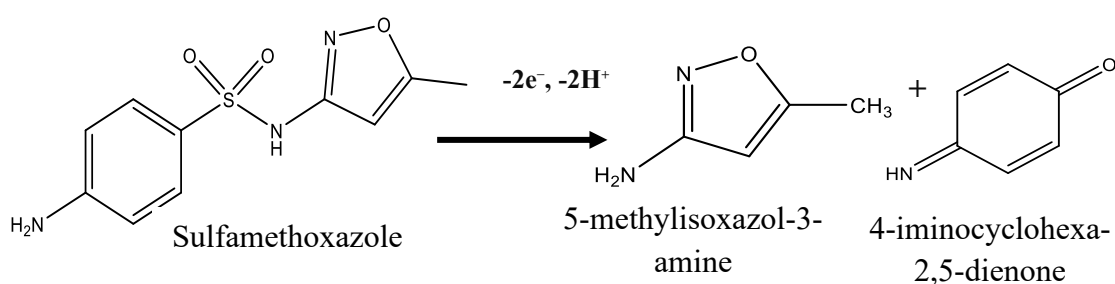
the electrochemical analysis of chloramphenicol, which are attributed to the formation of intermediates in its redox process. Specifically, the cathodic peak at -0.85 V corresponds to the irreversible reduction of the nitro group to a hydroxylamine derivative, while the anodic peak at 0.44 V is associated with the subsequent oxidation of the hydroxylamine to a nitroso derivative during the reverse scan (Chuanuwatanakul et al., 2008). Moreover, the redox couple at $+0.05$ V/ -0.07 V indicates a nearly reversible process; nevertheless, the peak-to-peak separation (ΔE_p) obtained from the voltammogram exceeded the predicted value of 59 mV expected for a reversible one-electron transfer mechanism (David et al., 2022; Svalova et al., 2022). This variation signifies that the electron transfer related to CRP does not occur through a completely reversible pathway, but instead follows via a quasi-reversible process. The incorporation of CeONC@GrO onto the GCE surface markedly improved the current responsiveness in comparison to bare and GrO modified electrodes. The presence of cerium oxide nanoclusters and graphene oxide, possibly, synergises the electrochemical response of these antibiotic compounds.

Figure 3.33 (b) displays the CV scans for sulfamethoxazole (SFX), which illustrates a pronounced anodic peak current, signifying that SFX oxidized efficiently at the electrode's surface. The oxidation reaction of SFX at the electrode material is suggested to occur via two-electron transfer reactions. The electrochemical oxidation occurs mainly through the amino ($-\text{NH}_2$) functional group, which involves the loss of two electrons, resulting in the cleavage and structural transformation of the SFX molecule, ultimately leading to the formation of two notable oxidation products: 4-iminocyclohexa-2,5-dienone and 5-methylisoxazol-3-amine (Lalmalsawmi & Tiwari, 2021). The possible reaction mechanism is illustrated in Scheme 3. The GrO GCE exhibited an enhanced current response, which is due to an enhanced ESA and the higher conductive nature of graphene oxide. Nonetheless, the CeONC@GrO composite-modified GCE showed significantly enhanced redox peak currents for CRP and SFX, underscoring its enhanced electrocatalytic performance. Previously reported that the graphene-based composites showed enhanced affinity towards the detection of antibiotics due to their exceptional surface adsorption properties and conductivity (Elgiddawy et al., 2023; Huang et al., 2021). Similarly, the cerium oxide nanoparticles exhibit significant electrocatalytic activity for redox-active biomolecules, attributable

to their distinctive oxygen storage capacity and proficiency in facilitating electron transport (Karimulla et al., 2025). Therefore, the well-defined peaks of CRP and SFX enabled us to sensitively detect CRP and SFX at trace levels. Therefore, DPV was utilized employing the anodic stripping method, which improves the sensitivity by preconcentrating the analytes onto the electrode's material before the voltammetric scan.



Scheme 3.2. Proposed mechanism for CRP detection



Scheme 3.3. Proposed mechanism for SFX detection

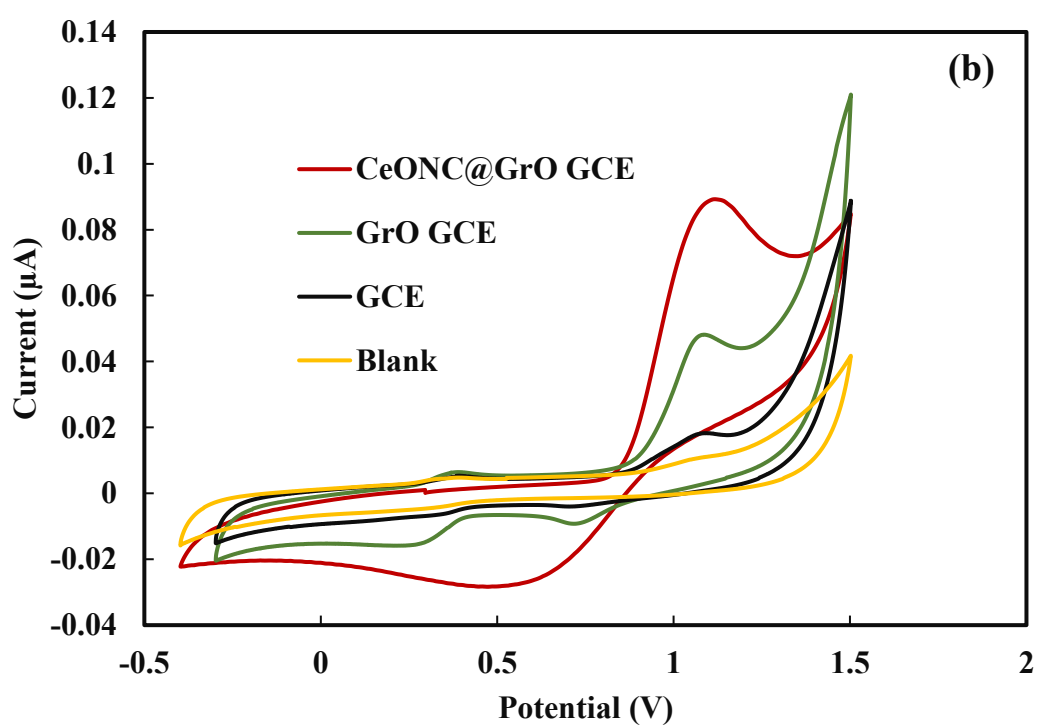
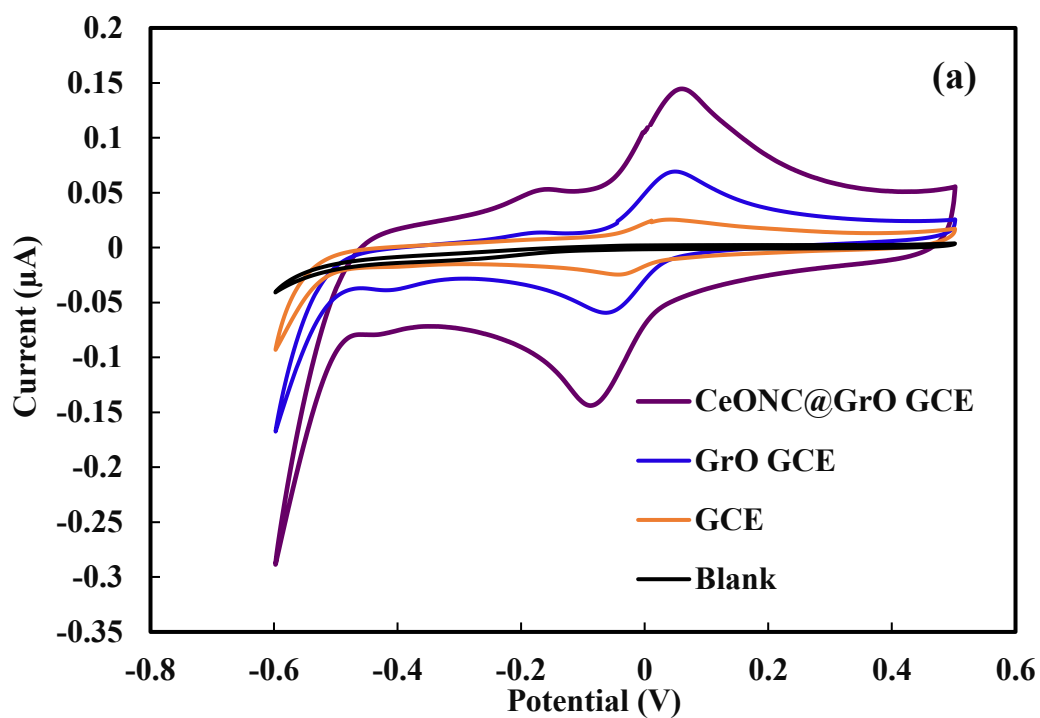


Figure 3.33. Cyclic voltammograms of 1.0 mgL^{-1} : (a) Chloramphenicol (CRP); (b) Sulfamethoxazole (SFX) using various electrodes.

3.4.2. Trace level determination of CRP and SFX using DPASV

Differential pulse anodic stripping voltammetry was employed for the detection of chloramphenicol (CRP) and sulfamethoxazole (SFX) due to its enhanced sensitivity and reduced detection limits relative to cyclic voltammetry (CV), establishing it as a reliable platform for prolonged electrochemical sensing. The detection mechanism of CRP and SFX at the CeONC@GrO modified electrode proceeds through the initial deposition of analyte molecules at the electrode surface during the deposition phase and then oxidized during the stripping phase. The magnitude of the anodic peak current during the oxidation process directly relates to the concentration of CRP or SFX in the solution, thereby enabling their quantitative determination. Figure 3.34 (a-b) illustrates the DPASV plots of CRP and SFX obtained at the CeONC@GrO-modified GCE under optimized conditions, recorded both in the absence and presence of 50.0 μgL^{-1} CRP and SFX in 0.1 molL^{-1} phosphate buffer solution (pH 7.0). In the blank solution, no noticeable peak appeared within the applied potential window, signifying the stability of the modified electrode and minimal background interference from the electrolyte or electrode surface. Upon the addition of 50.0 μgL^{-1} CRP and SFX, however, a well-defined and sharp oxidation peak appeared at potentials *Ca.* -0.037 V for CRP and 0.94 V for SFX, which is attributed to the electrochemical oxidation of CRP and SFX molecules on the CeONC@GrO surface. Furthermore, the sharp and reproducible nature of the anodic peak, along with the absence of interference in the blank, demonstrates the reliability of the CeONC@GrO modified GCE for precise and selective detection of these pharmaceutical compounds.

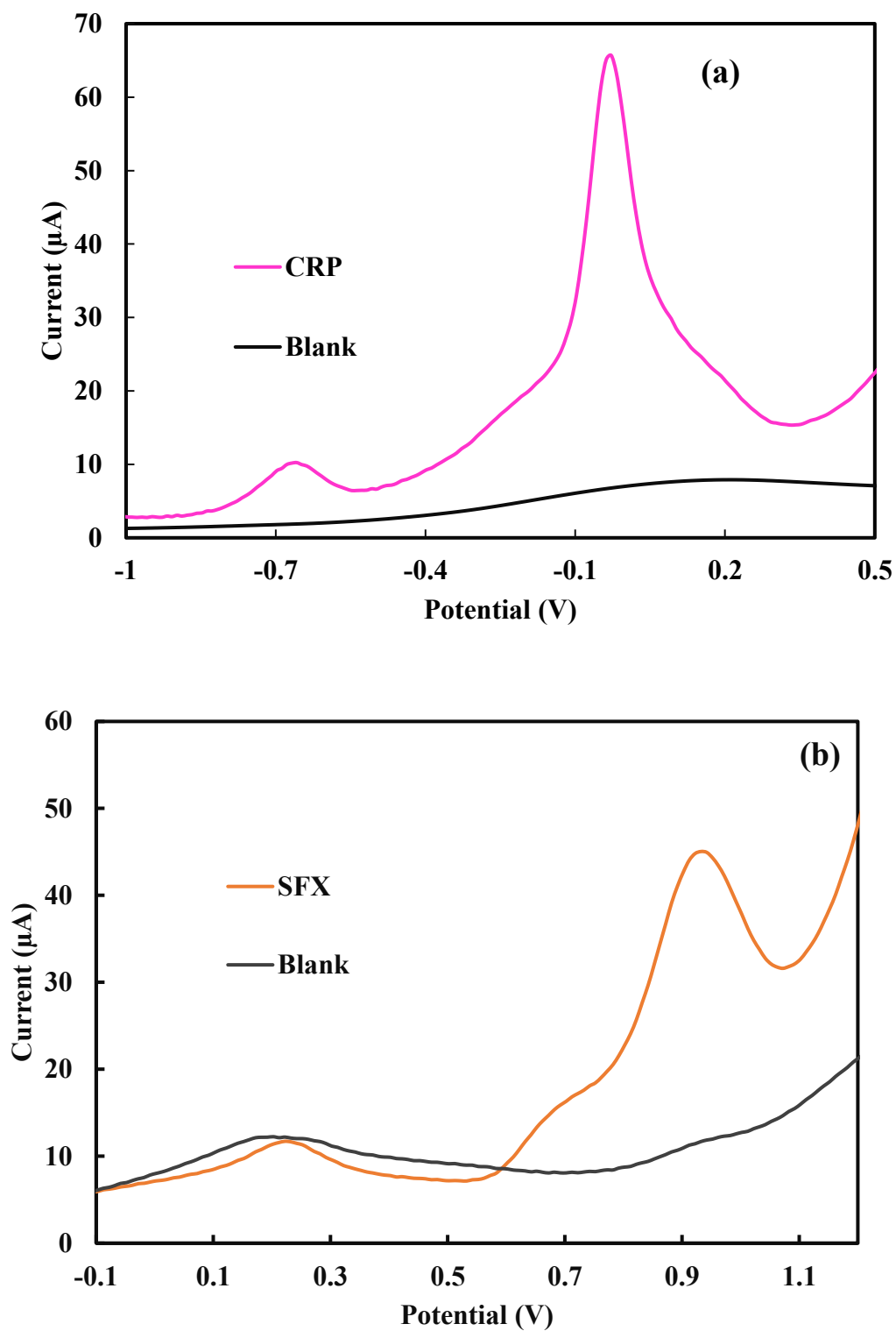


Figure 3.34. Differential pulse anodic stripping voltammograms in presence of $50.0 \mu\text{gL}^{-1}$ of: (a) Chloramphenicol (CRP); (b) Sulfamethoxazole (SFX) using CeONC@GrO GCE.

3.4.3. Optimization of pH

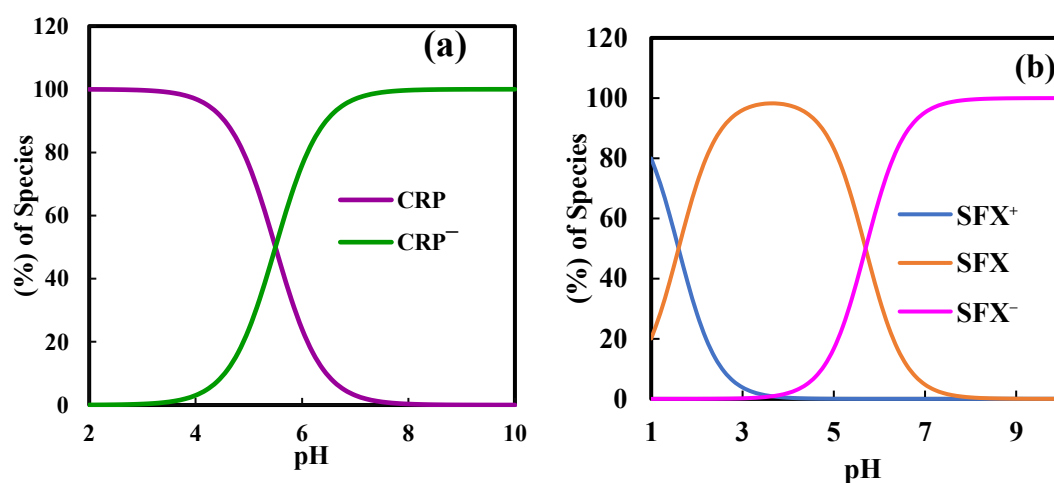
Figure 3.35(c-d) presents the DPASV curves of CRP and SFX using the CeONC@GrO modified GCE under different pH conditions, while Figure 3.35(c-d) shows the dependence of the anodic peak potential (E_{pa}) against the pH (5.0–9.0) (phosphate buffer solution). The data revealed that both the peak current intensity and peak potential are significantly influenced by the solution pH. Specifically, the anodic peak potential shifts toward more negative values with increasing the solution pH, which is primarily due to the protonic electrochemical processes. The observed negative shift in peak potentials suggested that the redox reactions of CRP and SFX on the CeONC@GrO GCE surface were associated with proton transfer reactions. Additionally, the oxidation potential exhibited a linear relationship described by equations: E_{pa} (CRP) (V) = $-0.0678 \text{ pH} + 0.3256$ ($R^2 = 0.990$) (Cf Figure 3.35 (c)) and E_{pa} (SFX) (V) = $-0.05 \text{ pH} + 1.238$ ($R^2 = 0.996$) (Cf Figure 3.35 (d)). It is important to note that the slope of -0.0678 V/pH and -0.05 V/pH unit is quite near to the predicted Nernstian value of -59 mV per pH unit at 25°C . This value often suggests a redox process that involves an equal amount of protons and electrons in redox processes. Therefore, it is assumed that the oxidation of CRP and SFX on the CeONC@GrO GCE surface is controlled by the transfer of one electron and one proton (Măgeruşan et al., 2025).

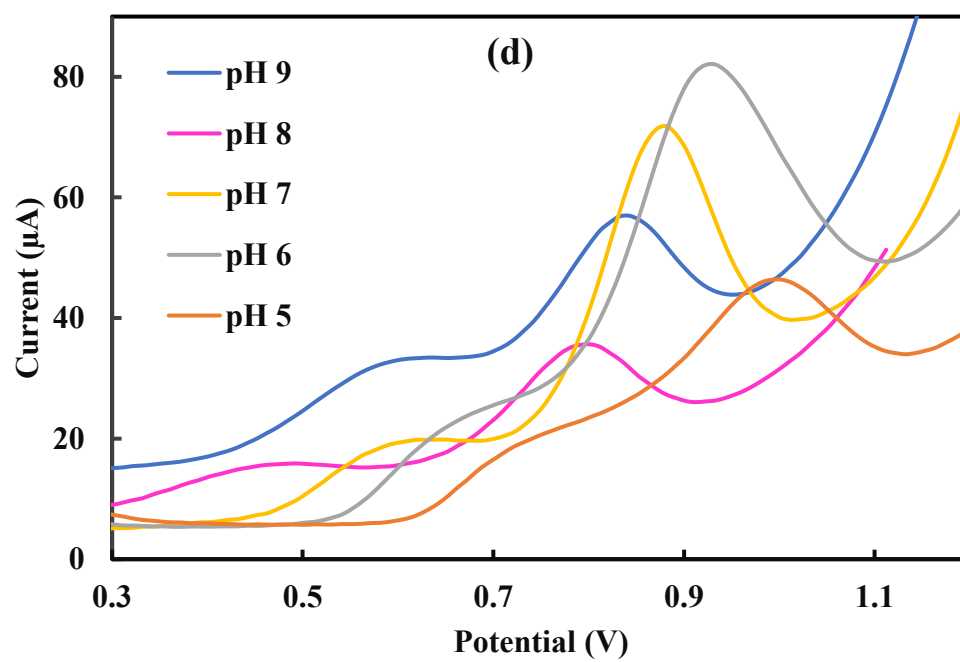
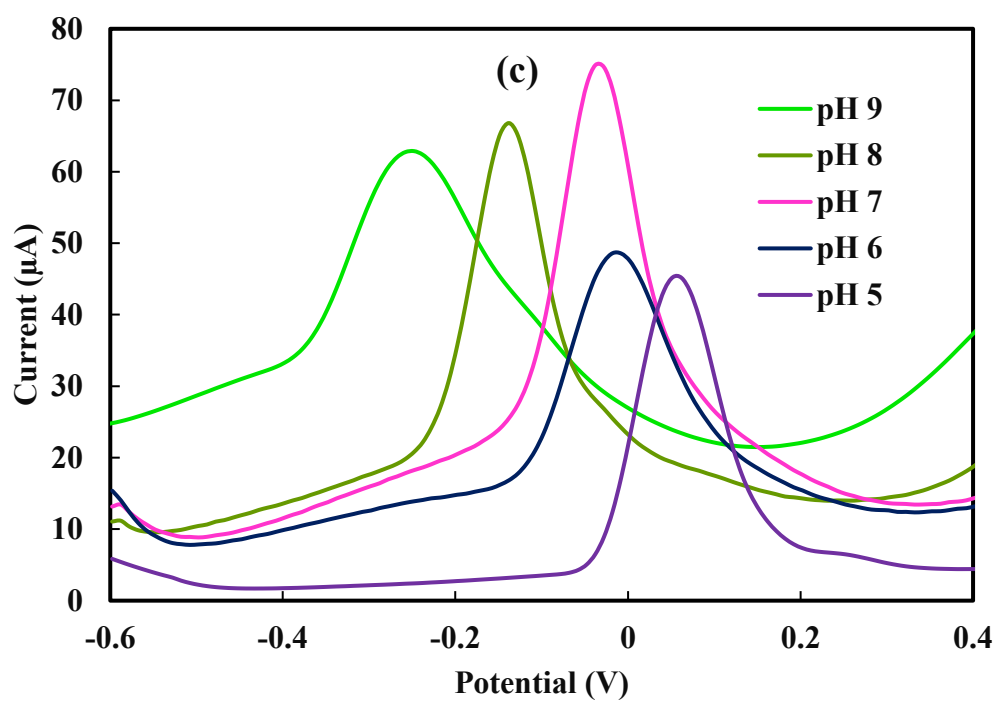
Figure 3.35 (e) illustrates that the anodic peak current for chloramphenicol (CRP) oxidation reaches its maximum value at pH 7.0. This suggests that pH 7.0 is an optimal pH for the electrochemical detection of CRP utilizing the CeONC@GrO GCE. The speciation study of CRP was conducted using the pK_a value of 5.5 (Khelifa et al., 2023). The species distribution of CRP is shown graphically in Figure 3.35 (a). Figure 3.34(a) shows that the CRP molecules primarily occur in their deprotonated species at $\text{pH} \sim 7.0$ (Cf Figure 3.35 (a)). On the other hand, the point pH_{PZC} of the CeONC@GrO nanocomposite was 6.4. This indicates that above this pH value, the surface of CeONC@GrO carries a net negative charge. Consequently, at pH 7.0, both CRP and the electrode surface are carrying a net negative charge. Therefore, the CRP species are possibly repelled at the CeONC@GrO electrode surface and suppress the faradaic

current response. Nonetheless, the experimental findings indicate a significant increase in current response at pH 7.0, which contradicts the predictions based only on electrostatic attraction. The CRP molecules interact at the surface with non-electrostatic interactions, consequently enhancing the electron transfer reactions at the electrode surface. The π - π stacking interactions between the aromatic rings of CRP and the extensive conjugated π -electron systems of graphene oxide facilitate the effective immobilization of CRP on the electrode surface (Zhang et al., 2017). These interactions not only counteract the repulsive electrostatic forces but also improve the orientation and accessibility of CRP for electron transfer reactions, resulting in an increased oxidation current. Similarly, the electron-withdrawing nitro group of chloramphenicol and the electron-donating functional groups present on the CeONC@GrO nanocomposite surface facilitate electron donor-acceptor (EDA) interactions (Tran et al., 2019). Furthermore, neutral pH conditions promote a stable proton environment and are ideal for proton-coupled electron transfer (PCET), a common mechanism in the redox processes of organic molecules, which enhances the electron transfer kinetics, leading to improved current responses that distinctly display an oxidative peak current in the electrochemical detection of CRP (Sayyad et al., 2024). Therefore, the improved electrochemical performance at pH 7.0 results from the synergistic combination of π - π stacking, EDA contacts, and PCET processes, which enhances the charge transfer reactions at the electrode surface for CRP molecules.

On the other hand, Figure 3.35 (f) illustrates that the anodic peak current for SFX oxidation reaches its maximum value at pH 6.0. The SFX possesses two ionizable functional groups, and its acid dissociation constants are $\text{p}K_{\text{a}1} = 1.39$ and $\text{p}K_{\text{a}2} = 5.7$ (Guo et al., 2015). Accordingly, through the $\text{p}K_{\text{a}}$ values of SFX, speciation studies were performed and returned in Figure 3.35 (b). Notably, within the pH range 3.0 to 4.5, the SFX is predominantly present in its neutral species. However, at pH >6.0, the SFX molecule is predominantly present as its anionic species (SFX^-) due to the deprotonation of the sulfonamide group (Y. Zhao et al., 2015). The pH_{pzc} of CeONC@GrO was 6.4; hence, pH < 6.4, the solid possessed a positive charge, which favoured the electrostatic attraction of SFX near the electrode's material and possibly sorbed on the surface. The sorbed SFX at the surface readily undergoes the redox

reaction. Moreover, at pH 6.0, the system reaches an apparent equilibrium where both electrostatic interactions and proton-coupled electron transfer (PCET) processes are enhanced (El-Azazy et al., 2022). The mildly acidic environment facilitates effective adsorption of SFX molecules and interactions like π - π stacking between the aromatic rings of SMX and the graphitic domains of GO, along with electron donor-acceptor (EDA) interactions, which potentially improve sorption of SMX onto the electrode surface. Consequently, pH 6.0 is identified as an optimum pH for the electrochemical detection of SFX at the CeONC@GrO-GCE surface, resulting in increased sensitivity, accelerated electron transfer kinetics, and superior analytical performance.





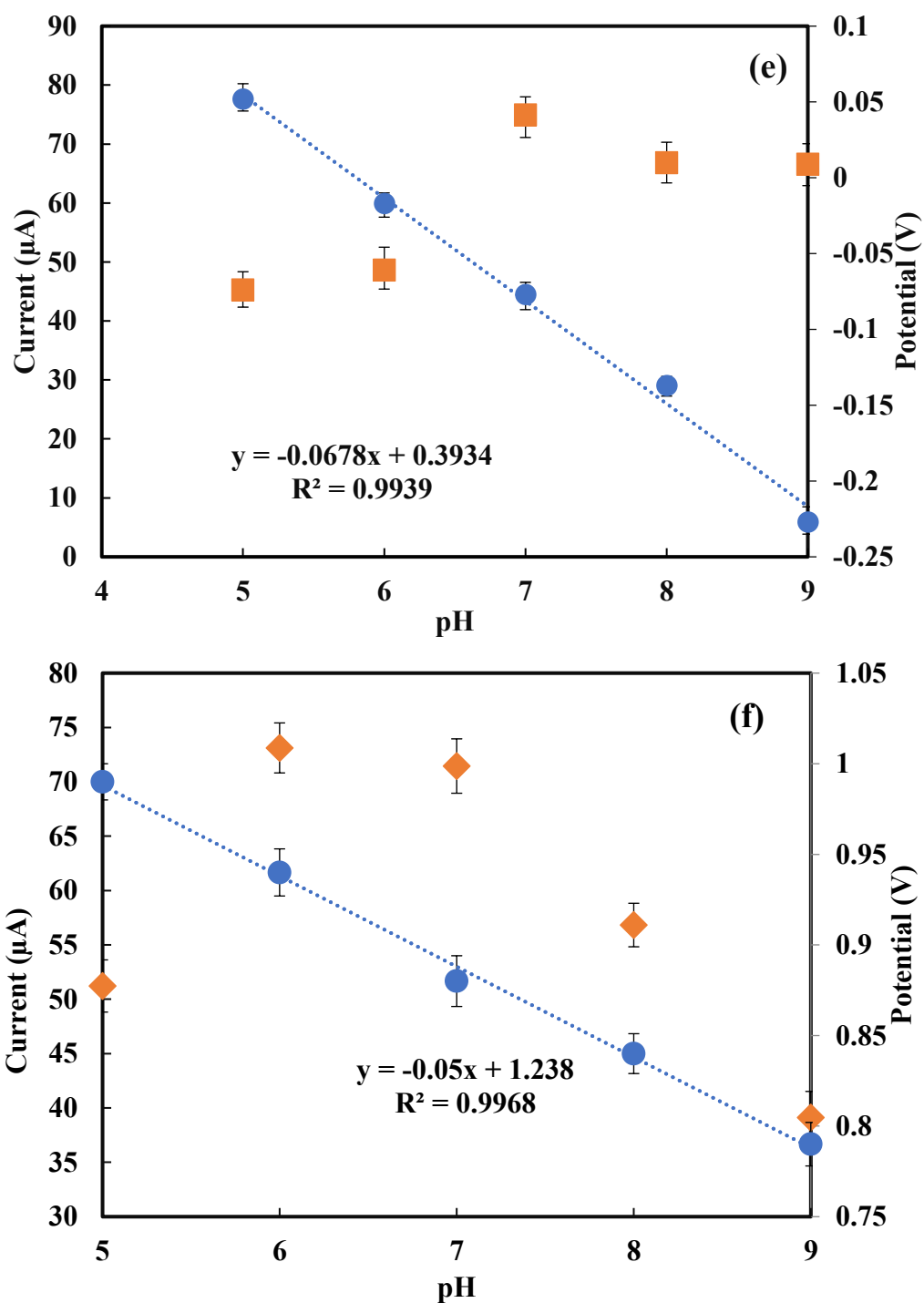


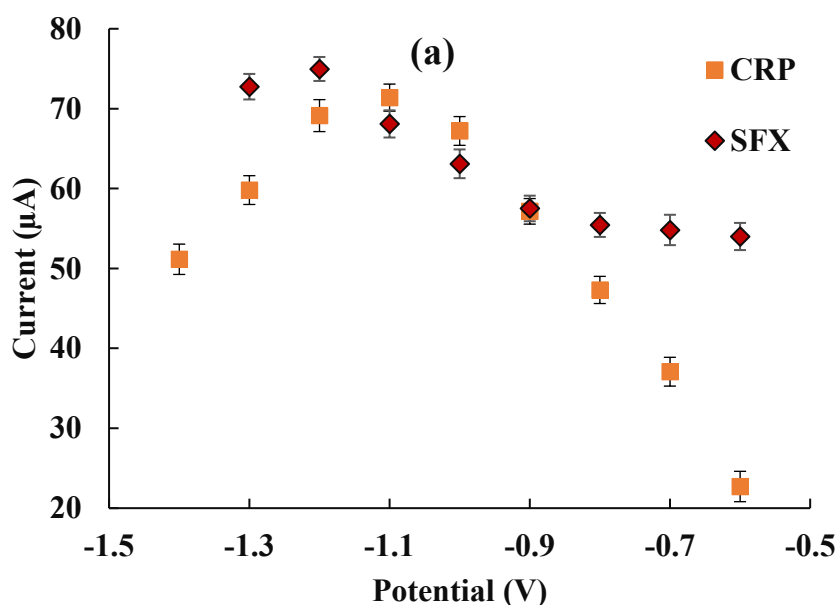
Figure 3.35. Speciation distribution of: (a) CRP; (b) SFX; Differential pulse anodic stripping voltammograms of $50.0 \mu\text{gL}^{-1}$ of: (c) CRP; (d) SFX at different pH values obtained with CeONC@GrO GCE; (e) Impacts on oxidized current and E_{pa} of CRP on pH of solution; and (f) Impacts on oxidized current and E_{pa} of SFX on pH of solution.

3.4.4. Optimization of preconcentration potential and time

The influence of preconcentration (or deposition) potential on the anodic response of CRP and CFX was systematically evaluated over the potential range of –1.4 V to –0.6 V and –1.3 V to –0.6 V, and results are shown in Figure 3.36(a). The results clearly demonstrate that the deposition potential plays a critical role in governing the accumulation of CRP and SFX molecules on the CeONC@GrO-modified electrode surface, thereby affecting the peak current intensity in subsequent anodic stripping measurements. As the deposition potential was shifted negatively from –0.5 V to –1.1 V for CRP and –0.6 V to –1.2 V for SFX, a steady increase in the anodic peak current was observed, reaching a maximum at –1.1 V for CRP and –1.2 V for SFX. This enhancement in peak current with an increase in negative potential was due to the greater driving force for electrostatic attraction and molecular accumulation at more negative potentials, which promotes the preconcentration of CRP and SFX molecules at the electrode–electrolyte interface. At this potential, the electrode surface provides sufficient energy to enhance the adsorption and stabilization of CRP and SFX, leading to enhanced sensitivity and signal amplification. However, further increase in negative potential, i.e., –1.2 V to –1.4 V for CRP and beyond –1.3 V for SFX, the anodic peak current is gradually decreased. This decrease in peak current is primarily due to two major factors: (i) the onset of excessive hydrogen evolution reactions (HER), which compete with CRP/SFX adsorption and blocking the surface active sites on the electrode, thereby decreasing the effective surface area available for analyte accumulation; and (ii) the possibility of desorption of previously adsorbed CRP/SFX molecules caused by strong local turbulence and bubble formation associated with hydrogen gas evolution (Lalhruaitluangi et al., 2025; Segura et al., 2015). Therefore, the optimal deposition potentials for the CRP and SFX are –1.1 V and –1.2 V.

Similarly, the influence of preconcentration time on the anodic peak currents of CRP and SFX was investigated over a time range of 30 to 270 sec, and results are illustrated in Figure 3.36(b). The results revealed that increasing the accumulation time from 30 to 180 sec for CRP and 30 to 210 sec for SFX caused for slight increase in anodic peak currents, reflecting the greater number of CRP and SFX molecules

adsorbed onto the CeONC@GrO-modified electrode surface. The results infer that the longer deposition periods allowed the diffusion of CRP or SFX molecules toward the electrode surface, which in turn enhanced the electrochemical oxidation of CRP and SFX during the stripping step. Nevertheless, with much prolonged accumulation duration, i.e., > 180 sec for CRP and > 210 sec for SFX, the anodic peak current slightly decreased. This decrease in peak current is explained by the fact that at much higher preconcentration times, the electrode surface is saturated with the analyte molecules, and no significant change in peak current is observed. In addition, excessive accumulation durations promote the desorption or reorientation of weakly bound analyte species or even lead to partial fouling of the electrode surface, which reduces the efficiency of electron transfer reactions. These results showed that a deposition time of 120 and 210 sec is the optimum condition for CRP and SFX detection.



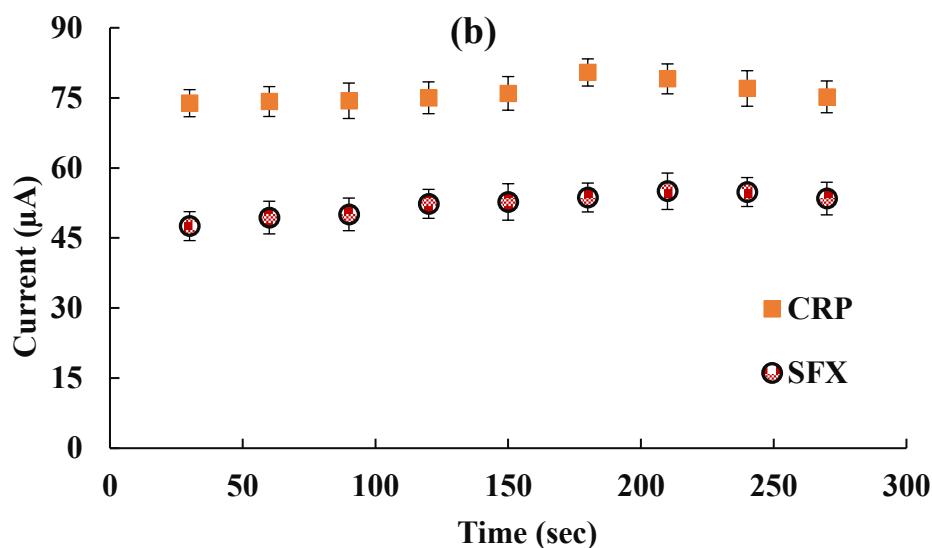
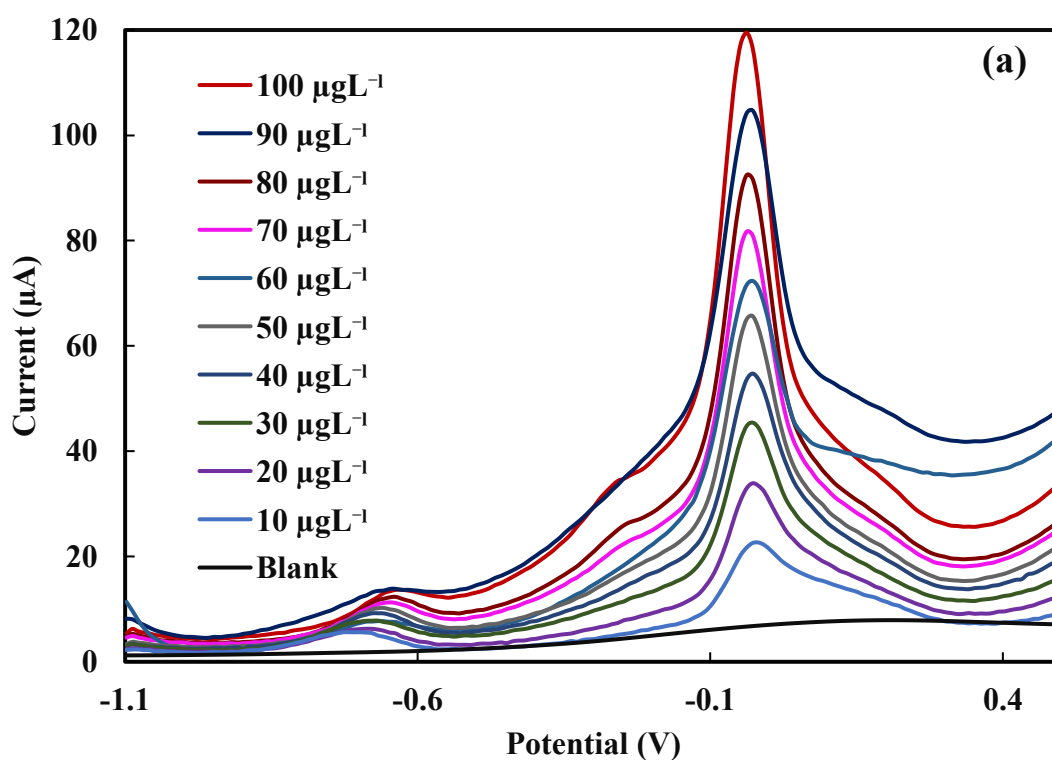


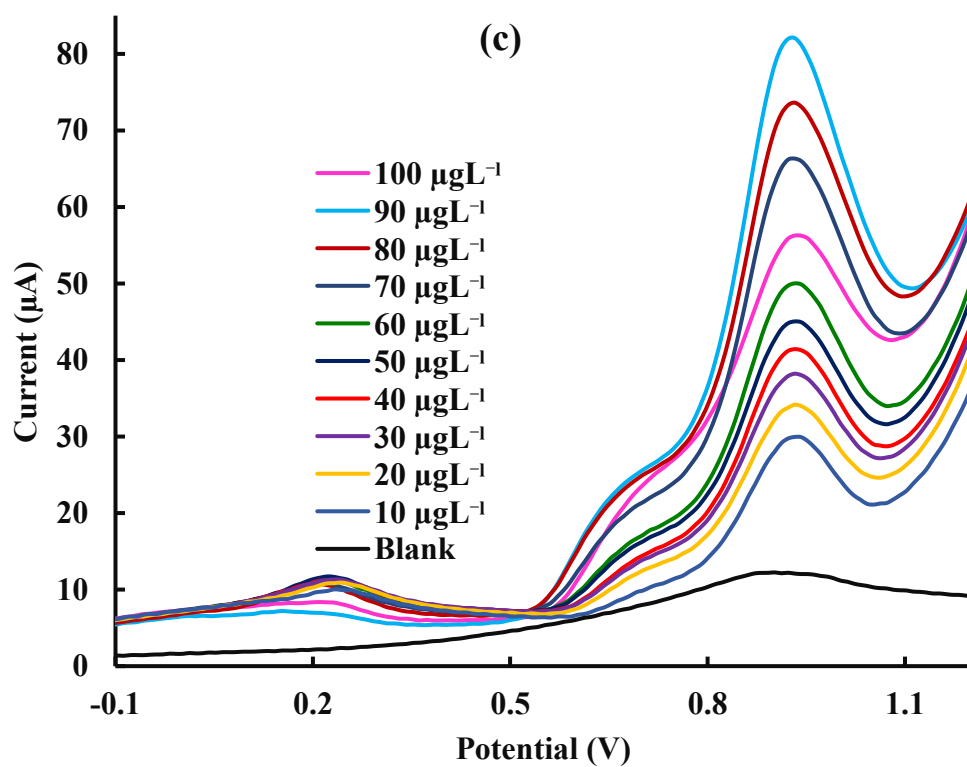
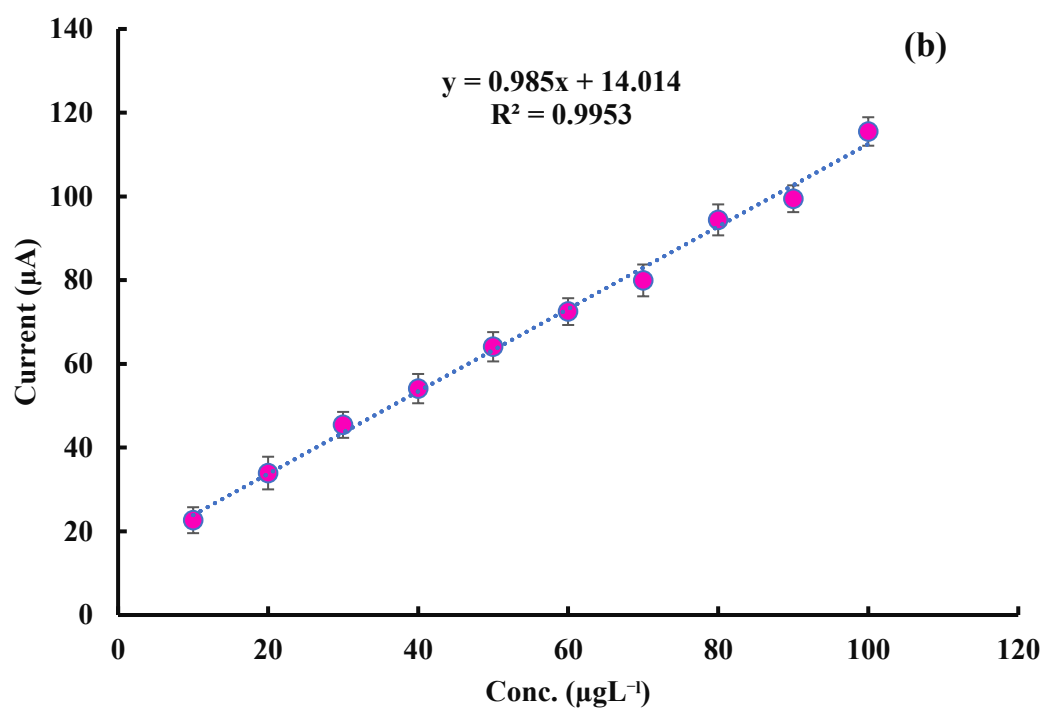
Figure 3.36. Impacts on oxidized current of CRP and SFX as a function of: (a) Preconcentration potential, (b) Preconcentration time using CeONC@GrO GCE in a 0.1 molL⁻¹ PhBs.

3.4.5. Concentration dependence study

Quantitative analyses of CRP and SFX were carried out using differential pulse anodic stripping voltammetry (DPASV) under the optimized experimental conditions, *viz.*, a deposition potential of -1.1 V and -1.2 V, a preconcentration time of 120 and 210 sec, and pH 7.0 and pH 6.0 for CRP and SFX, respectively. Figure 3.37 (a&c) presents the DPASV responses obtained for CRP and SFX over a concentration range of 0–100.0 μg L⁻¹. The voltammograms clearly demonstrate that with increasing analyte concentrations, the anodic peak current increases proportionally. The gradual increase in current intensity reflects the greater availability of electroactive molecules at the electrode surface, thereby confirming that the oxidation current is directly dependent on the concentration of the reactive species present in solution. The corresponding calibration plots, shown in Figure 3.37(b-d), exhibit excellent linearity within the studied concentration range. The regression equation for CRP and SFX was obtained as: $y \text{ (CRP)} = 0.985 x \text{ (}\mu\text{gL}^{-1}\text{)} + 14.014$, and $y \text{ (SFX)} = 0.5488 x \text{ (}\mu\text{gL}^{-1}\text{)} + 22.009$ with R^2 values of 0.995 and 0.99 for CRP and SFX, respectively. Moreover, the LOD and LOQ of CRP detection were determined to be 0.009 μg L⁻¹ and 0.03 μg

L^{-1} , while the LOD and LOQ of SFX detection were determined to be $0.016 \mu\text{g L}^{-1}$ and $0.05 \mu\text{g L}^{-1}$, respectively. These very low values of LOD clearly demonstrate the high sensitivity of the CeONC@GrO-based electrochemical sensor for the detection of these pollutants. The results offer a reliable analytical method for monitoring these pharmaceuticals in aqueous environments at required low levels. Additionally, Table 3.12 displayed the limit of detection (LOD) values obtained for CRP and SFX utilizing various materials. The findings of this investigation indicated that the LOD is either comparable to many other studies or perhaps much lower than those recorded in the literature.





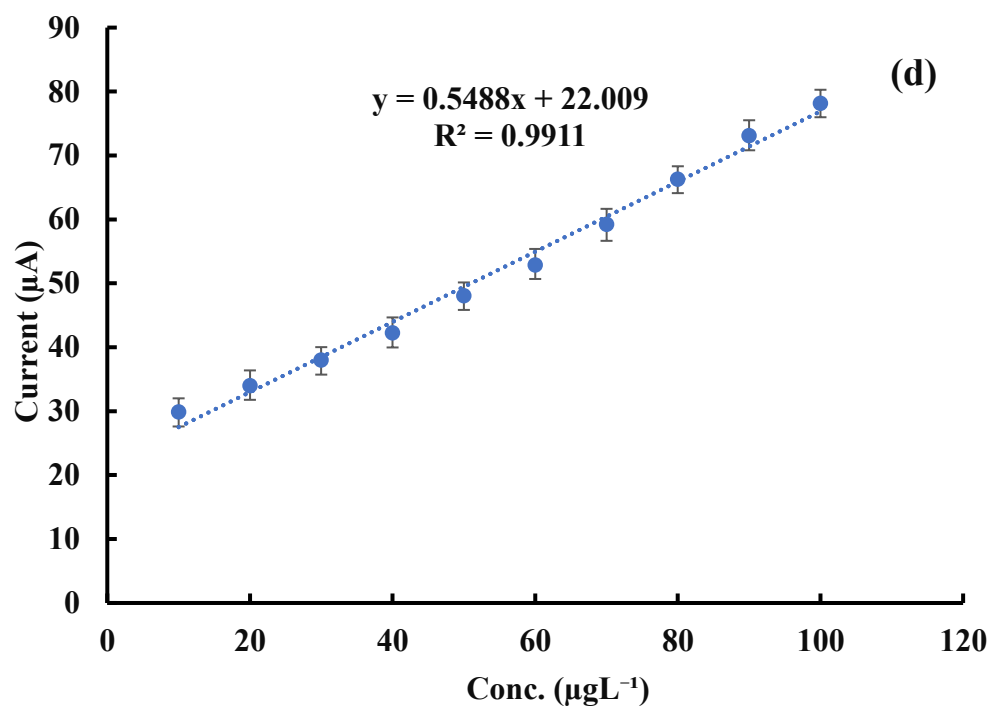


Figure 3.37. Differential pulse anodic stripping voltammograms of: (a) CRP, and (c) SFX at varied concentrations (10.0 to 100.0 $\mu\text{g/L}^{-1}$); and Calibration curves of anodic peak currents of CRP and SFX against: (b) CRP, and (d) SFX concentrations.

Table 3.12. Comparison of the CeONC@GrO material with other materials for CRP and SFX determination.

Material	Pollutant	pH	Concentration range (μM)	LOD (μM)	References
rGO-TiO ₂	CRP	7	0.1–900.0	0.036	(Anitha Devi et al., 2025)
rGO/NiCo-BTC MOFs	CRP	7	0.1-100.0	0.235	(Anitha Devi et al., 2025; Han et al., 2024)
AgNPs	CRP	7	0.0-80.0	0.265	(Batish & Rajput, 2023)
Short-MWNTs-COOH	CRP	7	0.3-229.0	0.049	(P. Zhang et al., 2019)
ZnWO ₄	CRP	7.4	30.0-500.0	0.32	(Shad et al., 2019)
NiMn ₂ O ₄ /CQD	CRP	7	0.5-143.0	0.471	(Nobari et al., 2025)
h-Ag-Cu ₂ O	CRP	7.4	0.5-150.0	0.16	(T.-A. Nguyen et al., 2025)
CeONC@GrO	CRP	7	0.0485-0.485	2.75x10⁻⁵	This work
SHL-GP/WP	SFX	7	5.0-100.0	0.40	(Melo Henrique et al., 2021)
rGNR	SFX	6	1.0-10.0	0.09	(Martins et al., 2021b)
GR-ZnO	SFX	7	1.0-220.0	0.40	(Yue et al., 2020b)
MIP-SiO ₂ @Nb ₂ CT _x	SFX	6	0.25-20.0	0.15	(H. Yang et al., 2025)
TFAB-COF@PANI	SFX	6.5	1.0-450.0	0.107	(Pan et al., 2023b)
Gpt/Al ₂ O ₃ /PLA	SFX	7	2.0-40.0	0.40	(de Faria et al., 2024; H. Yang et al., 2025)
GO/G/ITO	SFX	6	0.1–50.0	0.28	(Yeh et al., 2022)
CeONC@GrO	SFX	6	0.0485-0.485	6.32x10⁻⁵	This work

rGO-TiO₂: Titanium dioxide nanoparticles dispersed on a reduced graphene oxide.

rGO/NiCo-BTC MOFs : NiCo bimetallic MOFs-reduced graphene oxide composite thin film

AgNPs: Silver Nanoparticles

Short-MWNTs-COOH: Carboxylic short-chain multi-wall carbon nanotubes and silver nanoparticle

ZnWO₄: Zinc tungstate

NiMn₂O₄/CQD: NiMn₂O₄ spinel and carbon quantum dots

h-Ag-Cu₂O: Silver-Cuprous oxide nanohybrid

SHL-GP/WP: Shellac, a resin of natural origin, and graphite

rGNR: Reduced graphene nanoribbon

GR-ZnO: Graphene and zinc oxide nanorods

MIP-SiO₂@Nb₂CTx: Molecularly imprinted delaminating multi-layer tetramethylammonium hydroxide tetraethoxysilane

TFAB-COF@PANI: Covalent organic framework materials on polyaniline

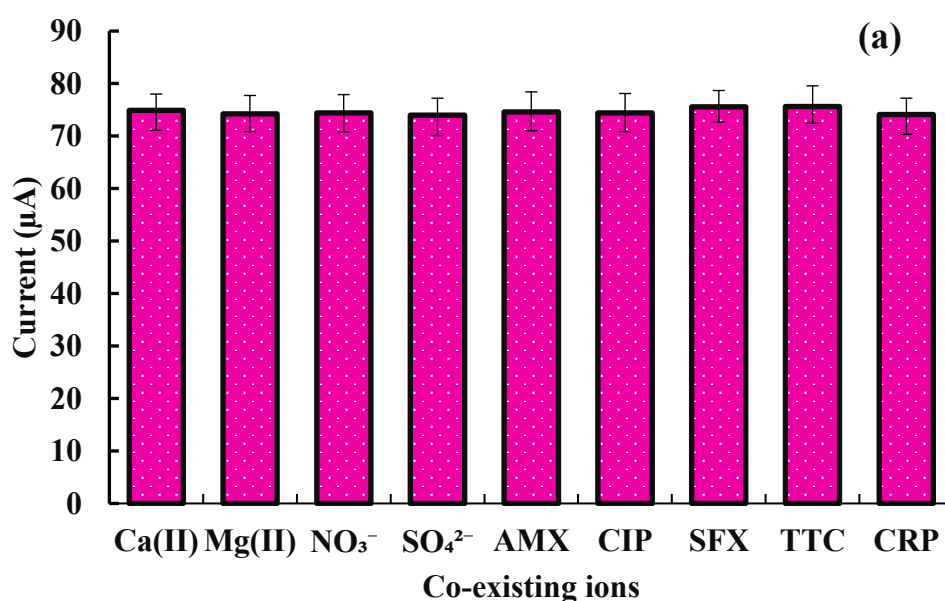
Gpt/Al₂O₃/PLA: Graphite/Aluminum oxide/polylactic acid

GO/G/ITO: Graphene oxide/graphene layered composite on indium tin oxide

3.4.6. Co-existing ion study on the detection of CRP and SFX

The selective detection of CRP and SFX in the presence of potentially co-existing species was systematically evaluated to assess the analytical reliability of the CeONC@GrO-modified electrode. The study included commonly occurring inorganic ions, such as calcium (Ca²⁺), magnesium (Mg²⁺), nitrate (NO₃⁻), and sulfate (SO₄²⁻), along with other pharmaceutical compounds, *viz.*, amoxicillin (AMX), ciprofloxacin (CFX), and tetracycline (TTC). In order to assess the electrode's selectivity towards these co-existing ions, the interferents were introduced at concentrations ten times higher (900.0 µg L⁻¹ for CRP and 300 µg L⁻¹ for SFX) than that of the target analytes (90.0 µg L⁻¹ for CRP and 30 µg L⁻¹ for SFX). Figure 3.38 (a&b) showed results in peak currents of CRP and SFX in the presence of these ions and pharmaceutical compounds. It is evident from the figure that these species caused only a negligible effect in the anodic peak current response for the CRP and SFX. The peak currents remained almost unchanged compared to those obtained in the absence of interferents, demonstrating that neither common inorganic ions nor drug molecules interfered with the detection of CRP and SFX. These results underscore the excellent selectivity of the CeONC@GrO GCE toward antibiotic detection, even in excessive presence of background species. The results clearly establish that the CeONC@GrO-modified electrode possesses high analytical specificity and robust anti-interference capacity, making it a reliable platform for CRP detection in complex real-world samples. Such

performance is particularly valuable for applications in pharmaceutical quality control, clinical diagnostics, and environmental monitoring, where samples often contain diverse ionic backgrounds and coexisting contaminants. In contrast, other electrochemical sensors for CRP and SFX detection have exhibited varied levels of selectivity. Another study, Fe_3O_4 was electrochemically deposited onto a glassy carbon electrode (GCE) and the selectivity studies demonstrated that inorganic ions at concentrations 80 times greater than chloramphenicol (CAP) and other antibiotics at fivefold higher concentrations did not appreciably influence the CAP detection (Giribabu et al., 2017). Similarly, the electrochemical performance of Fe_3O_4 doped cobalt (Co- Fe_3O_4 NS) supported on graphene oxide showed the selectivity with less than 5% variation in the CAP signal when subjected to metal ions and biomolecules as possible interferents (Nehru et al., 2021).



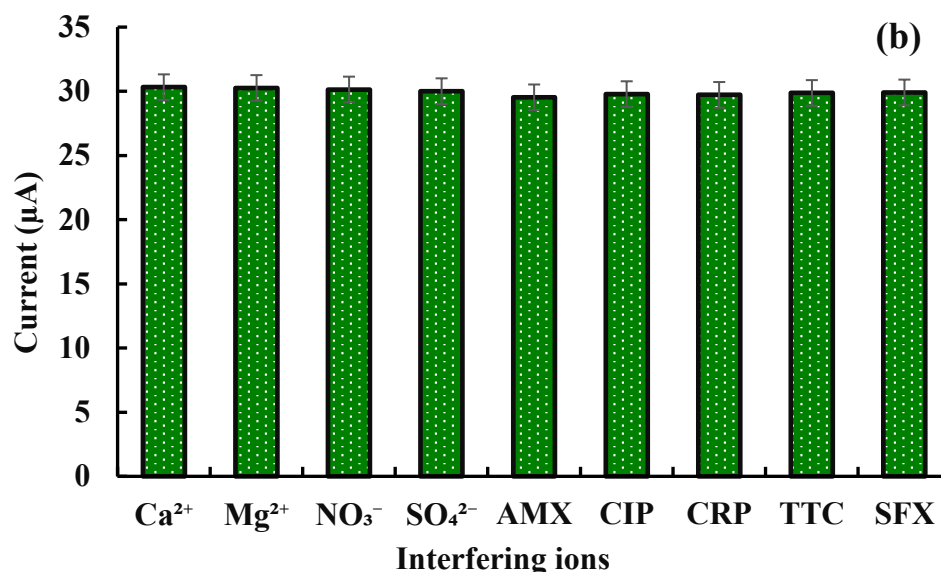


Figure 3.38. Effect of co-existing ions on electrochemical determination of: (a) CRP, and (b) SFX using CeONC@GrO modified electrode.

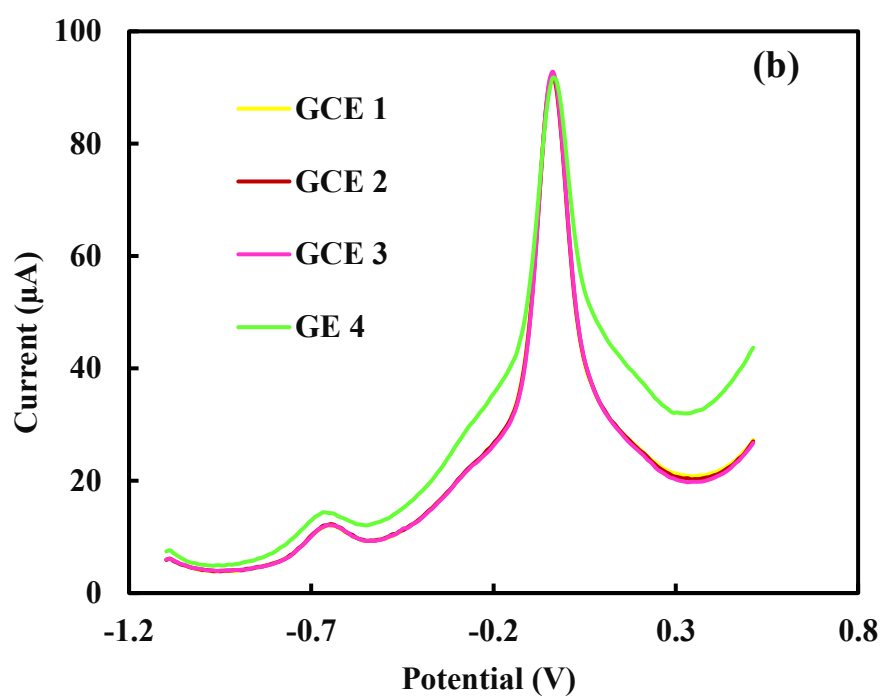
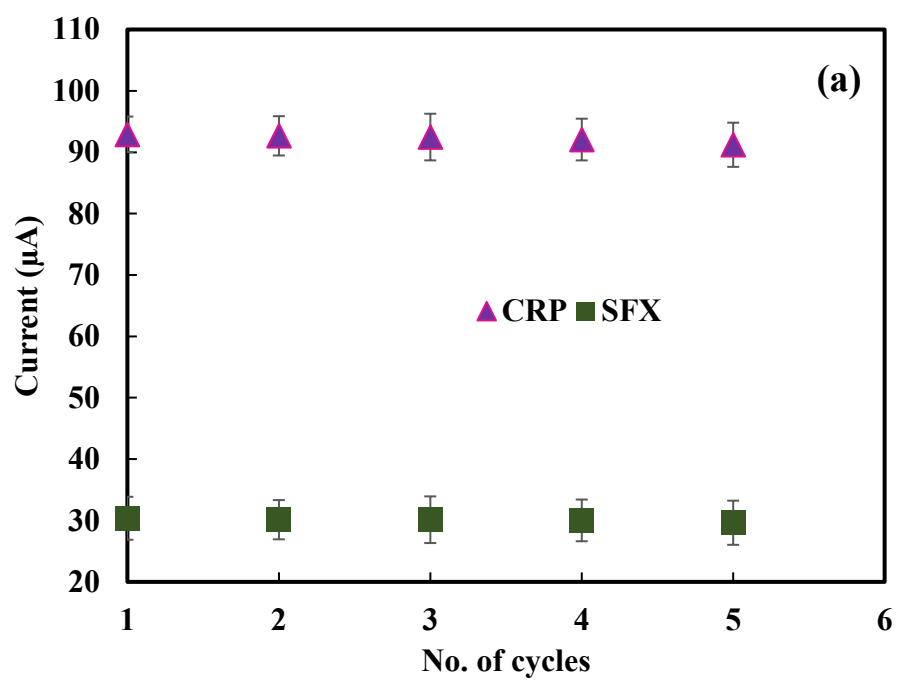
3.4.7. Repeatability, stability, and reproducibility of modified electrodes

The successive use of CeONC@GrO GCE for the detection of both CRP and SFX was investigated to assess the stability of the fabricated electrode. Five consecutive DPASV measurements were carried out using a freshly prepared analyte solution containing 90.0 $\mu\text{g L}^{-1}$ CRP (pH 7.0), and 30.0 $\mu\text{g L}^{-1}$ of SFX (pH 6.0), in 0.1 mol L^{-1} phosphate buffer, under optimized experimental conditions using the CeONC@GrO GCE. As depicted in Figure 3.39 (a), the anodic peak currents across the successive runs showed minimal variation, with both the peak shapes and intensities remaining unchanged. The relative standard deviation RSD (%) of the peak current was calculated, which was below 1%, confirming an excellent stability of the CeONC@GrO–GCE.

The reproducibility of the fabricated electrode was assessed by comparing the anodic peak current values obtained for several fabricated electrodes. Three glassy carbon electrodes modified with CeONC@GrO (designated as GCE 1, GCE 2, and

GCE 3) were prepared using the same fabrication method to evaluate the uniformity of electrode modification. Additionally, one gold electrode modified with CeONC@GrO (designated as GE 4) was tested to further validate the applicability of the nanocomposite across different electrode substrates. As shown in Figure 3.39 (b&c), the peak current responses recorded for CRP and SFX were highly consistent across all four electrodes, with only minor variations in intensity and no discernible changes in peak potential or shape. This uniformity demonstrates the reliability of the fabrication process in producing reproducible sensing interfaces.

Moreover, the stability of the CeONC@GrO-GCE was further examined by monitoring the current response toward CRP and SFX over five consecutive days under identical experimental conditions. As summarized in Table 3.13, the relative standard deviation RSD (%) for these measurements, performed at 24 hour intervals, was less than 1.5%. Moreover, the electrode retained approximately 96% for CRP and 98% for SFX of its initial current response after four days of continuous use (Figure 3.39 (d)), underscoring its excellent operational stability and durability. The minimal loss in current response confirmed that the electrode surface is largely resistant to fouling, passivation during repeated measurements. These findings demonstrated the sensor's long shelf life, which pointed to CeONC@GrO as a reliable sensing platform that produces accurate, reproducible, and long-term electrochemical detection of CRP and SFX. These results are in line with the prior work on Co-doped CeO₂ nanoparticles, which showed that over 95% of the initial peak currents for xanthine (XA), hypoxanthine (HXA), as well as uric acid (UA) were retained after one month, thereby affirming the remarkable durability of the fabricated electrodes (Lavanya et al., 2016).



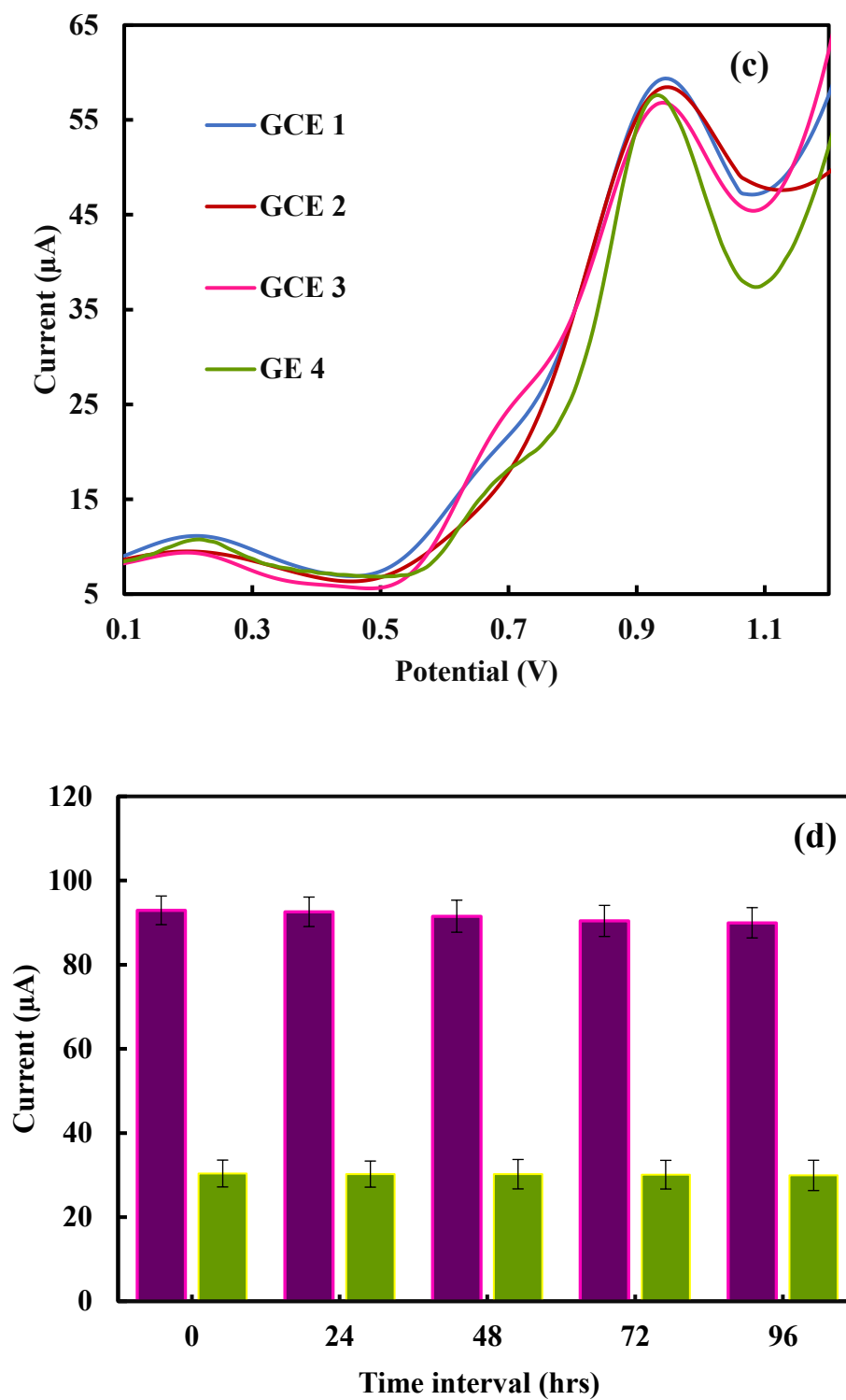


Figure 3.39. (a) Anodic current changes of CRP and SFX for 5 repetitive measurements; Effect of anodic current of: (b) CRP; (c) SFX using four different

CeONC@GrO fabricated electrodes; (d) Anodic current changes of CRP and SFX using CeONC@GrO GCE conducted at 24 hrs intervals.

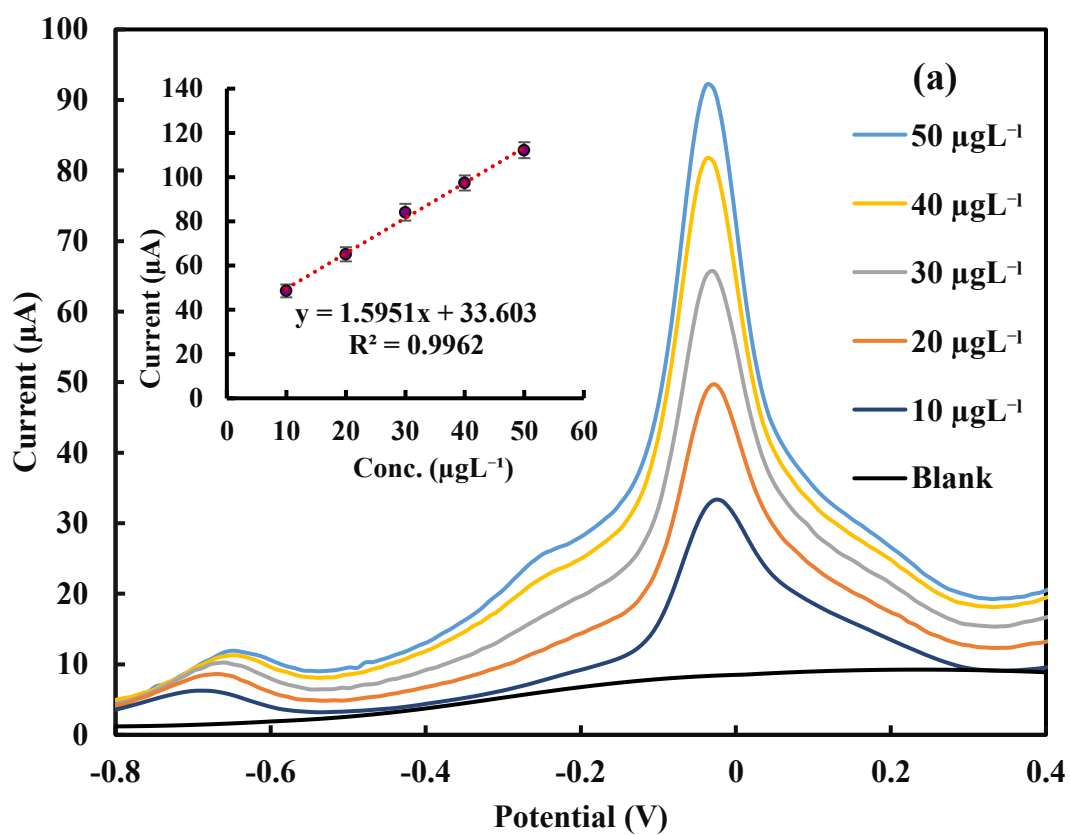
Table 3.13. Stability tests for CeONC@GrO GCE in the detection of CRP and SFX.

Time interval (hrs)	Repetition	RSD (%)	
		CRP	SFX
0	5	0.72	0.88
24	5	1.04	1.02
48	5	1.02	0.87
72	5	0.98	0.73
96	5	1.05	0.67

3.4.8. Real water analysis

To assess the practical applicability of CeONC@GrO in detecting pharmaceutical compounds, studies were performed utilizing actual environmental water samples. The outlet sewage water sample was collected from the sewage treatment plant, SIPMIU, Aizawl, Mizoram, India. The collected samples underwent initial filtration through a filter paper (pore size of 11 μm) to eliminate unwanted particulate matter. Further, physicochemical analyses were conducted to obtain the baseline quality of the water. Table 3.14 indicated that the water sample contained an increased concentration of inorganic carbon, possibly due to dissolved carbonate or bicarbonate ions. Furthermore, non-purgeable organic carbon (NPOC) assays revealed a concentration of 36.7 mgL^{-1} , indicating significant organic content, likely either from decomposing biological material or anthropogenic contamination. In contrast, the concentrations of prevalent anions such as SO_4^{2-} , PO_4^{3-} , and F^- were very low. Likewise, concentrations of potentially hazardous metals, such as Ni, Pb, Mn, and Fe, were at trace quantities. To evaluate the sensor's efficacy under actual settings, the

wastewater sample was spiked with known quantities of CRP and SFX (10.0 to 50.0 μgL^{-1}), prepared in a 0.1 molL^{-1} PhBs at optimized pH values. The electrochemical detection was performed utilizing the CeONC@GrO GCE under previously optimized voltametric conditions as illustrated in Figure 3.40 (a&b). Additionally, a strong linear correlation was obtained between the oxidative peak current values against the CRP or SFX concentrations (Cf Figure 3.40 Inset (a&b)). The straight-line correlation between the oxidized current of CRP or SFX and their concentrations showed the promise of CeONC@GrO GCE in the quantitative determination of CRP and SFX in natural water assessment. The regression equation for CRP and SFX was obtained as: $y (\text{CRP}) = 1.5951 \times (\mu\text{gL}^{-1}) + 33.603$, and $y (\text{SFX}) = 0.5744 \times (\mu\text{gL}^{-1}) + 22$, with R^2 values of 0.996 and 0.995 for CRP and SFX, respectively. Moreover, Table 3.15 showed the recovery percentages of the CRP and SFX under the experimental conditions. The method exhibited very high recovery rates, ranging from 93.14 to 105.39% for CRP and 94.01 to 105.67% for SFX, affirming its accuracy and reliability of detection in real water samples. Therefore, the findings indicate that the synthesized CeONC@GrO GCE exhibits both sensitivity and selectivity, which makes it effective for detecting trace concentrations of pharmaceutical residue, *viz.*, CRP and SFX, in intricate environmental water matrices. Polyethyleneimine-functionalized reduced graphene oxide coated onto the gold nanocubes was utilized for the electrochemical determination of chloramphenicol (CAP) in natural water samples, which showed high recovery rates ranging from 97.70 to 109.36% (M. Lu et al., 2021). Similarly, sulfamethoxazole (SFX) was detected in real water samples using graphene incorporated with ZnO nanorods (GR-ZnO/GCE), achieving high recovery values (Yue et al., 2020).



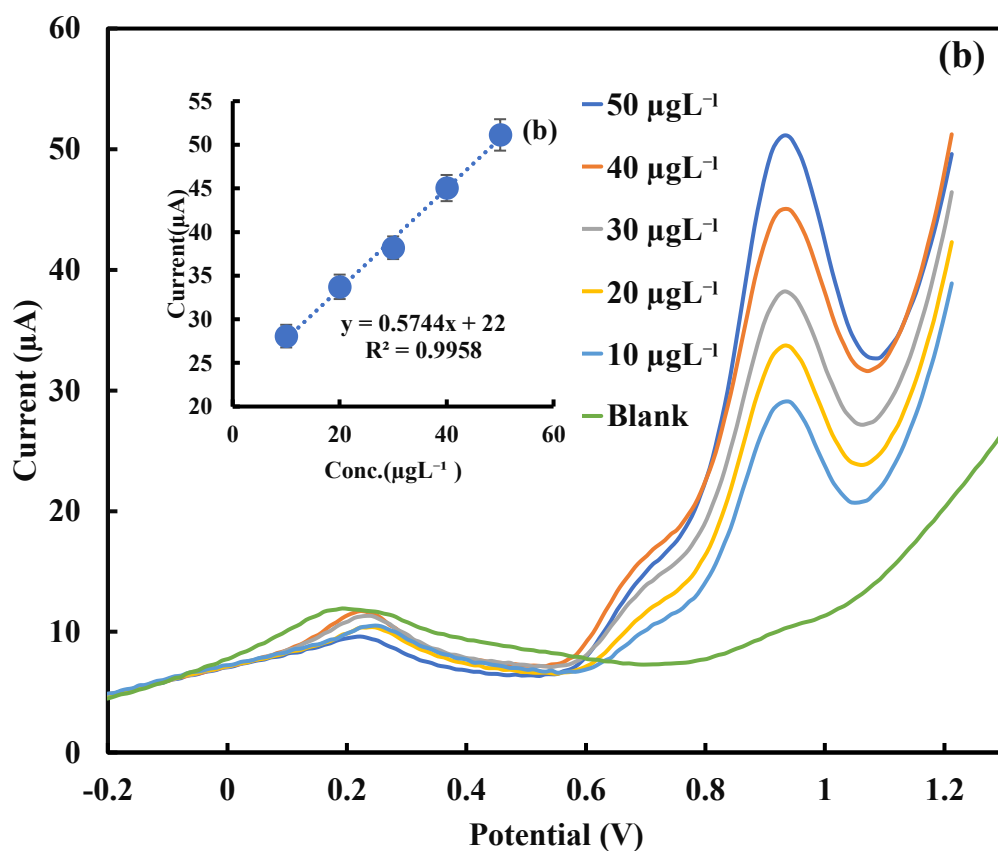


Figure 3.40. Differential pulse anodic stripping voltammograms of: (a) CRP at varied concentrations (10.0 to 50.0 µg/L⁻¹) [Inset: Calibration line obtained between oxidized peak current and CRP concentration]; (b) SFX at varied concentrations (10.0 to 50.0 µg/L⁻¹) obtained using CeONC@GrO GCE in sewage water samples; [Inset: Calibration line obtained between oxidized peak current and SFX concentration].

Table 3.14. Physicochemical parameters of sewage water (outlet) sample, SIPMIU, Aizawl, Mizoram, India.

Parameter	SIPMIU
pH	7.2
Oxidation Reduction Potential (Mv)	164.2
Conductivity EC ($\mu\text{S/cm}$)	820
Resistivity ($\text{M}\Omega\text{cm}$)	0.0012
Total Dissolved Solid (ppm)	409
Salinity(PSU)	0.44
NO_3^-	133 mgL^{-1}
SO_4^{2-}	29 mgL^{-1}
PO_4^{3-}	2.5 mgL^{-1}
F^-	2.15 mgL^{-1}
Al^{3+}	0.06 mgL^{-1}
Ni^{2+}	0.535 mgL^{-1}
Mg^{2+}	23 mgL^{-1}
Ca^{2+}	147 mgL^{-1}
Pb	0.2142 mgL^{-1}
Mn	0.054 mgL^{-1}
Fe	BDL
IC	31.9 mgL^{-1}
NPOC	36.7 mgL^{-1}

BDL: Below detection limit

Table 3.15. Recovery percentage of CRP and SFX in sewage water (outlet) samples.

Spiked concentration of analyte (μgL^{-1})	Found (μgL^{-1}) $\pm 3\sigma$		Recovery (%)	
	CRP	SFX	CRP	SFX
10	9.31 $\pm$ 0.69	10.56 $\pm$ 0.56	93.14	105.67
20	19.69 $\pm$ 0.31	20.40 $\pm$ 0.4	98.47	102.01
30	31.61 $\pm$ 1.61	28.20 $\pm$ 1.8	105.39	94.01
40	39.91 $\pm$ 0.09	40.11 $\pm$ 0.11	99.78	100.27
50	49.20 $\pm$ 0.8	50.71 $\pm$ 0.71	98.41	101.42

3.4.9. Conclusion

The CeONC@GrO nanocomposite-modified glassy carbon electrode (GCE) was employed for the sensitive electrochemical detection of two antibiotics, *viz.*, chloramphenicol (CRP) and sulfamethoxazole (SFX). Cyclic voltammetry studies revealed distinct redox behaviour of these pharmaceuticals. The CRP exhibited a pair of redox peaks at approximately 0.05 V and -0.07 V, whereas SFX displayed redox at 1.14 V and 0.55 V. Compared with the bare GCE, the CeONC@GrO-GCE showed a substantially enhanced electrochemical response, underscoring the catalytic activity of the nanocomposite. The optimal pH, accumulation potential, and accumulation time are 7.0, -1.1 , and 120 s, respectively, for CRP. Similarly, the optimized pH, accumulation potential, and accumulation time are 6.0, -1.2 V, and 210 s, respectively, for SFX. Under these conditions, the regression equations for CRP and SFX were obtained as: y (CRP) = $0.985 x$ (μgL^{-1}) + 14.014, and y (SFX) = $0.5488 x$ (μgL^{-1}) + 22.009 with R^2 values of 0.995 and 0.99 for CRP and SFX, respectively. Moreover, the sensor achieved remarkably low detection limits of $0.009 \mu\text{gL}^{-1}$ for CRP and $0.016 \mu\text{gL}^{-1}$ for SFX and a limit of quantification of 0.030 and $0.054 \mu\text{gL}^{-1}$ for CRP and SFX, respectively. Selectivity tests demonstrated that common co-existing ions, even at concentrations ten times higher than the target analytes, showed negligible interference, confirming the robustness of the detection method using the CeONC@GrO-GCE. Furthermore, the CeONC@GrO-GCE displayed minimal variation in anodic peak currents across 5 successive measurements, and independently, four fabricated electrodes confirmed the uniformity and reliability of

the electrode performance. Furthermore, the electrode showed high shelf life even after 96 hrs of successive operations, having 96% and 98% of recovery with RSD (%) below 1.5%. The practical applicability of the CeONC@GrO GCE showed high recovery rates ranging from 93.14% to 105.39% for CRP and 94.01% to 105.67% for SFX using the sewage treatment plant effluent water. Collectively, these findings confirm that the CeONC@GrO-modified electrode exhibited strong affinity, high selectivity, and excellent sensitivity toward CRP and SFX, making them highly efficient for trace-level monitoring of pharmaceutical contaminants in complex aqueous environments.

3.5. PHOTO-FENTON LIKE DEGRADATION OF CHLORAMPHENICOL AND SULFAMETHOXAZOLE UNDER VISIBLE LIGHT

3.5.1. Modelling and interaction of two factors in the photo-Fenton-like degradation (PFD) process using Response Surface Methodology (RSM)

The correlation between the response variables, i.e., A: pH; B: Time; and C: Concentration of CRP and SFX and their respective degradation efficiencies was examined using the RSM based on a Central Composite Design (CCD). The results of the CCD experiments, including both the actual and predicted performances of CeONC@GrO, as well as the Analysis of Variance (ANOVA) results for CRP degradation, are presented in Tables 3.16 and 3.17, while Tables 3.18 and 3.19 show the corresponding data for SFX. The experimental design involved varying the pH from 3-9, reaction time from 60-120 min, and antibiotic concentrations between 200-1000 μgL^{-1} , with a fixed H_2O_2 concentration of 0.2 mLL^{-1} and catalyst dosage below the toxicity threshold (100 mgL^{-1}). The resulting degradation efficiency responses, expressed in terms of the coded factors, are represented in equation (3.3) for CRP and equation (3.4) for SFX.

$$Y = 69.74 - 7.64A + 8.61B - 4.37C + 1.51AB + 0.9613AC - 0.7612BC - 11.30A^2 - 7.16B^2 + 0.7264C^2 \quad \dots(3.3)$$

$$Y = 42.06 - 7.48A + 8.96B - 8.33C - 5.01AB + 1.82AC - 0.1225BC + 7.43A^2 + 6.59B^2 - 3.58C^2 \quad \dots(3.4)$$

ANOVA was applied to evaluate the statistical significance and adequacy of the quadratic regression model, as well as to explore the individual and interactive

effects of various parameters on the removal efficiencies of the antibiotics. The Fisher test produced F-values of 1056.11 for CRP and 3077.36 for SFX, highlighting the strong influence of each factor and confirming the appropriateness of the selected regression model. Additionally, the p-value of 0.0001 for the removal of both CRP and SFX, being considerably lower than the 0.05 significance threshold, indicates the model's high statistical validity at a 95% confidence level and minimal likelihood of random error. The significance of each independent variable was further examined to determine its contribution to the overall response. The strong agreement between predicted and experimental degradation efficiencies was evident from the R^2 values of 0.9989 for CRP and 0.996 for SFX. Moreover, the adjusted R^2 values of 0.9980 and 0.993 for CRP and SFX, respectively, confirm the robustness of the model after accounting for insignificant factors. The adequate precision values of 111.69 (CRP) and 239.10 (SFX) further demonstrate the model's reliability, as values exceeding 4 are considered acceptable.

Table 3.16. Central composite design matrix with variables (A, B, and C), actual and predicted degradation percentage in the degradation of CRP.

Run No.	A: pH	B: Time (min)	C: Concentration (μgL^{-1})	CRP Removal (%) (Predicted)	CRP Removal (%) (Actual)
1	6	60	600	53.97	54.34
2	6	90	600	69.74	69.81
3	9	60	1000	31.59	31.44
4	6	90	600	69.74	69.89
5	3	120	200	72.84	72.77
6	6	120	600	71.19	71.66
7	6	90	600	69.74	68.96
8	3	60	200	57.11	57.22
9	6	90	1000	66.1	66.66
10	6	90	600	69.74	69.54
11	6	90	600	69.74	69.66
12	6	90	600	69.74	68.89

13	9	60	200	36.88	36.66
14	9	90	600	50.79	51.58
15	3	60	1000	47.97	47.86
16	9	120	1000	50.31	49.99
17	3	120	1000	60.65	60.66
18	6	90	200	74.84	75.12
19	9	120	200	58.65	58.55
20	3	90	600	66.08	66.14

Table 3.17. Results of the statistical analysis for the degradation of the CRP regression model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2850.46	9	316.72	1056.11	< 0.0001	significant
A-pH	584.15	1	584.15	1947.89	< 0.0001	
B-Time	741.49	1	741.49	2472.54	< 0.0001	
C-Concentration	191.06	1	191.06	637.08	< 0.0001	
AB	18.27	1	18.27	60.93	< 0.0001	
AC	7.39	1	7.39	24.65	0.0006	
BC	4.64	1	4.64	15.46	0.0028	
A ²	351.37	1	351.37	1171.67	< 0.0001	
B ²	141.12	1	141.12	470.58	< 0.0001	
C ²	1.45	1	1.45	4.84	0.0525	
Residual	3	10	0.2999			
Lack of Fit	2.07	5	0.414	2.23	0.1998	not significant
Pure Error	0.9287	5	0.1857			
Cor Total	2853.46	19				

Std. Dev.:	0.5476	R ² value:	0.9989
Mean:	60.87	Predicted R ² :	0.9958
Adequate Precision:	111.6964		

Table 3.18. Central composite design matrix with variables (A, B, and C), actual and predicted degradation percentage in the degradation of SFX.

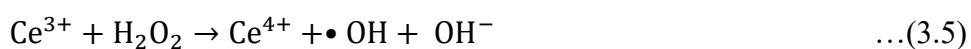
Run No.	A: pH	B: Time (min)	C: Concentration ($\mu\text{g L}^{-1}$)	SFX Removal (%) (Predicted)	SFX Removal (%) (Actual)
1	3	120	1000	63.67	63.54
2	6	90	600	42.06	42.42
3	9	90	600	42.01	41.86
4	3	90	600	56.98	56.82
5	9	120	1000	42.34	42.44
6	6	120	600	57.61	57.66
7	6	90	600	42.06	42.66
8	6	90	1000	30.15	29.99
9	3	120	200	84.23	84.33
10	9	60	200	47.45	47.66
11	3	60	200	56.05	56.02
12	9	60	1000	34.69	34.66
13	6	90	600	42.06	41.89
14	3	60	1000	35.98	36.19
15	6	90	600	42.06	41.72
16	6	90	600	42.06	42.18
17	6	60	600	39.69	39.33
18	6	90	600	42.06	42.12
19	6	90	200	46.81	46.66
20	9	120	200	55.59	55.46

Table 3.19. Results of the statistical analysis for the degradation of CRP regression model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2833.42	9	314.82	3077.36	< 0.0001	significant
A-pH	559.8	1	559.8	5471.99	< 0.0001	
B-Time	802.28	1	802.28	7842.14	< 0.0001	
C-Concentration	694.06	1	694.06	6784.28	< 0.0001	
AB	200.8	1	200.8	1962.8	< 0.0001	
AC	26.64	1	26.64	260.45	< 0.0001	
BC	0.12	1	0.12	1.17	0.3041	
A ²	151.91	1	151.91	1484.86	< 0.0001	
B ²	119.33	1	119.33	1166.42	< 0.0001	
C ²	35.3	1	35.3	345.04	< 0.0001	
Residual	1.02	10	0.1023			
Lack of Fit	0.4371	5	0.0874	0.7459	0.6222	not significant
Pure Error	0.5859	5	0.1172			
Cor Total	2834.44	19				
Std. Dev.:	0.3198			R ² value:	0.9996	
Mean:	47.28			Predicted R ² :	0.9982	
Adequate Precision:	239.1062					

The pH of the solution and the reaction time were identified as the primary factors affecting the degradation of both CRP and SFX, as shown in Figure 3.41 (a & b). Among the variables studied, the one exhibiting the greatest deviation from the reference point was considered the most significant. The effects of the independent parameters A, B, and C on the experimental removal efficiencies of the antibiotics were further examined through 3D surface plots. Figure 3.42 (a & d) presents the interaction between initial pH and reaction time, demonstrating that degradation efficiency increased up to an optimal point for both parameters, achieving maximum predicted removals of 77.04% for CRP at pH 6.0 and 84.22% for SFX at pH 3.0, with

a reaction duration of 120 min. The analysis revealed a strong correlation between pH and reaction time in the photocatalytic Fenton-like degradation (PFD) of the antibiotics. The results suggest that cerium-based catalysts effectively promote antibiotic degradation under acidic or slightly acidic conditions. In the case of CRP, with a reported pK_a of 5.5, the reaction was primarily governed by non-electrostatic interactions, minimizing surface repulsion effects (Khelifa et al., 2023). Hence, the antibiotic is efficiently adsorbed on the reactive sites of the CeONC@GrO for degradation (Zhao et al., 2016). Furthermore, unlike the traditional Fenton process, Ce-based catalysts are capable of maintaining redox cycling even under near-neutral pH conditions (*Cf* Equation (3.5)). In contrast, for SFX, the degradation efficiency was increased at lower pH levels, which is attributed to the enhanced formation of reactive species and more favourable surface interactions. The generation of highly reactive $\bullet OH$ radicals in the photo-Fenton-like system is more pronounced under acidic conditions, while the likelihood of $\bullet OH$ scavenging also increases in the lower pH values (Ralte et al., 2025). As a result, the efficiency is lower at higher pH values in the PFD of SFX. As a result, the efficiency is lower at higher pH values in the PFD of SFX. Furthermore, the higher reaction time showed a positive impact on the degradation of these antibiotics [*Cf* Figure 3.42 (a, c, d & f)]. The results from the prolonged exposure of reactive species and prolonged interaction between the catalyst and the antibiotic molecules caused an enhanced breakdown of these compounds and their intermediates (Mousavi et al., 2025).



Additionally, the influence of antibiotic concentration on their degradation was also examined. For both CRP and SFX, an increase in concentration exhibited an adverse effect on the photocatalytic Fenton-like degradation (PFD) process [*Cf* Figure 3.42 (b, c, e & f)]. The observed decrease in degradation efficiency with an increase in concentrations of CRP and SFX is ascribed to the reduced generation of oxidizing species, suggesting that the available $\bullet OH$ radicals are insufficient to effectively oxidize the higher number of antibiotic molecules present in the system (Sadeghi et al., 2019). At lower concentrations of CRP and SFX, a greater number of active sites on the catalyst surface are accessible for adsorption, enabling the antibiotic molecules to attach effectively and achieve higher degradation efficiency. Conversely, as the

concentrations of CRP and SFX increased, the number of available active sites became insufficient relative to the larger number of antibiotic molecules, resulting in a decrease in removal efficiency (Coin et al., 2024).

3.5.2. Identification of reactive radical

Experiments were conducted to determine the primary reactive species responsible for the degradation of CRP and SFX during the photocatalytic Fenton-like (PFD) process. As illustrated in Figure 3.42 (g), the removal efficiencies of CRP and SFX were evaluated in the presence of various radical scavengers. A significant reduction in antibiotic degradation was observed when isopropanol, a known hydroxyl radical ($\bullet\text{OH}$) scavenger (Dihingia et al., 2023), was introduced into the reaction system. Additionally, NaHCO_3 , also known to scavenge $\bullet\text{OH}$ radical, moderately reduced the degradation efficiency of CRP and SFX (Dihingia et al., 2025). These results highlight that $\bullet\text{OH}$ serves as a primary reactive species in the PFD of CRP and SFX.

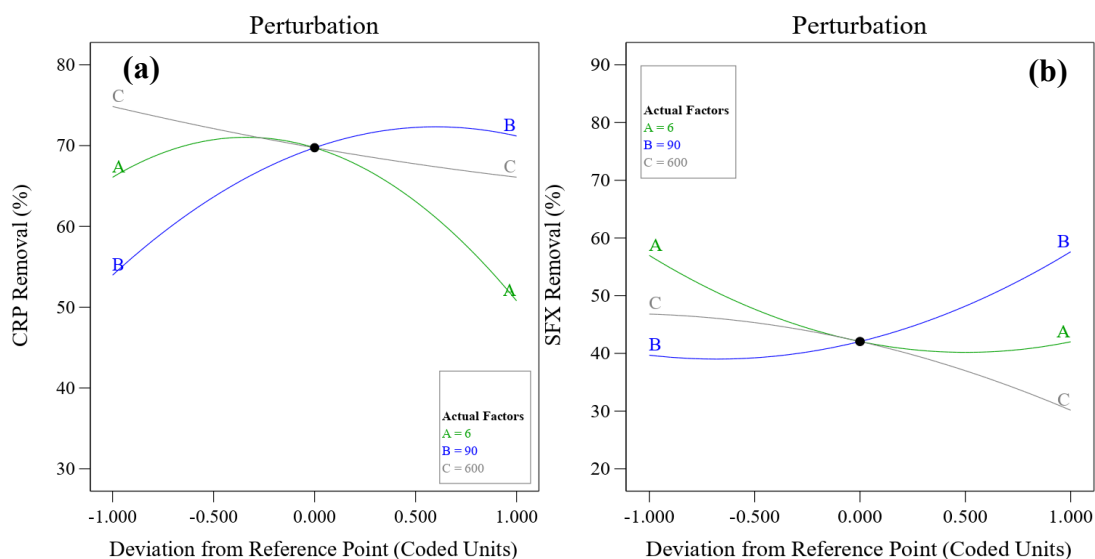
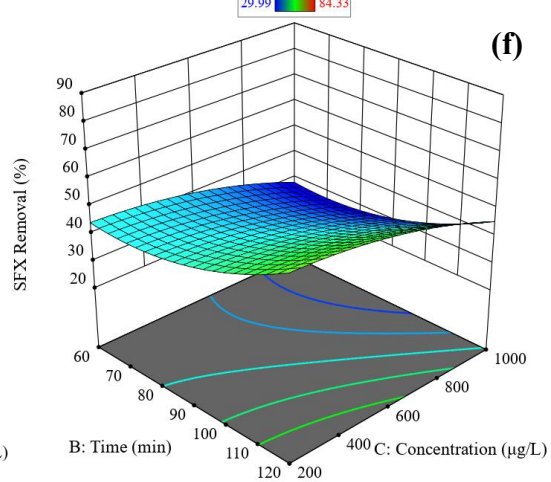
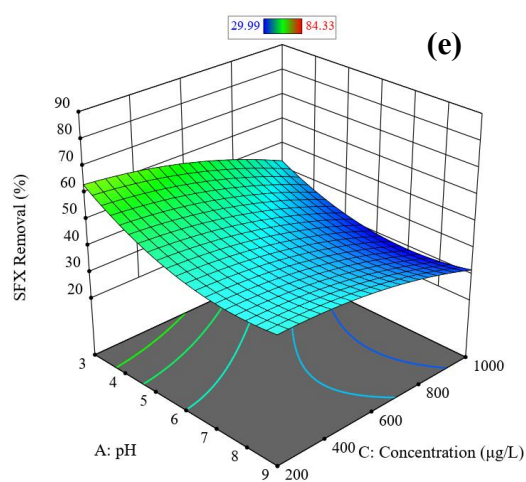
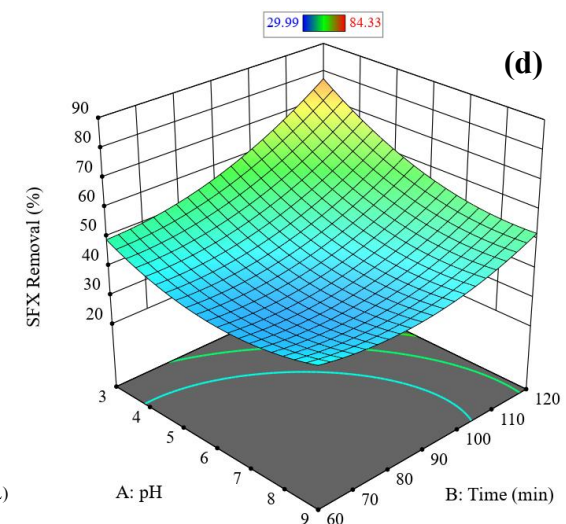
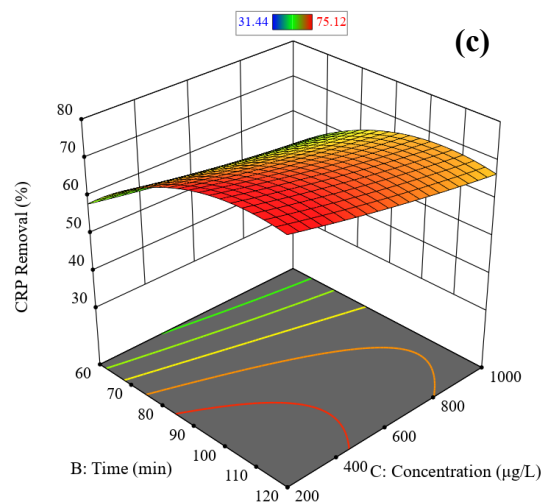
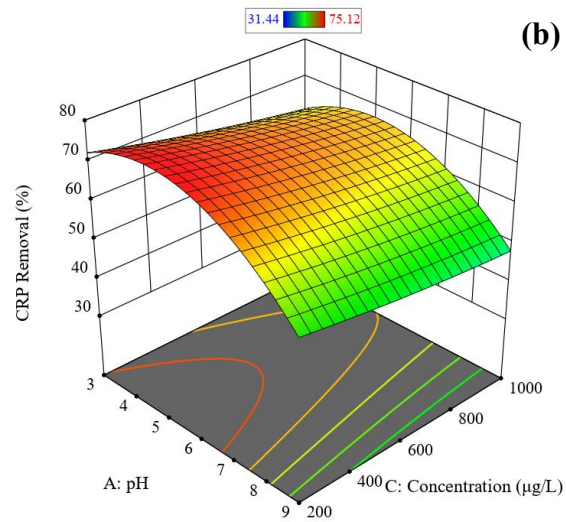
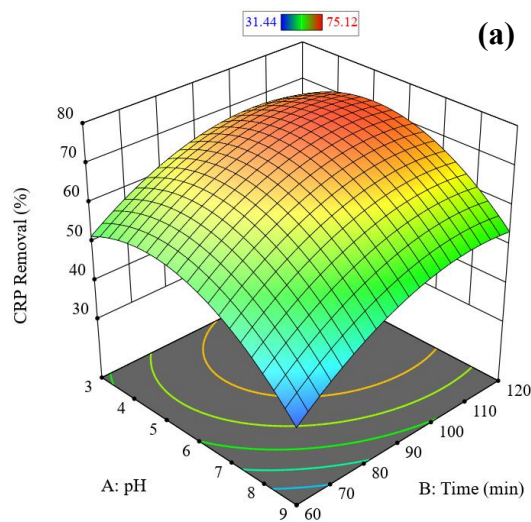


Figure 3.41. Variables with a substantial impact on the degradation process on the perturbation plot of: (a) CRP; and (b) SFX.



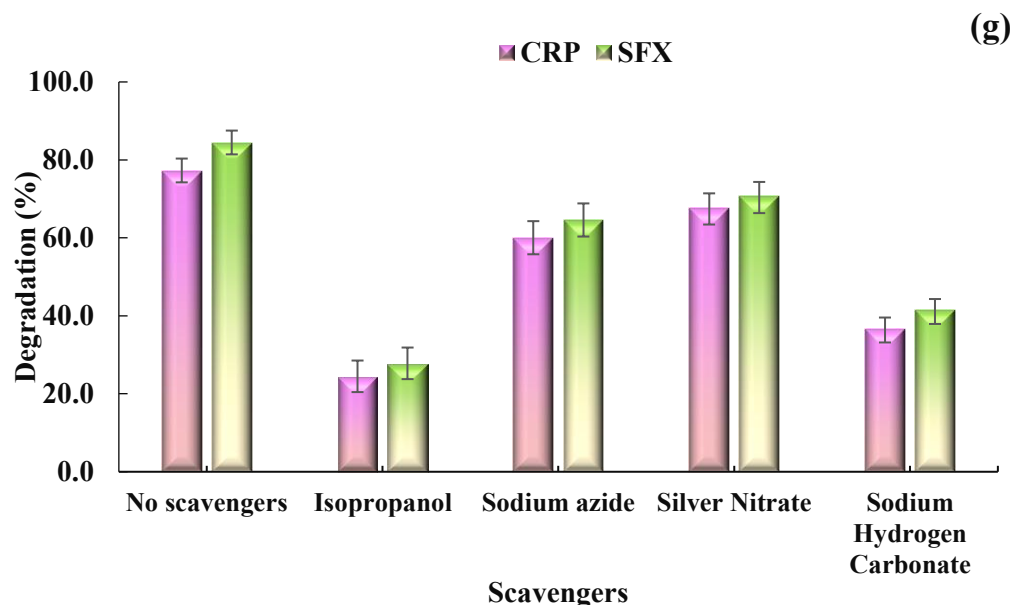


Figure 3.42. Degradation efficiency of CRP in a 3D surface plot between two factors of: (a) pH and time; (c) pH and CRP concentration; and (d) time and concentration; degradation efficiency of SFX in a 3D surface plot between two factors of: (d) pH and time; (e) pH and CRP concentration; and (f) time and concentration under visible light [H_2O_2 : 0.2 mL/L]; (g) Degradation of CRP and SFX in the presence of radical scavengers [SFX: pH = 6; H_2O_2 = 0.2 mL/L; catalyst dosage = 100 mgL^{-1} ; concentration = 2 mgL^{-1} ; CRP: pH = 3; H_2O_2 = 0.2 mL/L; catalyst dosage = 100 mgL^{-1} ; concentration = 2 mgL^{-1}].

3.5.3. Degradation mechanism and toxicity of by-products

Density Functional Theory (DFT) calculations were carried out to model the electronic structures of CRP and SFX, with the objective of identifying the atomic sites most vulnerable to radical attack, specifically the electrophilic and nucleophilic regions (Salahshoori et al., 2024). Additionally, the Hirshfeld surface analysis was conducted to assess the electron density distribution across individual atoms for the CRP and SFX molecules (Akhileshwari et al., 2022). The Fukui functions were then computed for the neutral, cationic, and anionic states of both antibiotics, where elevated values of f^+ , f^- , and f^0 highlight the areas that are most reactive towards nucleophiles, electrophiles, and radical attacks, respectively (Vanlalthmingmawia et al., 2025). The computed Fukui index values for CRP and SFX are presented in Tables

3.20 and 3.21, respectively. The electronic structures of CRP and SFX were also examined through their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states. Atoms with higher electron density in the HOMO region were found to be more prone to oxidation, as these sites readily donate electrons during the reaction process (Vanlalhmingmawia et al., 2025). Conversely, atoms exhibiting higher electron density in the LUMO demonstrate increased susceptibility to reduction, as these locations can readily accept electrons. Nevertheless, the change in Gibbs free energy (ΔG) was also calculated to show the viability of the process.

Table 3.20 Fukui index of CRP.

Atom	f^-	f^+	f^0
1(C)	0.0108	0.0602	0.0355
2(C)	0.0082	0.0374	0.0228
3(C)	-0.0039	0.0607	0.0284
4(C)	0.0103	0.0369	0.0236
5(C)	0.0111	0.0639	0.0375
6(C)	0.0142	0.0439	0.0291
7(H)	0.0066	0.032	0.0193
8(H)	0.006	0.0211	0.0135
9(H)	0.0072	0.0215	0.0144
10(H)	0.0064	0.033	0.0197
11(C)	0.0504	0.0048	0.0276
12(C)	0.0254	0.0091	0.0172
13(N)	0.0042	0.1288	0.0665
14(O)	0.0098	0.1841	0.0969
15(O)	0.01	0.1838	0.0969
16(N)	0.0169	0.0005	0.0087
17(C)	0.0185	0.0021	0.0103
18(C)	0.0049	0.0006	0.0028
19(O)	0.0434	0.003	0.0232

20(Cl)	0.0206	0.0039	0.0123
21(Cl)	0.0202	0.0039	0.0121
22(C)	0.3708	0.0119	0.1914
23(O)	0.1183	0.0046	0.0615
24(O)	0.0508	0.012	0.0314
25(H)	0.0174	0.0059	0.0116
26(H)	0.0583	0.0047	0.0315
27(H)	0.0071	0.0013	0.0042
28(H)	0.0184	0.0033	0.0109
29(H)	0.0187	0.0128	0.0158
30(H)	0.039	0.0082	0.0236

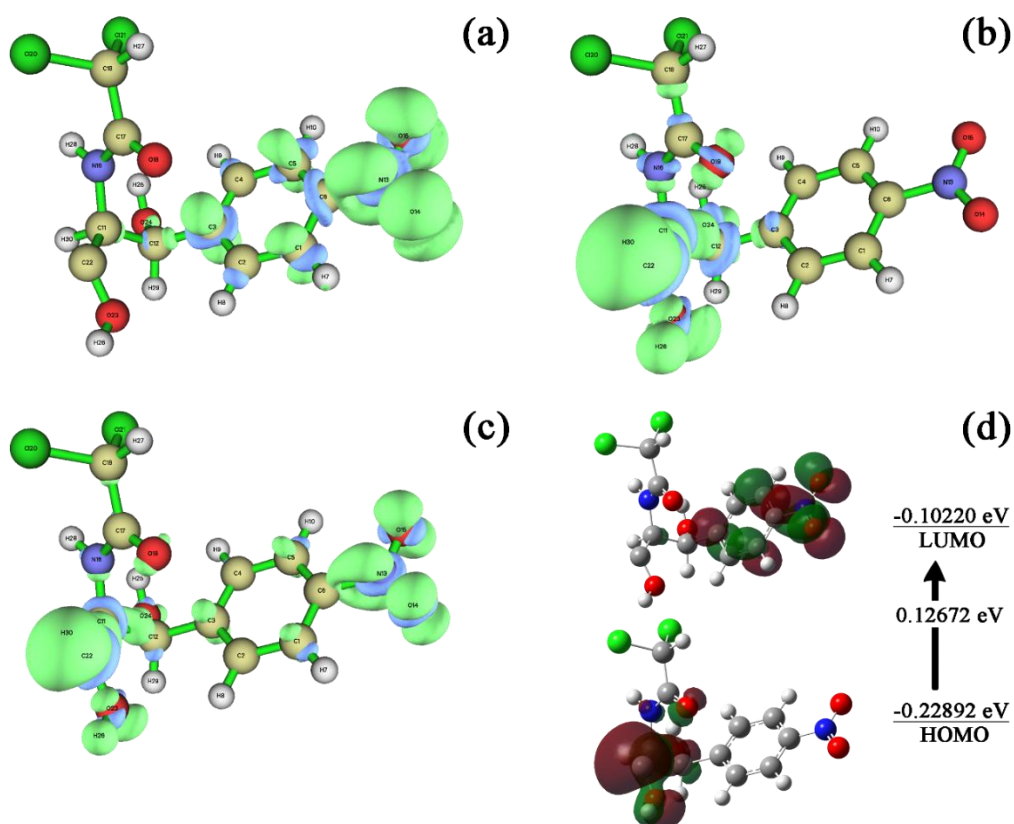
Table 3.21 Fukui index of SFX.

Atom	f^-	f^+	f^0
1(C)	0.077	0.0705	0.0737
2(C)	0.0614	0.0728	0.0671
3(C)	0.0687	0.0545	0.0616
4(C)	0.038	0.1046	0.0713
5(C)	0.0711	0.0469	0.059
6(C)	0.0423	0.0427	0.0425
7(H)	0.0325	0.0347	0.0336
8(H)	0.0307	0.0295	0.0301
9(H)	0.0226	0.0447	0.0336
10(H)	0.0252	0.0293	0.0273
11(N)	0.143	0.0455	0.0942
12(H)	0.0461	0.0244	0.0352
13(H)	0.0462	0.022	0.0341
14(S)	0.046	0.1214	0.0837
15(O)	0.045	0.0472	0.0461
16(O)	0.1228	0.0567	0.0898

17(N)	0.0198	0.0251	0.0224
18(H)	0.0122	0.0184	0.0153
19(C)	0.0051	0.0162	0.0106
20(C)	0.005	0.01	0.0075
21(C)	0.0055	0.0127	0.0091
22(O)	0.0091	0.0172	0.0131
23(N)	0.0135	0.0277	0.0206
24(C)	0.002	0.0044	0.0032
25(H)	0.0018	0.0043	0.0031
26(H)	0.0019	0.0041	0.003
27(H)	0.0016	0.0034	0.0025
28(H)	0.0042	0.0091	0.0066

The Fukui function analysis revealed that, in CRP, the atoms most susceptible to nucleophilic attack are 14(O) (0.1841), 15(O) (0.1838), 13(N) (0.1288), 5(C) (0.0639), and 3(C) (0.0607), as illustrated in Figure 3.43(a). As shown in Figure 3.43(b), the atoms most reactive toward electrophilic attack include 22(C) (0.3708), 23(O) (0.1183), 16(N) (0.0583), 24(O) (0.0508), and 11(C) (0.0504). Meanwhile, Figure 3.43(c) indicates that the preferred sites for radical attack are 22(C) (0.1914), 14(O) (0.0969), 15(O) (0.0969), 13(N) (0.0665), and 23(O) (0.0615). The Mayer bond order analysis further showed that the bonds between 22(C)–23(O), 13(N)–14(O), and 13(N)–15(O) exhibited the lowest bond order values, implying these bonds are the most likely to undergo cleavage. Based on the frontier molecular orbital (FMO) model, the HOMO and LUMO energies for CRP were -0.22892 eV and -0.10220 eV, respectively, with an energy gap (ΔE) of 0.12672 eV. The HOMO electron density mapping (Figure 3.43d) indicated that the carbonyl group in CRP is the most oxidation-prone site. On the other hand, for SFX, the atoms most reactive toward nucleophilic attack were identified as 14(S) (0.0705), 4(C) (0.1046), 2(C) (0.0728), 1(C) (0.0705), and 16(O) (0.0567), as depicted in Figure 3.43(e). The atoms most vulnerable to electrophilic attack, shown in Figure 3.43(f), include 11(N) (0.1430), 16(O) (0.1228), 1(C) (0.0770), 5(C) (0.0711), and 3(C) (0.0687). Similarly, the sites

most prone to radical attack were 11(N) (0.0942), 16(O) (0.0898), 14(S) (0.0837), 1(C) (0.0737), and 4(C) (0.0713), as presented in Figure 3.43(g). According to the FMO analysis, SFX exhibited HOMO and LUMO energies of -0.22221 eV and -0.03464 eV, respectively, with an energy gap (ΔE) of 0.18757 eV. The HOMO electron density distribution, shown in Figure 3.43(h), suggests that the phenolic group in SFX is particularly prone to electron donation.



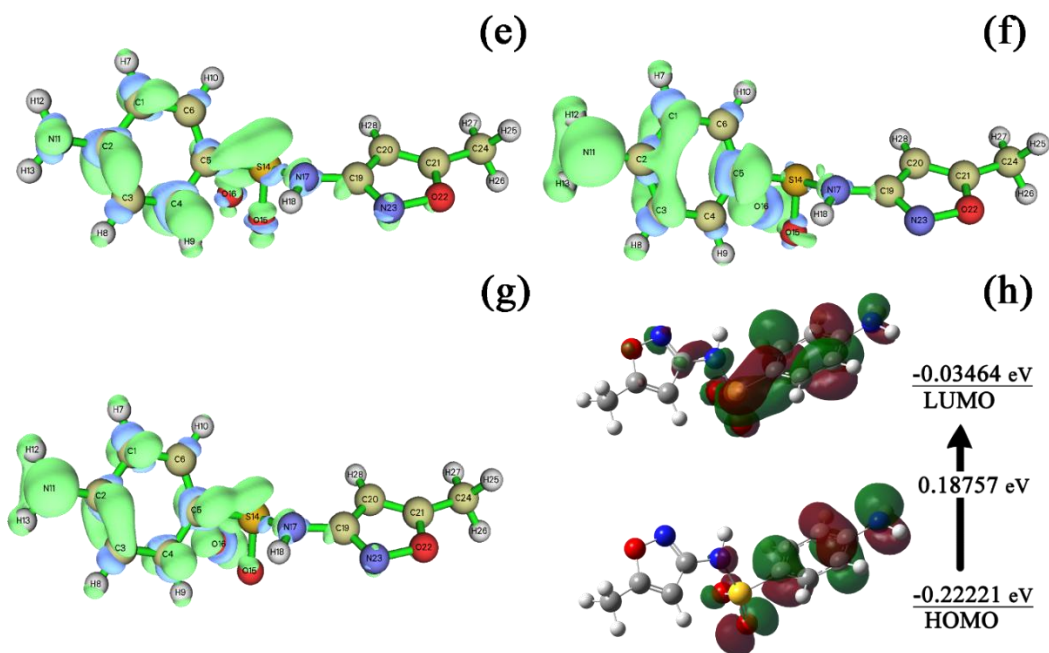


Figure 3.43. CRP Fukui values of: (a) f^+ , (b) f^- , and (c) f^0 indices; (d) HOMO and LUMO distribution of CRP; SFX Fukui values of: (e) f^+ , (f) f^- , and (g) f^0 indices; (h) HOMO and LUMO distribution of SFX.

During the degradation process, the parent compound CRP was first attacked by $\bullet\text{OH}$ radicals, resulting in the cleavage of the N–C bond within the benzene ring and the formation of intermediate C1 ($m/z = 227$), as supported by the f^0 calculation [see Figure 3.43(c)], where the 23(O)–26(H) bond undergoes radical attack. This step is thermodynamically favorable, as evidenced by a low Gibbs free energy change ($\Delta G = -3.3 \times 10^5 \text{ kJmol}^{-1}$). The intermediate C1 subsequently converts into C2 ($m/z = 197$) through C–N bond cleavage ($\Delta G = -2.6 \times 10^6 \text{ kJmol}^{-1}$). The negative ΔG values indicate that these transformations proceed spontaneously under ambient conditions. Alternatively, CRP can undergo oxy-dehydrogenation, producing intermediate C4 ($m/z = 319$; $\Delta G = -1.1 \times 10^4 \text{ kJmol}^{-1}$) due to the electrophilic attack of $\bullet\text{OH}$ radicals (f^0), as discussed earlier. Further dehydration of C4 leads to the formation of C5 ($m/z = 300$; $\Delta G = -1.7 \times 10^5 \text{ kJmol}^{-1}$). The intermediates C2 and C5 are subsequently oxidized into low-molecular-weight compounds, including C3 ($m/z = 122$), C6 ($m/z = 126$), and C7 ($m/z = 96$). These smaller intermediates then undergo additional oxidation steps, where $\bullet\text{OH}$ radicals promote ring-opening reactions to form short-chain organic acids. Ultimately, these degradation products are further oxidized and mineralized into

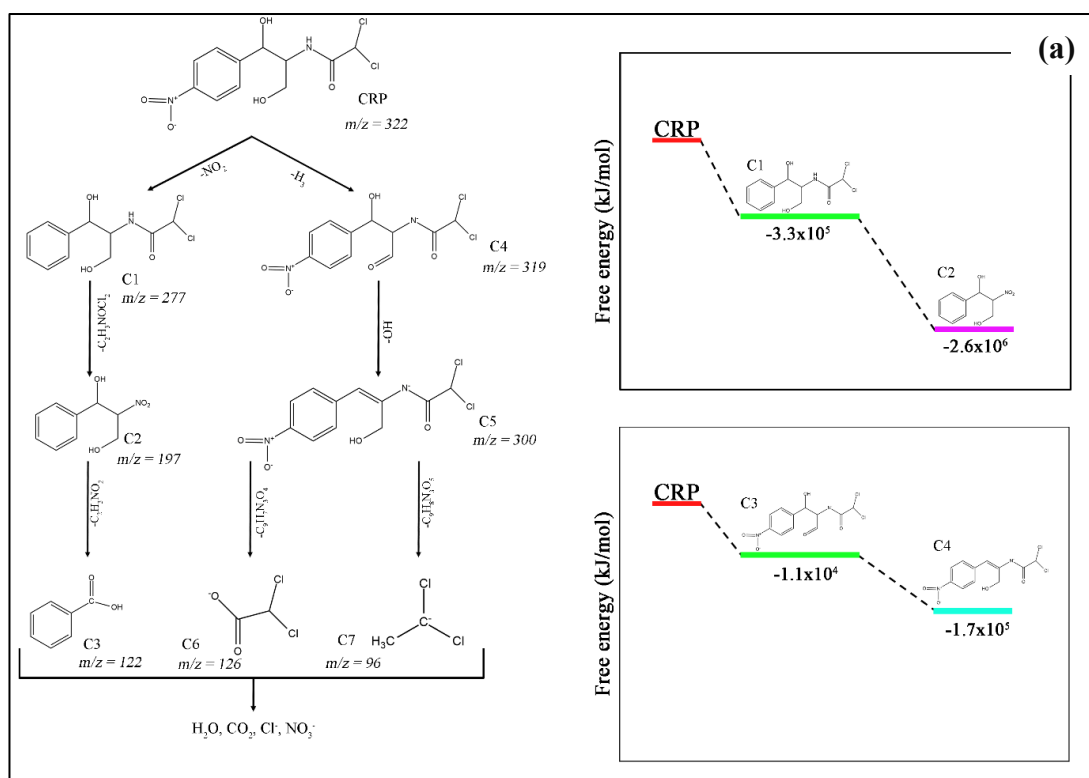
inorganic species such as H_2O , CO_2 , Cl^- , and NO_3^- . The proposed degradation pathway of CRP, along with the corresponding Gibbs free energy variations, is illustrated in Figure 3.44(a).

The LC-MS analysis of SFX degradation revealed a stepwise process involving both bond cleavage and oxidative transformations. In the first pathway, degradation initiates with the cleavage of the sulfonamide S–N bond in the parent SFX molecule ($m/z = 253$), generating two major fragments through radical attack ($f^\bullet$). The first fragment, S1 ($m/z = 179$; $\Delta G = -5.5 \times 10^5 \text{ kJmol}^{-1}$), corresponds to a sulfanilamide-like compound that retains the aniline and sulfonamide groups. The second fragment, S2 ($m/z = 93$; $\Delta G = -2.3 \times 10^6 \text{ kJmol}^{-1}$), represents a simplified aniline derivative, likely originating from the isoxazole moiety. The intermediate S1 ($m/z = 179$) is subsequently oxidized by reactive oxygen species, particularly hydroxyl radicals ($\bullet\text{OH}$), which facilitate cleavage of the remaining S–N bond and further oxidation of the molecule, forming intermediate S3 ($m/z = 136$; $\Delta G = -1.19 \times 10^6 \text{ kJmol}^{-1}$). This compound likely represents a hydroxylated and ring-modified degradation product. In the second pathway, SFX undergoes a sequence of oxidative transformations via electrophilic attack (f^-), producing intermediates S4 ($m/z = 252$; $\Delta G = -2.9 \times 10^4 \text{ kJmol}^{-1}$), S5 ($m/z = 239$; $\Delta G = -2.1 \times 10^4 \text{ kJmol}^{-1}$), and S6 ($m/z = 226$; $\Delta G = -1.9 \times 10^5 \text{ kJmol}^{-1}$). These intermediates correspond to hydroxylated and demethylated derivatives of SFX, reflecting successive oxidation, ring-opening, and removal of substituent groups. The final aromatic intermediate, S7 ($m/z = 108$), exhibits a benzoquinone-like structure, indicating an advanced stage of degradation.

In the third pathway, SFX experiences direct bond dissociation, primarily through the cleavage of the sulfonamide S–N linkage, resulting in two smaller fragments. The first, S8 ($m/z = 156$; $\Delta G = -8.9 \times 10^5 \text{ kJmol}^{-1}$), likely corresponds to a cleaved aromatic sulfonyl derivative, while the second, S9 ($m/z = 96$; $\Delta G = -2.1 \times 10^6 \text{ kJmol}^{-1}$), is attributed to a low-molecular-weight product derived from the isoxazole ring. All these reactions are thermodynamically favorable and occur spontaneously at room temperature, as indicated by the negative ΔG values. The three proposed pathways represent distinct degradation routes of SFX fragmentation, stepwise oxidation, and direct bond cleavage, eventually leading to complete mineralization

into CO₂ and H₂O, as supported by the detected end products. The degradation mechanism of SFX and the corresponding Gibbs free energy changes are illustrated in Figure 3.44(b).

Additionally, the degradation products of CRP and SFX exhibited significantly reduced toxicity, as illustrated in Figure 3.44(c) and Figure 3.44(d). Nonetheless, some intermediates generated during CRP degradation retained partial toxicity. With extended treatment duration, these intermediates were further decomposed into smaller and less harmful compounds, indicating ongoing mineralization with time. After 120 min of visible-light irradiation using CeONC@GrO, most of the CRP and SFX molecules were completely mineralized into CO₂ and H₂O. Overall, the final degradation products were found to be non-toxic and environmentally benign. The detailed toxicity parameters (EC₅₀/LC₅₀/ChV) are summarized in Table 3.22 and Table 3.23.



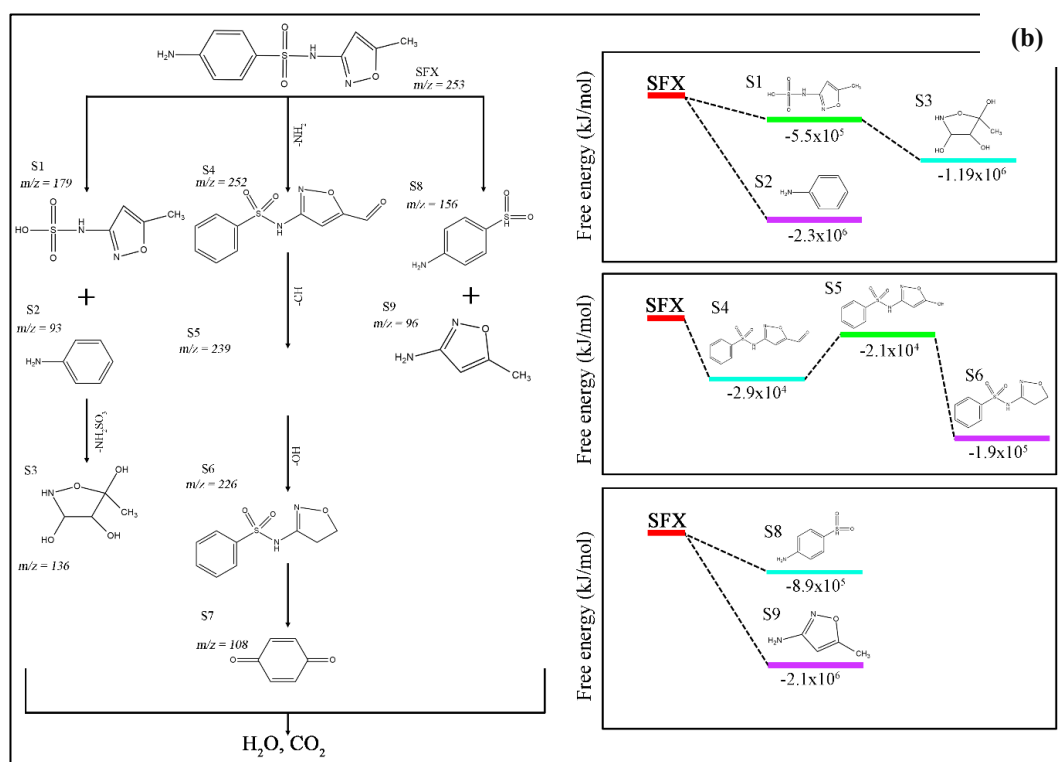


Figure 3.44. (a) Degradation mechanism of CRP along with its ΔG values; (b) Degradation mechanism of SFX along with its ΔG values; (c) Acute toxicity (EC_{50}/LC_{50}) values of CRP, SFX, and their degradation products; and (d) Chronic values (ChV) CRP, SFX, and their degradation products towards fish, daphnia, and green algae.

Table 3.22. Acute toxicity (LC₅₀/EC₅₀) values of CRP, SFX, and their degradation products towards fish, *daphnia*, and green algae.

Molecule	Fish (LC ₅₀)	<i>Daphnia</i> (LC ₅₀)	Green Algae (EC ₅₀)	
CRP	651	692	25.8	
C1	26.5	51.5	0.245	
C2	84.1	22.8	2.15	
C3	2763.235	2206.215	219	
C4	358	424	10.9	
C5	330	179	111	
C6	1300	730	518	
C7	134	74.4	50.6	
C8	2411.7	194	0.032	
SFX	4783.172	236.154	986	
S1	8651	3007	2947	
S2	517	270	141	
S3	4475	1754	1621	
S4	6642	3230	1268	
S5	430	89	511	
S6	1186	620	328	Not harmful
S7	3333	1609	614	Harmful
S8	5210	2263	5568	Toxic
S9	6946	3232	1057	Very Toxic

Table 3.23. Chronic (ChV) values of CRP, SFX, and their degradation products towards fish, *daphnia*, and green algae.

Molecule	Fish (ChV)	<i>Daphnia</i> (ChV)	Green Algae (ChV)	
CRP	335	1283	52.2	
C1	10	31.2	0.119	
C2	5.68	1.7	0.89	
C3	2707.372	6959.801	876	
C4	230	643	17.1	
C5	30.6	15.5	26.5	
C6	125	68	132	
C7	12.8	6.82	12.6	
C8	249	32.5	0.0084	
SFX	396	156	189	
S1	4741	1488	2588	
S2	45.7	20.7	30.6	
S4	541	205	235	
S5	36	7	51	
S6	105	48	71	
S7	269	100	112	
S8	3712	1047	903	
S9	536	181	177	

Not harmful

Harmful

Toxic

Very Toxic

3.5.4. Conclusion

In addition to their application as electrochemical sensing interfaces for the detection of chloramphenicol (CRP) and sulfamethoxazole (SFX), the CeONC@GrO nanocomposite was also explored for its potential in photocatalytic degradation of these pharmaceutical contaminants via a photo-Fenton-like degradation (PFD) process. The nanocomposite exhibited fair photocatalytic efficiency under LED light irradiation, achieving degradation rates of 77.04% for CRP at pH 6 and 84.22% for SFX at pH 3 within 120 minutes of treatment. The reactive oxygen species (ROS) trapping experiments confirmed that hydroxyl radicals ($\bullet\text{OH}$) played the predominant role in the oxidative degradation of CRP and SFX molecules, with superoxide ($\text{O}_2^{\bullet-}$) and singlet oxygen contributing as a secondary species. Furthermore, the frontier molecular orbital analysis shows that the carbonyl group and phenolic group of CRP and SFX are most prone to oxidation. The proposed degradation pathways were systematically investigated, and the transformation products were identified using intermediate analysis. Interestingly, only two degradation intermediates of CRP, such as C1 ($m/z = 227$) and C2 ($m/z = 197$), exhibited measurable ecotoxicity towards green algae, whereas the intermediates of SFX were found to be non-toxic to fish, *Daphnia*, and green algae, suggesting that the PFD process minimizes risks associated with harmful by-products. Furthermore, the thermodynamic feasibility of the reactions was supported by the negative Gibbs free energy (ΔG) values obtained for all intermediate formation steps, demonstrating the spontaneity and viability of the degradation process under ambient conditions. These findings establish CeONC@GrO as a multifunctional nanomaterial capable not only of highly sensitive and selective electrochemical detection of trace pharmaceuticals but also of efficient photocatalytic elimination of these contaminants from aqueous environments. The dual functionality, coupled with the low toxicity of degradation intermediates and strong catalytic stability, underscores its potential as a sustainable platform for environmental monitoring and treatment of emerging pollutants.

CHAPTER 4

CONCLUSIONS

4. CONCLUSION

An electrochemical detection approach employing chemically modified glassy carbon electrodes was successfully developed in this study. The electrodes were fabricated using nanocomposite materials synthesized via a simple and eco-friendly green synthesis route. The nanocomposites consisted of biosynthesized zinc oxide and cerium oxide nanoparticles integrated with graphene oxide, providing excellent structural and electrochemical properties. Comprehensive investigations were carried out on the synthesis procedure, characterization of the materials, and their application in detecting selected target pollutants—namely Cd^{2+} , Hg^{2+} , Pb^{2+} , Zn^{2+} , ibuprofen (IBP), chloramphenicol (CRP), and sulfamethoxazole (SFX). The detailed findings demonstrate the efficiency and versatility of the developed sensors for multi-analyte environmental monitoring.

Graphene oxide (GrO) was synthesized using the modified Hummer's method, ensuring the successful oxidation and exfoliation of graphite into layered graphene oxide sheets with abundant oxygen-containing functional groups. These functional groups (such as hydroxyl, carboxyl, and epoxy) provide excellent anchoring sites for the immobilization of metal oxide nanoparticles. Subsequently, the synthesized GrO material was impregnated with zinc oxide nanoparticles ($\text{ZnO}(\text{NP})$) and cerium oxide nanoclusters (CeONC) through an *in-situ* immobilization process, resulting in the formation of nanostructured composites such as $\text{ZnO}(\text{NP})@\text{GrO}$ and $\text{CeONC}@\text{GrO}$. These nanocomposite materials showed a synergistic effect in the efficient detection of these water contaminants. A green, sustainable method was used to synthesize $\text{ZnO}(\text{NP})$ and CeONC nanoparticles utilizing *Acmella oleracea* (toothache plant) leaf extracts as natural reducing and stabilizing agents. This biosynthetic route uses no harmful chemicals, saves energy, and is environmentally friendly. Flavonoids and phenolic compounds in plant-derived phytochemicals influence metal precursor reduction and stabilization, resulting in uniformly dispersed and small-sized nanoparticles. The resulting $\text{ZnO}(\text{NP})@\text{GrO}$ and $\text{CeONC}@\text{GrO}$ nanocomposites were used to modify glassy carbon electrodes (GCEs), enhancing their electrocatalytic activity, electron transfer rate, and sensitivity. Modified electrodes detect a variety of

environmental pollutants such as heavy metals (Cd^{2+} , Hg^{2+} , Pb^{2+} , Zn^{2+}) and pharmaceutical contaminants (IBP, CRP, and SFX).

The ZnO(NP) sample showed an absorption peak around 370–378 nm, indicating electronic excitation from the valence band to the conduction band (near-band-edge transition typical of semiconducting ZnO). The absorption spectrum of CeONC nanostructures showed two cerium oxide nanoparticle-like peaks at 317 and 258 nm. The 317 nm band is due to the $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$ charge transfer transition, while the 258 nm band is due to the $\text{Ce}^{3+} (4f^1 \rightarrow 5d^1)$ electronic transition. The broad spectrum profile and coexistence of these transitions indicate the presence of mixed valence states ($\text{Ce}^{3+}/\text{Ce}^{4+}$) and oxygen vacancy defects in the CeONC lattice. These characteristics suggest that phytochemicals of *Acmella oleracea* extract reduce Ce^{4+} to Ce^{3+} during biosynthesis, resulting in oxygen-deficient cerium oxide nanoclusters with increased redox activity. The SEM study shows morphological evidence of nanocomposite material and structural integration. Graphene oxide (GrO) has layered, wrinkled, and sheet-like morphology, indicating its two-dimensional structure with numerous surface functional groups such as hydroxyl, epoxy, and carboxyl moieties. ZnO(NP)@GrO SEM micrographs showed uniform integration of hexagonally structured ZnO nanoparticles across GrO sheets, corresponding with ZnO's wurtzite crystalline structure. Moreover, the CeONC@GrO composite exhibited a uniform distribution of finely dispersed CeONC across the graphene oxide layers, signifying robust bonding interactions between CeONC and the oxygenated functional groups of GrO. The lack of substantial agglomeration indicates that the green synthesis of these nanoparticles is stabilized and uniformly deposited onto the GrO surface. The EDX spectra of GrO, ZnO(NP)@GrO, and CeONC@GrO exhibited prominent peaks corresponding to carbon (C) and oxygen (O) elements. In addition, the ZnO(NP)@GrO and CeONC@GrO displayed distinct peaks of zinc and cerium, respectively, confirming the successful incorporation of zinc oxide and cerium oxide nanoparticles onto the graphene oxide framework. The HRTEM investigation validated the successful synthesis and structural stability of the nanocomposites, ZnO(NP)@GrO and CeONC@GrO. The HR TEM images of ZnO(NP)@GrO and CeONC@GrO exhibited evenly distributed hexagonal ZnO(NP) and CeONC

throughout the GrO sheets, with lattice fringe spacings of 0.26 nm and 0.29 nm, respectively, corresponding to the (002) plane of hexagonal wurtzite ZnO and the (220) plane of cubic fluorite CeO₂. The unique diffraction spots in the SAED signals for both composites validated their crystalline characteristics and clearly delineated crystal structures. Moreover, the particle size distribution of ZnO(NP)@GrO and CeONC@GrO nanocomposites showed an average particle size of 18 nm and 9 nm for ZnO(NP)@GrO and CeONC@GrO, respectively. The surface roughness of ZnO(NP)@GrO and CeONC@GrO modified glassy carbon plates was examined using AFM. The results showed that the ZnO(NP)@GrO coated carbon sheet exhibited R_a and R_q values of 9.65 nm and 15.23 nm, respectively, while the CeONC@GrO coated carbon sheet had roughness values, with $R_a = 3.55$ nm and $R_q = 4.37$ nm.

XRD peaks at 2θ values of 31.83°, 34.45°, 36.29°, 47.62°, 56.57°, 62.88°, 66.39°, 67.97°, 72.6° and 76.94° referring to the ZnO(NP) diffraction planes of (100), (002), (101), (102), (110), (103), (200), (112), (201) and (004) (JCPDS card no. 89-1397), which indicate a typical hexagonal wurtzite structure while XRD peaks at 2θ values of 28.49°, 33.07°, 47.44°, 56.31°, 58.78°, 69.60°, 76.69°, and 78.77°, corresponding to the CeONC diffraction planes of (111), (200), (220), (331), (222), (400), (311), and (420) (JCPDS card no: 34-0394), indicating the characteristic face-centered cubic phase of CeO₂ nanoparticles and a distinctive diffraction peak of GrO was seen at 2θ value of 10.57° in both samples, which corresponds to the (001) plane of graphene oxide. The XPS survey confirms the elemental composition of the nanocomposites, with Zn, O, and C detected in ZnO(NP)@GrO and Ce, O, and C in CeONC@GrO. Further, the Zn 2p peaks at 1045.0 and 1021.8 eV indicate the presence of Zn²⁺, confirming ZnO formation in the ZnO(NP)@GrO. Similarly, the XPS of CeONC@GrO showed the Ce 3d XPS peaks occurred at 882.0, 885.4, 888.6, 898.3, 900.9, 903.04, 907.4, and 916.7 eV binding energies, demonstrating that cerium is present in both +4 and +3 oxidation states. The detection of signature peaks for Ce³⁺, alongside Ce⁴⁺, confirms the partial reduction of Ce⁴⁺ to Ce³⁺. Moreover, acute toxicity and application investigations examined the environmental safety and multifunctional potential of ZnO(NP)@GrO and CeONC@GrO. After 48 hours, the ZnO(NP)@GrO nanocomposite showed moderate toxicity to *Daphnia magna*, with an EC₅₀ value of 115.7 mgL⁻¹. GrO matrix containing ZnO nanoparticles enhanced stability, reduced

ion leaching, and lowered toxicity. Compared to typical metal oxide catalysts, the CeONC@GrO nanocomposite showed a higher EC₅₀ value of 150.8 mgL⁻¹ after 48 hrs, indicating reduced acute toxicity and greater environmental compatibility. The biocompatibility of cerium and the stabilizing effect of GrO preclude a stable phase of the nanocomposite, resulting in low toxicity.

The GrO, ZnO(NP)@GrO, and CeONC@GrO nanocomposites were employed to cast the glassy carbon electrodes (GCEs), which served as the working electrodes in a three-electrode electrochemical setup, having Ag/AgCl and platinum electrodes as reference and counter electrodes, respectively. Both the modified and unmodified electrodes were characterized using electrochemical techniques. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a standard redox probe of 0.001 M Fe²⁺/Fe³⁺ in 0.1 molL⁻¹ sodium acetate buffer (pH 4.5). Increasing the scan rate led to a proportional rise in the oxidation and reduction peak currents of the Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ redox couple using the GCE, GrO GCE, ZnO(NP)@GrO GCE, and CeONC@GrO GCE. A plot of the anodic peak current versus the square root of the scan rate exhibited linear relationships, indicating a diffusion-controlled process, and was subsequently used to calculate the electroactive surface area via the Randles–Sevcik equation. The electroactive surface area (ESA) values were 8.0×10^{-4} , 17.0×10^{-4} , 38.0×10^{-4} , and 66.0×10^{-4} mm² for bare GCE, GrO GCE, ZnO(NP)@GrO GCE, and CeONC@GrO GCE, respectively, indicating a significant increase in the electroactive surface area using the nanocomposite solids. The EIS studies were performed to obtain the interfacial charge transfer resistance (R_{ct}) of various electrodes. The EIS studies were performed in a 0.001 molL⁻¹ solution of the ferric/ferrocyanide, and the experimental data are fitted with an equivalent circuit through the Nyquist plots. The size of the semicircle region in Nyquist plots correlated directly to the R_{ct} , and a progressive reduction in semicircle region was followed by the trend: bare GCE > GrO GCE > ZnO(NP)@GrO GCE > CeONC@GrO GCE. The electron transfer resistance for the bare GCE was 8.4×10^3 Ohms. On the other hand, the modified electrodes exhibited significantly reduced R_{ct} values, measuring $2.6 \times 10^3 \Omega$ for GrO GCE, $0.7 \times 10^3 \Omega$ for ZnO(NP)@GrO GCE, and $0.3 \times 10^3 \Omega$ for CeONC@GrO GCE.

The individual and simultaneous detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} ions was investigated using the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE, through cyclic voltammetry and DPASV techniques. CV data showed that Cd^{2+} and Pb^{2+} possess sharp redox peaks at -0.67 V, -0.87 V (for Cd^{2+}), and -0.46 V, and -0.69 V (for Pb^{2+}). However, the Hg^{2+} and Zn^{2+} exhibit prominent oxidized current at E_{pa} of 0.29 V and -0.98 V, respectively, using $\text{ZnO}(\text{NP})@\text{GrO}$ GCE. A significantly enhanced current response was observed at $\text{ZnO}(\text{NP})@\text{GrO}$ GCE for all these metal ions compared to bare and GO-modified electrodes. Moreover, at pH 5.0 and preconcentration parameters, i.e., deposition potential and time of -1.0 V and 120 sec, are the optimum conditions for detection of these ions using the $\text{ZnO}(\text{NP})@\text{GrO}$ GCE by DPASV technique. Further, the calibration curves were obtained for individual detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} with the linear equations: $\text{Cd}^{2+} \rightarrow y (\mu\text{A}) = 0.1923x (\mu\text{gL}^{-1}) + 8.3614$ ($R^2 = 0.996$), $\text{Hg}^{2+} \rightarrow y (\mu\text{A}) = 0.3039x (\mu\text{gL}^{-1}) + 9.4908$ ($R^2 = 0.993$), $\text{Pb}^{2+} \rightarrow y (\mu\text{A}) = 0.6766x (\mu\text{gL}^{-1}) + 18.979$ ($R^2 = 0.995$), and $\text{Zn}^{2+} \rightarrow y (\mu\text{A}) = 0.4501x (\mu\text{gL}^{-1}) + 18.551$ ($R^2 = 0.971$). Additionally, the nanocomposite efficiently detects these ions simultaneously with the detection limits of 0.026, 0.030, 0.010, and 0.020 μgL^{-1} for Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} , respectively. Furthermore, the applicability of the sensor was validated with real water matrices, yielding high recovery rates in the range of 91.6–101.2% for Cd^{2+} , 89.9–99.92% for Hg^{2+} , 99.42–104.6% for Pb^{2+} , and 90.9–106.4% for Zn^{2+} . The presence of common interfering ions such as Ca^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Mg^{2+} , and Ni^{2+} did not significantly affect the detection of the target metal ions. In addition, the $\text{ZnO}(\text{NP})@\text{GrO}$ thin-film electrode exhibited excellent repeatability after 5 repeated measurements and long-term stability for repeated applications, with RSD(%) less than 2 even after 48 hrs, indicating enhanced shelf life of the fabricated electrode.

On the other hand, the $\text{CeONC}@\text{GrO}$ nanocomposite-modified glassy carbon electrode (GCE) was employed for the sensitive electrochemical detection of pharmaceuticals such as ibuprofen (IBP), chloramphenicol (CRP), and sulfamethoxazole (SFX). Cyclic voltammetry studies revealed distinct redox behaviour for these pharmaceutical compounds: IBP shows anodic peak at +0.76 V and a corresponding cathodic peak at +0.46 V, CRP exhibited a pair of well-defined peaks at approximately 0.05 V and -0.07 V, whereas SFX displayed redox peaks at

1.14 V and 0.55 V. Compared with the bare GCE, the CeONC@GrO GCE showed a substantially enhanced electrochemical peak currents. The optimal experimental conditions were determined as follows: pH 5.5, pH 7.0, and pH 6.0, respectively, for the IBP, CRP and SFX. Similarly, the accumulation potentials of -0.6V (IBP), -1.1 V (CRP), and -1.2 V (SFX), and accumulation times of 180 sec, 120 sec, and 210 sec for IBP, CRP, and SFX, respectively. The regression equations for IBP, CRP, and SFX was: $y \text{ (IBP)} = 0.2533 \times (\mu\text{gL}^{-1}) + 8.678$; $y \text{ (CRP)} = 0.985 \times (\mu\text{gL}^{-1}) + 14.014$; and $y \text{ (SFX)} = 0.5488 \times (\mu\text{gL}^{-1}) + 22.009$ with R^2 values of 0.992, 0.995 and 0.99 for IBP, CRP and SFX, respectively. Under these conditions, the sensor achieved remarkably low detection limits of $0.030 \mu\text{gL}^{-1}$, $0.009 \mu\text{gL}^{-1}$ and $0.016 \mu\text{gL}^{-1}$ for IBP, CRP and SFX, respectively. Similarly, the limit of quantification of 1.02, 0.030 and $0.054 \mu\text{g L}^{-1}$ for IBP, CRP and SFX, respectively using the CeONC@GrO GCE. Selectivity tests demonstrated that common co-existing ions, even at concentrations ten times higher than the target analytes, showed negligible interference, confirming the robustness of the method. However, a slight decrease in the anodic peak of IBP was recorded in the presence of diclofenac. The percentage change in peak current was less than 5% in the presence of diclofenac. Furthermore, the CeONC@GrO GCE displayed minimal variation in anodic peak currents for 5 successive measurements, and independently, four fabricated electrodes confirmed the reliability of the fabricated electrode. Moreover, the CeONC@GrO GCE maintained over 97%, 96% and 98% of its initial current response for IBP, CRP and SFX, respectively, after 96 hrs of continuous operation, with RSD (%) values below 1.5%. The practical applicability of the sensor was validated by analysing a real wastewater sample collected from hospital effluents (Ebenezer Hospital) near Tuikual Lui, Aizawl (India), and the outlet of the sewage treatment plant at SIPMIU, Aizawl, Mizoram, India. The method yielded high recovery values, ranging from 90.43% and 104.8% for IBP (RSD (%) <1.3), 93.14% to 105.39% for CRP (RSD (%) <1), and 94.01% to 105.67% for SFX (RSD (%) <1), highlighting the accuracy and reliability of the fabricated electrode. These studies confirm that the CeONC@GrO GCE exhibits strong affinity, high selectivity, and excellent sensitivity toward the IBP, CRP, and SFX, making them highly efficient for trace-level monitoring of pharmaceutical contaminants in complex aqueous environments.

In summary, the limits of detection (LOD) obtained in this study for heavy metals and pharmaceuticals are compiled in Table 4.1. A comparative value revealed that the LODs are well below the maximum contamination levels (MCLs) set by the World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA). This indicates that the developed electrochemical method exhibits exceptional sensitivity, capable of detecting trace amounts of target analytes well within safe regulatory limits. Furthermore, the low LODs, combined with the reproducibility and stability of the nanocomposite-modified electrodes, highlight the practical applicability of the fabricated electrodes for real-world environmental monitoring.

Table 4.1: LOD values of several contaminants obtained with fabricated electrodes compared to MCL levels prescribed by the WHO/or US-EPA.

Sl. No.	Working Electrodes	Pollutants	LOD (μgL^{-1})	MCL (μgL^{-1})
1	ZnO(NP)@GrO GCE	Cd^{2+}	0.026	5 (WHO) 3 (USEPA)
2	ZnO(NP)@GrO GCE	Hg^{2+}	0.030	10 (WHO) 15 (USEPA)
3	ZnO(NP)@GrO GCE	Pb^{2+}	0.010	10 (WHO) 15 (USEPA)
4	ZnO(NP)@GrO GCE	Zn^{2+}	0.020	5000 (WHO)
5	CeONC@GrO GCE	Ibuprofen (IBP)	0.03	-
6	CeONC@GrO GCE	Chloramphenicol (CRP)	0.009	-

6	CeONC@GrO GCE	Sulfamethoxazole (SFX)	0.016	-

MCL: Maximum contamination level

In addition to serving as an efficient electrochemical sensing interface for the detection of chloramphenicol (CRP) and sulfamethoxazole (SFX), the CeONC@GrO nanocomposite was further evaluated for its photocatalytic performance in the degradation of these two pharmaceutical contaminants through a photo-Fenton-like degradation (PFD) process. Under LED light irradiation, the nanocomposite demonstrated excellent photocatalytic activity, achieving degradation efficiencies of 77.04% for CRP at pH 6.0 and 84.22% for SFX at pH 3.0 within 120 min. Reactive oxygen species (ROS) scavenging experiments revealed that hydroxyl radicals ($\bullet\text{OH}$) were the dominant oxidative agents responsible for pollutant degradation, while superoxide ($\text{O}_2\bullet^-$) and singlet oxygen additionally took part in the degradation mechanism. The frontier molecular orbital analysis showed that the carbonyl group and phenolic group of CRP and SFX are most prone to oxidative degradation. Detailed intermediate analyses elucidated the degradation pathways, showing that only two CRP ($\text{C1}(\text{m/z} = 227)$ and $\text{C2}(\text{m/z} = 197)$) intermediates exhibited slight ecotoxicity toward green algae, whereas all SFX intermediates were non-toxic to fish, *Daphnia*, and algae. These results suggest that the PFD process effectively minimizes the generation of harmful by-products. Moreover, the calculated negative Gibbs free energy (ΔG) values for all intermediate formation steps confirmed the thermodynamic spontaneity and feasibility of the reactions under ambient conditions. Overall, the CeONC@GrO nanocomposite demonstrates multifunctionality—combining high electrochemical sensitivity with enhanced photocatalytic capability—making it a sustainable and environmentally benign material for both detection and remediation of emerging pharmaceutical pollutants in water systems.

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BIO-DATA

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5. EDUCATIONAL QUALIFICATIONS : M.Sc. (Chemistry)

Qualification	Year of Passing	Board/University	Subjects	% Of Marks	Div.
HSLC	2013	Mizoram Board of School Education (MBSE)	Mathematics, Science, Social Science, English, Mizo, Information Technology	69.2	First
HSSLC	2015	Mizoram Board of School Education (MBSE)	Physics, Chemistry, Mathematics, English, Mizo	54.6	Second
B.Sc. (Chemistry)	2018	Mizoram University	Chemistry	76.75	First
M.Sc. (Chemistry)	2020	Mizoram University	Organic Chemistry (Specialisation)	71.25	First

LIST OF PUBLICATIONS

A. Journals (Published)

1. **Melody Lalhrualtuangi**, Lalruatkima Ralte, Diwakar Tiwari, Jinho Jung (2025). Highly efficient and toxicologically safe ZnO(NP)@GO nanocomposite in the simultaneous detection of Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ in aqueous medium. *Sensors and Actuators Reports*, 100373. <https://doi.org/10.1016/j.snr.2025.100373>. [IF:7.6]
2. **Melody Lalhrualtuangi**, Lalruatkima Ralte, Diwakar Tiwari, and Dong Jin Kim. Sustainable nanocomposite catalyst for ultra-sensitive detection and photo-Fenton-like degradation of emerging contaminants. *Separation and Purification Technology*. [IF: 9.0]
3. **Melody Lalhrualtuangi**, Ricky Lalawmpuia, Diwakar Tiwari, Rama Dubey (2025). Nanocomposite material in the trace and simultaneous electrochemical detection of As (III) and As (V). *Environmental Engineering Research*, (30)5. <https://doi.org/10.4491/eer.2024.663>. [IF:3.0]
4. Ricky Lalawmpuia, **Melody Lalhrualtuangi**, Diwakar Tiwari (2024). Metal organic framework (MOF): Synthesis and fabrication for the application of electrochemical sensing. *Environmental Engineering Research*, (29)5. <https://doi.org/10.4491/eer.2023.636>. [IF:3.0]
5. Ricky Lalawmpuia, **Melody Lalhrualtuangi**, Lalhmunsiamia, Suk Soon Choi, Diwakar Tiwari (2025). Novel titanium-based metal organic framework (MOF) in efficient and ultra-trace electrochemical detection of arsenic (III). *Journal of Applied Electrochemistry*, 1-14. <https://doi.org/10.1007/s10800-025-02314-0>. [IF:3.0]
6. Ricky Lalawmpuia, **Melody Lalhrualtuangi**, and Diwakar Tiwari (2025). Electrochemical sensing of ciprofloxacin and carbamazepine using highly sensitive metal-organic framework. *Journal of The Electrochemical Society*, 172 105504. [DOI: 10.1149/1945-7111/ae0bb7]. [IF:3.3]
7. Ricky Lalawmpuia, **Melody Lalhrualtuangi**, and Sandhya Pathak, Diwakar Tiwari. Highly sensitive Titanium based Metal Organic Framework for the

simultaneous detection of Lead (II) and Cadmium (II) in aqueous media.
Inorganica Chimica Acta. [IF:3.2]

CONFERENCES AND SEMINAR

1. Melody Lalhrualtuangi and Diwakar Tiwari. use of novel nanocomposite material in the trace detection of Lead (II) and Zinc (II) in aqueous solution. International Conference on Chemical Advances in Chemical Science Research and Education Education (CASCRE-2024) and National Convention of Chemistry Teachers (NCCT-2024) during 6th – 8th November, 2024, organised by department of Chemistry, Industrial Chemistry, Chemistry (PUC), Mizoram University and the Association of Chemistry Teachers (ACT), Aizawl, Mizoram.
2. Melody Lalhrualtuangi and Diwakar Tiwari. Novel nanocomposite material in the development of electrochemical sensors for detection of arsenic (III), iron (III) and fluoride. National Conference on Chemical Physics (NCCP-2024) during 18th – 19th March, 2024, organised by department of Physics, Assam University, Silchar.
3. Melody Lalhrualtuangi and Diwakar Tiwari. Novel Nanocomposite Material in the Trace and Simultaneous Electrochemical Detection of Arsenic (III) & Arsenic (V). International Conference on Recent Advances in Mathematical, Physical, and Chemical Sciences (ICRAMPC-2024) organized by School of Physical Sciences, Mizoram University, Aizawl during 21st-23rd February, 2024.
4. Melody Lalhrualtuangi and Diwakar Tiwari. Novel and highly efficient silver nanoparticles decorated Silane-grafted bentonite for simultaneous detection of Arsenic (III) and Arsenic (V) in aqueous solution. International Conference on Science and Technology for Innovative and Sustainable Development (STISD-2023) jointly organized by Department of Chemistry and Department of Industrial Chemistry, Mizoram University, Aizawl during 28th -30th June, 2023.



Highly efficient and toxicologically safe ZnO(NP)@GO nanocomposite in the simultaneous detection of Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ in aqueous medium

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ABSTRACT

Miniaturised devices for trace, simultaneous and off-site detection are the need of the hour for protecting public health and the environment at large. Using sustainable and greener approach, the current study explores using *Acmella oleracea* extract to derive zinc oxide nanoparticles. Further, ZnO incorporates graphene oxide to obtain the nanocomposite material (ZnO(NP)@GO). The thin film electrode using the ZnO(NP)@GO efficiently detects potential heavy metal ions viz., Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ individually and simultaneously at trace level concentrations. The thin film electrode using the ZnO(NP)@GO showed significantly enhanced electroactive surface area and reduced electron transfer resistance compared to the unmodified glassy carbon electrode. The calibration curve for detecting Cd²⁺, Hg²⁺, Pb²⁺, and Zn²⁺ shows the limits of detection of 0.026, 0.03, 0.010 and 0.020 µg/L, respectively, in their simultaneous detection. The ZnO(NP)@GO thin film electrode possesses good shelf life and stability for repeated detections of these heavy metal toxic ions. Furthermore, the thin film electrode detects simultaneously these ions at trace levels in the hospital effluent waters with real implications. Moreover, the acute toxicity of ZnO(NP)@GO towards *D. magna* shows an EC₅₀ value of 115.7 mg/L after 48 hrs, proving the safety and environmental sustainability of the modified electrode.

1. Introduction

Accumulation of heavy metals in biological systems poses a serious threat to human health [1]. Lead, mercury, arsenic, cadmium, chromium, and zinc are naturally occurring heavy metals necessary in small quantities but highly toxic. Bioaccumulation of these ions by the bio-system poses severe and prolonged health hazards to living beings [2,3]. Examples of human activities, including mining, industrial operations, agricultural practices, and improper treatment of wastes, significantly contribute to heavy metal contamination of the aquatic environment, adversely impacting the natural ecosystems by diminishing soil fertility, polluting water sources, and harming aquatic organisms [4]. Detecting and constantly monitoring heavy metals in aqueous solutions is essential for safeguarding public health and preventing them from entering the food chain.

Various analytical techniques, such as atomic/molecular spectroscopic and chromatographic, efficiently detect the heavy metals in different matrices [5–7]. However, these techniques are expensive, need cumbersome sample preparations, are time-consuming and are performed off-site for measurements [8]. On the other hand, the

electrochemical techniques, including voltammetry, amperometry, and potentiometry, are particularly advantageous for on-site use because of their high sensitivity, cost-effectiveness, and portability [9]. It detects trace levels of heavy metals simultaneously with high accuracy, and suitable for real-time monitoring in environmental settings [10].

Carbon-based nanomaterials, particularly graphene oxide (GO), can be employed in sensor technologies since they possess large surface area with outstanding electrical conductivity while having robust mechanical strength [11]. It possesses an array of functional groups that include oxygen, like hydroxyl, epoxide, and carboxyl groups, making it highly versatile in chemical and biological sensing applications [12]. Similarly, ZnO exhibits distinct advantages as an electrochemical sensor material resulting from its large band gap energy, intense binding energy, high excitability, as well as exceptional biocompatibility [13]. Their high mechanical strength and stability ensure durability in testing conditions, making it highly suitable for various sensing applications. The ZnO nanotube/reduced graphene oxide modified GCE was synthesized for detecting Pb²⁺ ions, and it shows a low LOD of 4.8×10^{-12} M within a straight-line variation of 2.4×10^{-8} to 4.8×10^{-7} M [14]. Further, ZnO nanorods mixed with graphene efficiently measures Cd²⁺ and Pb²⁺

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Sustainable nanocomposite catalyst for ultra-sensitive detection and photo-Fenton-like degradation of emerging contaminants

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ABSTRACT

As environmental concerns grow over the extensive use and disposal of antibiotics into the aquatic environment, the study reports the environmentally friendly synthesis of nanocubical cerium oxide particles (CeONC@GrO) using *Spilanthes acmella* extract incorporated with graphene oxide. The study demonstrated the ability of the synthesized nanocomposite for low-level electrochemical sensing and photo-Fenton-like degradation (PFD) of the antibiotics chloramphenicol (CRP) and sulfamethoxazole (SFX). Several spectroscopic/microscopic techniques characterize the CeONC@GrO in detail. The fabricated CeONC@GrO electrode shows an 8-fold increase in electroactive surface area (ESA) and a 28-fold decrease in charge transfer resistance compared to the pristine electrode. The CeONC@GrO electrode efficiently detected CRP and SFX, with detection limits of 9.0×10^{-3} and 1.6×10^{-2} $\mu\text{g/L}$, respectively, and demonstrated high shelf life and stability. Moreover, high recovery efficiencies were achieved in real water samples using the synthesized CeONC@GrO nanocomposite, demonstrating remarkable photo-Fenton-like degradation: 77.04 and 84.22 % for CRP and SFX, respectively, at a catalyst concentration of 100 mg/L, which is well below to the EC_{50} , suggesting minimal environmental toxicity. The insights into the degradation mechanism and pathways were extensively demonstrated using LC-MS, along with density functional theory (DFT) calculations for thermodynamic feasibility (ΔG values). Furthermore, the toxicity of the intermediates was studied for safer and integrated detection and treatment processes.

1. Introduction

The utilization of antibiotics, including both human and animal care medications, has become essential in health management, control, and prevention [1]. These compounds often infiltrate the environment through the effluent from wastewater treatment facilities, sewage overflows, and manufacturing facilities [2,3]. Humans or livestock excrete a significant amount of antibiotics through faeces and urine, as liver enzymes such as glucuronidation, sulfation, and methylation partially break down of various medications in the body [4–6]. Therefore, these compounds, or even their active metabolites, enter sewage waters, are often not eliminated in wastewater treatment plants, and escape as residuals through effluents, entering the aquatic environment [7,8]. Although the concentration of these compounds was found at low levels in surface water, they have a higher potential to change the microecological system, which ultimately affects the food chain,

resulting in several health complications, including several allergic reactions, chronic toxic consequences from extended exposure, and disruptions in the normal functioning of the digestive system [9,10].

Chloramphenicol (CRP) is an extensively used antibiotic [11] employed to treat diseases such as dysentery, anthrax, and ocular disorders, and is also used in veterinary medicines [12,13]. Nonetheless, due to its affordability and potent efficacy, CRP is a widely used antibiotic, resulting in increased concentration in the food and water, which causes serious health concerns, including aplastic anaemia and cardiovascular collapse. Several countries have banned the utilization of chloramphenicol in animal farming [14], implementing stringent regulations to ensure that chloramphenicol residues are undetectable in food products. Moreover, sulfamethoxazole (SFX), a class of antibiotics used in animals and humans for the treatment of infections (urinary tract infections, bronchitis, and prostatitis, etc.) [5], is considered a pseudo-persistent pollutant owing to its environmental prevalence.

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Nanocomposite material in the trace and simultaneous electrochemical detection of As(III) and As(V)

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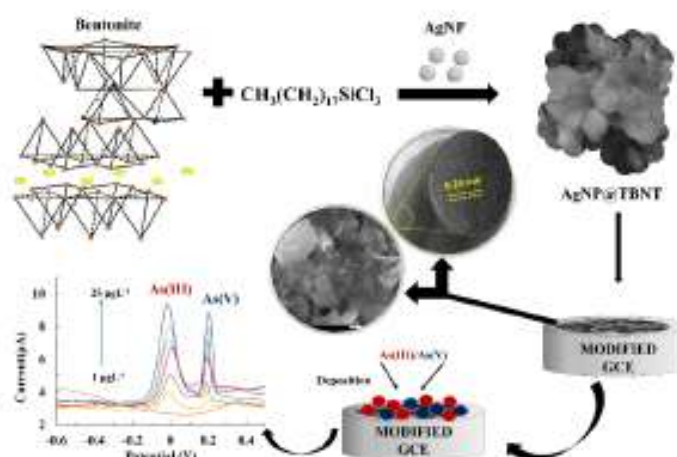
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ABSTRACT

Arsenic contamination in groundwater is severely impacting millions in North Eastern India, causing significant health issues. This communication discusses the use of a novel material for simultaneously detecting As(III) and As(V) at very low concentrations to address monitoring and safety concerns. Butter fruit (*Persea americana*) synthesized the silver nanoparticles (AgNP). These nanoparticles are then embedded directly into silane-functionalized bentonite to produce AgNP@TBNT. Several analytical methods characterize amicably the material and are utilized in fabricating the thin film glassy carbon electrode. An enhanced electroactive surface area and accelerated electron transfer processes are observed from the scan rate and EIS studies when compared with an unmodified glassy carbon electrode (GCE). Extensive parametric studies are conducted to optimize analyte detection, focusing on factors including pH, preconcentrated time, and potential, as well as the presence of ions that could interfere. The produced calibration graph for detecting As(III) and As(V) is quite satisfactory showing quite promising low limit of detection (LOD) of 0.037 and 0.087 $\mu\text{g/L}$ for As(III) and As(V), respectively. Further, the AgNP@TBNT fabricated electrode is fairly stable, reasonable self-life and detects efficiently arsenic in river water samples.

Keywords: Fabrication of electrode, Mechanism of detection, Nanocomposite material, Real water implications, Self-life electrode, Simultaneous detection

Graphical Abstract



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ABSTRACT

NANOCOMPOSITE MATERIALS IN THE DEVELOPMENT OF ELECTROCHEMICAL SENSORS FOR PHARMACEUTICALS AND HEAVY METAL IONS

**AN ABSTRACT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY**

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**DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES**

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**NANOCOMPOSITE MATERIALS IN THE DEVELOPMENT
OF ELECTROCHEMICAL SENSORS FOR
PHARMACEUTICALS AND HEAVY METAL IONS**

BY

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Department of Chemistry

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Submitted

In partial fulfillment of the requirement of the Degree of Doctor of Philosophy in
Chemistry of Mizoram University, Aizawl

ABSTRACT

Water is essential for all forms of life; however, the increasingly contaminated by anthropogenic activities, including industrialization, urbanization, agriculture, and the widespread use of pharmaceuticals. Contaminated water threatens food security by contaminating crops and adversely affecting fish populations. Moreover, the contamination of the aquatic environment significantly affects human health and the global economy. Globally, about 25% of people lack access to safe drinking water, 50% lack with basic sanitation, and 30% lack with hygiene facilities, that caused to exposes around 2.4 billion people. Over 1.15 billion people still live without clean drinking water, and more than 2 million—mostly children—die annually from waterborne diseases. Pollutants such as heavy metals and micro-pollutants, even at trace concentrations, pose severe ecological and public health risks, including disruption of aquatic ecosystems, bioaccumulation, food contamination, and waterborne diseases. Pharmaceuticals, including antibiotics, non-steroidal anti-inflammatory drugs, hormones, and neuroleptics, enter water bodies through wastewater discharge, improper disposal, and incomplete metabolism, adversely impacting the microecological systems and potentially causing chronic health effects. Ibuprofen (IBP), chloramphenicol (CRP), and sulfamethoxazole (SFX) are emerging water pollutants often detected, at low levels, in many aquatic environments, such as groundwater, surface water, wastewater, sewage sludge, and river streams. The presence of these pharmaceuticals in various water matrices underscores the pressing necessity for efficient wastewater treatment technology to meet various environmental regulations.

Heavy metals such as lead, cadmium, mercury, arsenic, and chromium are persistent, non-biodegradable, and bioaccumulative, originating from natural sources and anthropogenic activities, leading to long-term ecological imbalances and toxicity in humans and wildlife. Although zinc is crucial in trace quantities for biological processes, its environmental excess has emerged as a significant concern, with exposure levels rising markedly. Prolonged use of zinc significantly above the prescribed dietary allowances (generally exceeding 150 mg/day, and in extreme

instances reaching 1–2 grams per day) may lead to hazardous impacts, emphasizing the need for careful monitoring of environmental zinc contamination and its pathways of human exposure.

Therefore, accurate and on-site monitoring of these contaminants is challenging to prevent their entry into the food chain and mitigate their adverse effects at the source itself. Although advanced analytical techniques such as atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), chromatography, inductively coupled plasma mass spectrometry (ICP-MS), laser-induced breakdown spectroscopy (LIBS), liquid chromatography–tandem mass spectrometry (LC-MS/MS), high-performance liquid chromatography–mass spectrometry (HPLC/MS), and gas chromatography–mass spectrometry (GC/MS) are highly effective in detecting trace levels of heavy metals and pharmaceutical contaminants. However, these techniques possess several inherent limitations, such as high instrument cost, the need for skilled personnel, complex sample preparation, and off-site analysis, which restrict their practical applicability for routine and real-time monitoring. Consequently, there is a growing necessity for robust, portable, and cost-effective devices capable of rapid on-site detection. In this context, electrochemical sensing devices are emerging as a promising alternative, offering high sensitivity, simplicity, and real-time detection capabilities compared to conventional analytical methods. Electrochemical sensors have emerged as powerful analytical tools for the detection and quantification of environmental contaminants in aqueous environments. The voltammetry, amperometry, and potentiometry offer notable advantages, including high sensitivity, low cost, portability, and the capability for real-time, on-site monitoring of trace-level heavy metals and pharmaceutical pollutants. Their rapid response, robustness, and minimal operational requirements make them highly suitable for environmental applications. Recent advancements in electrochemical sensing focus on enhanced performance through the development of electrode materials that enhance the sensitivity, selectivity, and stability. The integration of these advanced materials into electrochemical systems is promising for the possible miniaturized device development, and enables a sustainable monitoring of water quality in diverse environmental settings.

Carbon-based nanomaterials, particularly graphene oxide (GrO), have emerged as promising materials utilized in sensor technology due to their exceptionally large surface area, high electrical conductivity, and remarkable mechanical strength. The presence of oxygen-containing functional groups such as hydroxyl, epoxide, and carboxyl enhances their versatility in chemical and biological sensing applications. Moreover, the green synthesis approaches have attracted significant interest for the sustainable production of nanomaterials and their composites. Among these, metal oxide nanoparticles have been utilized for electroanalytical applications owing to their nanoscale size, large surface area, biocompatibility, chemical stability, and rapid electron transport properties. Their superior electrochemical properties and durability under testing conditions enable them to be highly efficient for the detection of several heavy metal ions.

The current study presents the design and fabrication of a highly sensitive and selective electrochemical sensing platform for the trace detection of heavy metal ions and pharmaceuticals in aqueous media. A glassy carbon electrode (GCE) is employed as the working electrode owing to its excellent stability, broad potential window, and ease of surface modification. The graphene oxide (GrO) is synthesized using a known Hummer's method precursor to graphite. On the other hand, zinc oxide (ZnONPs) and cerium oxide (CeONCs) nanoparticles are synthesized via a green route using *Acmella oleracea* leaf extract. UV–Vis absorption spectra of these colloidal solutions showed absorption peaks at 370 nm for ZnO(NP), while CeONC showed two peaks at 317 and 258 nm. These metal oxide nanoparticles promote electrochemical redox reactions by facilitating faster electron transfer and increasing the effective surface area, thereby enhancing the sensor's sensitivity and selectivity. The impregnation of GrO with ZnONPs and CeONCs results in the formation of nanocomposites, viz., ZnO(NP)@GrO and CeONC@GrO, which are utilized in the trace detection of pharmaceutical contaminants such as chloramphenicol (CRP), ibuprofen (IBP), and sulfamethoxazole (SFX), as well as heavy metal toxic ions viz., Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} in aqueous medium.

The morphology and structural characteristics of the nanocomposite materials were studied using Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM/EDX), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), and X-ray Diffraction (XRD). The UV–Vis spectra indicated ZnO absorption at 370 nm and CeONC peaks at 317 nm and 258 nm, demonstrating the presence of mixed $\text{Ce}^{3+}/\text{Ce}^{4+}$ states and oxygen vacancies. SEM and HRTEM demonstrated a homogeneous distribution of hexagonal ZnO and cubic CeO_2 nanoclusters over graphene oxide, with average dimensions of 18 nm and 9 nm, respectively. XRD verified the wurtzite ZnO, fluorite CeO_2 , and (001) GrO structures, whereas XPS and EDX verified the existence of Zn^{2+} and $\text{Ce}^{3+}/\text{Ce}^{4+}$ species. AFM revealed more surface roughness for $\text{ZnO}(\text{NP})@\text{GrO}$ compared to $\text{CeONC}@\text{GrO}$, signifying a different morphology. Moreover, the ecotoxicity of the $\text{ZnO}(\text{NP})@\text{GrO}$ and $\text{CeONC}@\text{GrO}$ showed an EC_{50} value of 115.7 mgL^{-1} and 150.80 mgL^{-1} for its acute toxicity toward *Daphnia magna* after 48 hrs. The glassy carbon electrode surface is modified with the $\text{ZnO}(\text{NP})@\text{GrO}$ and $\text{CeONC}@\text{GrO}$ nanocomposites using the drop cast method, and the modified electrodes are known as $\text{ZnO}(\text{NP})@\text{GrO}$ GCE and $\text{CeONC}@\text{GrO}$ GCE, respectively. These modified electrodes are then utilized for the efficient electrochemical detection of various pollutants, including heavy metals (Cd, Hg, Pb, and Zn) and pharmaceutical contaminants (ibuprofen, chloramphenicol, and sulfamethoxazole). The fabricated electrodes were electrochemically characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) with a standard redox probe consisting of $0.001 \text{ M Fe}^{2+}/\text{Fe}^{3+}$ prepared in 0.1 molL^{-1} sodium acetate buffer (pH 4.5). The cyclic voltammetry CV was carried out at a range of different scan rates, and the oxidative peak current was plotted versus the square root of the scan rate for each electrode, viz., bare GCE, GrO GCE, $\text{ZnO}(\text{NP})@\text{GrO}$, and $\text{CeONC}@\text{GrO}$. The linear relationship was obtained between the oxidative peak current was plotted versus the square root of the scan rate. Further, employing the Randles–Sevcik equation, the electroactive surface area (ESA) of the electrodes were obtained and are found to be 8.0×10^{-4} , 17.0×10^{-4} , 38.0×10^{-4} , and $66.0 \times 10^{-4} \text{ mm}^2$ for bare GCE, GrO GCE, $\text{ZnO}(\text{NP})@\text{GrO}$ GCE, and $\text{CeONC}@\text{GrO}$ GCE, respectively. The EIS results showed that the interfacial charge transfer resistance (R_{ct}) of various electrodes was found to be 8.4×10^3 , $2.6 \times 10^3 \Omega$, $0.7 \times 10^3 \Omega$, and $0.3 \times$

$10^3 \Omega$ for the bare GCE, GrO GCE, ZnO(NP)@GrO GCE, and CeONC@GrO GCE, respectively. The nanocomposite modified GCE electrodes exhibited significantly reduced R_{ct} values.

Furthermore, the individual and simultaneous detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} ions was carried out using the ZnO(NP)@GrO GCE, employing cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV). The ZnO(NP)@GrO GCE exhibited significantly higher current responses for all metal ions compared to bare and GrO-modified electrodes. The detection of these heavy metal ions was optimized at pH 5.0, with a deposition potential of -1.0 V and a deposition time of 120 sec under the DPASV measurements. Under these conditions, the ZnO(NP)@GrO GCE enabled simultaneous detection of these four metal ions, achieving detection limits of 0.026, 0.030, 0.010, and 0.020 μgL^{-1} for Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} , respectively. Additionally, the CeONC@GrO GCE was utilized for the electrochemical detection of ibuprofen (IBP), chloramphenicol (CRP), and sulfamethoxazole (SFX). Optimal detection conditions were established as follows: pH 5.5, 7.0, and 6.0 for IBP, CRP, and SFX, respectively. The optimized accumulation potentials were -0.6 V, -1.1 V, and -1.2 V for IBP, CRP, and SFX, respectively. Similarly, the optimized accumulation times were 180 sec, 120 sec, and 210 sec for IBP, CRP, and SFX, respectively. Under these optimized conditions, the sensor demonstrated excellent sensitivity, achieving detection limits of 0.030 μgL^{-1} , 0.009 μgL^{-1} , and 0.016 μgL^{-1} for IBP, CRP, and SFX, respectively.

The selectivity of the nanocomposite-modified electrodes for respective pollutant detection was rigorously assessed in the presence of co-existing ions at concentrations tenfold greater than the target analyte. The ZnO(NP)@GrO-GCE demonstrated that common interfering metal ions, including Ca^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Mg^{2+} , and Ni^{2+} , did not significantly affect the electrochemical detection of Cd^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} . This indicates that the ZnO(NP)@GrO-GCE displays significant selectivity for heavy metal ions, even in intricate matrices with potentially competing cations. Similarly, the CeONC@GrO GCE showed excellent selectivity in electrochemical detection of IBP, CRP, and SFX in the presence of various cations and anions *viz.*, Ca^{2+} , Mg^{2+} , NO_3^- , and SO_4^{2-} , along with the amoxicillin and

ciprofloxacin molecules. The detection of IBP was also assessed in the presence of diclofenac, paracetamol, and tetracycline. The presence of PRT and TTC did not affect IBP detection; however, diclofenac slightly affected the detection of IBP.

Furthermore, the ZnO(NP)@GrO and CeONC@GrO modified electrodes demonstrated reasonably good reproducibility and long-term stability during repeated measurements, with relative standard deviations (RSD%) below 2%, indicating a stable and reliable performance over extended operational use.

The practical applicability and reliability of these electrodes were thoroughly utilized in the real wastewater samples collected from hospital effluents at Ebenezer Hospital near Tuikual Lui, Aizawl, India, and the outlet of the sewage treatment plant at SIPMIU, Aizawl, Mizoram, India. To remove any unwanted particulate matter, the collected samples were first filtered through filter (pore size of 11 μ m). Prior to electrochemical measurements, the samples underwent detailed physico-chemical characterization, including measurements of pH, conductivity, resistivity, salinity, oxidation-reduction potential (ORP), total dissolved solids (TDS), non-purgeable organic carbon (NPOC), and inorganic carbon (IC). Additionally, the elemental composition of the water samples was determined using atomic absorption spectroscopy (AAS). The real water samples were spiked with known concentrations of target pollutants. The hospital wastewater showed the recovery percentages of: 91.6–101.2% for Cd²⁺, 89.9–99.92% for Hg²⁺, 99.42–104.6% for Pb²⁺, and 90.9–106.4% for Zn²⁺ utilizing the ZnO(NP)@GrO GCE. Similarly, the recovery of IBP, CRP and SFX was 90.43% -104.8%, 93.14% - 105.39% and 94.01% - 105.67%, respectively, utilizing the sewage treatment plant effluent water. These results demonstrate that the ZnO(NP)@GrO GCE and CeONC@GrO GCE are highly effective, accurate, and reliable for real water applications, capable of detecting trace levels of both heavy metals and pharmaceuticals in complex wastewater matrices.

Additionally, the CeONC@GrO nanocomposite was explored as a multifunctional material for degrading CRP and SFX under the photo-Fenton like process. Besides its excellent electrochemical sensing performance, it exhibited seemingly high photocatalytic activity under LED irradiation, achieving 77.0% and 84.2% degradation of CRP and SFX, respectively, within 120 min at dosages below

the EC₅₀ threshold (100 mgL⁻¹). Hydroxyl radicals (•OH) were identified as the dominant reactive species, with minimal toxicity observed in degradation intermediates. Negative Gibbs free energy values confirmed the reactions' spontaneity, highlighting CeONC@GrO as an efficient, low- or non-toxic, and sustainable material for simultaneous detection and remediation of these pharmaceuticals.