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Review of Developments of Modified Carbon-Based Electrodes on Electrochemical Sensors for Water Environment Monitoring

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Environmental components, especially water, are important for human life and other organisms and the sustainability of the earth. Recently, environmental pollution has been one of the most crucial problems globally. Therefore, analytical methods are needed to monitor the water environment pollutant. Electrochemical techniques have been developed for pollutant determination in water environments due to low cost, simplified operations, shorter time for analysis, increased sensitivity, and capabilities for simultaneous detection of multiple substances. One of the most common electrochemical sensors is based on carbon electrodes. Carbon electrodes have many advantages, such as low background current, mechanical strength, inhibition of water electrolysis, and ease of modification. In this review, we described the development of carbon electrodes in electrochemical sensors to determine water pollutants including 4-nitrophenol, tetracycline, diazinon, and heavy metal. This review mentioned the various modified sensors that increase the performance of the sensor including sensitivity, selectivity, and reproducibility. We expect that this review can be used as the basis for developing further modified sensors with excellent performance.

Keywords: Electrochemical sensor, Carbon electrode, 4-Nitrophenol, Tetracycline, Diazinon, Heavy metal

INTRODUCTION

Environmental components such as water and the sustainability of these components are essential for all living organisms and the earth's sustainability. Water is the separated environment component from the land that is the primary source of life and cannot be substituted with other components. However, most environmental problems recently caused by human activity are related to water quality [1]. Environmental pollution is one of the most critical problems facing humanity and the other life forms on our planet today. During human activity such as industrialization, urbanization, endangering wildfire, and human health, many hazardous substances such as heavy metals, petrochemicals, pharmaceuticals, nanomaterials, pesticides, and herbicides are released into the water environment intentionally or unintentionally. That caused pollution when the substances were above the natural level [2,3]. In most developing countries, water pollution is caused by domestic sewage, industrial effluents, leaches, and runoff from solid waste dumps and agricultural land [4]. Water pollution has many negative effects on the ecosystem, humans, and other organisms. There is an essential correlation between water pollution and health problems in human life. Polluted water could cause many different diseases such as respiratory disease, cancer, reproductive system diseases, diarrheal disease, neurological disorders, and cardiovascular disease. Moreover, water pollution could cause the loss of the stability of the water ecosystem, where many organisms live [1]. Consequently, analytical methods are required to control various substances in the water environment at a safe level.

Several analytical methods are used to detect the substances that cause water pollutants. There is Liquid

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Chromatography [5], High-Performance Liquid Chromatography [6-8], Gas Chromatography [9,10], UV spectrophotometry [11], and Mass Spectrometry [12]. Although those common methods are relatively sensitive and specific, they are expensive, complicated, require well-trained personnel for operation and maintenance, and are time-consuming [13,14]. Therefore, it is necessary to develop analytical methods that are affordable, simple, rapid, sensitive, and selective.

Recently, electrochemical techniques have been developed and found in various application areas. Electrochemical methods have some advantages such as cost-effective, simplified operations, shorter time for analysis, increased sensitivity, and capabilities for simultaneous detection of multiple substances [15,16]. Electrochemical sensors were developed to obtain accurate and real-time analysis results of a specific compound. The electrochemical sensor consists of a transducer and electrodes, which are coated with a chemical or biological recognition layer. Electrode modifications can improve sensor performance, such as sensitivity and selectivity [17]. The electrochemical sensor can be recognized depending on the type of transducer of the sensor: potentiometric, conductometric, impedimetric, and voltammetric or amperometric [18]. Voltammetry is a powerful electroanalytical technique that refers to the current measurement at a working electrode as a potential at a limited range was applied. Some common methods in voltammetry are cyclic voltammetry, squarewave, stripping voltammetry, and amperometry, a sub-class of voltammetry in which the electrode is held at constant potentials for certain periods. Voltammetric sensors were successfully applied for the sensitive analysis of various pollutants (*i.e.*, heavy metals, herbicides, pesticides, dye, pharmaceutical compounds, *etc.*) in environmental samples [16,19].

The most important part of an electrochemical sensor is a working electrode that can be modified to become a sensitive and selective sensor. Common working electrodes are carbon-based electrodes that are widely used in voltammetric sensors for some reasons, including low cost, availability, stability, and easiness of modifying the morphology of carbon. There are some carbon-based electrodes such as carbon paste electrodes (CPEs), glassy carbon electrodes (GCEss), screen printed electrodes (SPEs), carbon nanotubes, and graphene. The use of carbon as a working electrode has some advantages, such as low background current, mechanical strength, and inhibition of water electrolysis [15,20]. Therefore, the electrode materials were an important component in developing the excellent performance of electrochemical sensors and detecting target analytes [21]. Many electrochemical reactions can occur at electrodes of carbon materials, whereas electrochemical transformations at electrodes with other materials can occur or cause electrolyte decomposition. In addition, carbon-based electrodes are the most suitable for on-field analysis [17]. Accordingly, in this review, the environmental application of carbon-based electrodes with various developments in electrochemical sensors that can improve the performance of the sensors was briefly described. The comparison of the sensor performance for some pollutants is also shown in Table 1.

Electrochemical Sensors for 4-Nitrophenol Detection

4-Nitrophenol (4-NP) is one of the most hazardous and toxic phenols for human health and the environment. 4-NP is a phenolic compound generally found in wastewater from pharmaceutical, agriculture, petrochemical, coke ovens, and steel foundry. 4-NP can be a pollutant in water due to its properties, including high solubility, stability, and toxicity in water. 4-NP affected human health. Ingestion of 4-NP can cause headaches, drowsiness, nausea, and cyanosis [22]. The limit of 4-NP in drinking water was 0.43 μM according to the United States Environmental Protection Agency (EPA) [23]. Thus, it leads to the development of electrochemical analysis methods for 4-NP in the environment.

4-NP is a weak acid that has a pKa value of 7.15. In the acidic condition (pH less than 6), most 4-NP was in the molecular form. Therefore, 4-NP was dissociated into anions form in the alkaline condition [22]. 4-NP undergoes an electro-reduction process into 4-hydroxyaminophenol, which involves an equal number of protons and electrons transfer ($+4e^-$, $+4H^+$). Furthermore, 4-(hydroxyamino)phenol is reduced into 4-nitrosophenol involved with the $2e^-$ and $2H^+$ transfer process (Fig. 1) [24]. However, Li *et al.* also proposed another plausible reduction mechanism for 4-NP in their experiment. The electro-reduction process of 4-NP involved two-electron and three-proton with two routes. The free radicals of OH and O might appear in the intermediate

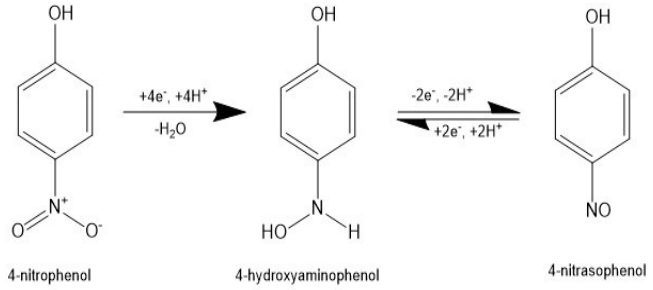

Fig. 1. Possible mechanism scheme for 4-nitrophenol reduction.

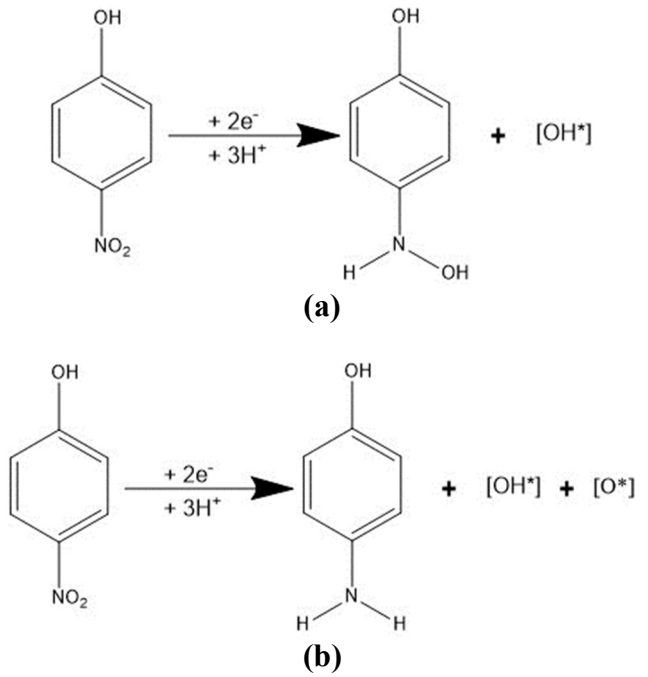

Fig. 2. Another possible mechanism scheme for 4-nitrophenol reduction involved free radical OH and O (a) mechanism 1 (b) mechanism 2.

product of 4-NP reduction in acidic conditions (Fig. 2) [25]. As reported by previous studies, the electro-oxidation process also occurred in the electrochemical detection of 4-NP. 4-NP electro-oxidation converted to p-quinoimine involved the formation of p-(hydroxyamino)phenol-p-nitrosophenol [26]. Giribabu *et al.* modified GCE with poly(methylene blue) (PMB) for 4-NP determination. Hydrogen bonding and ion pairs interaction between PMB and 4-NP caused the potential shift to a more negative potential. It indicated that PMB could improve the electron transfer rate between the electrode and 4-NP molecules. The electrode showed a linear response in the concentration range of 15 nM to 250 nM. The sensor has a low detection limit of 90 nM. The linear concentration response was obtained in the range of 15-250 nM. The limit of detection was estimated to be 90 nm. The sensor obtained the recoveries value in the range of 97%-101.6% for analysis of 4-NP in water samples [26].

Pfeifer *et al.* carried out a comparative study of 4-NP cathodic and anodic quantification using the DPV technique at GCE. To increase the reproducibility, GCE was polished with alumina powder and washed in an ultrasonic bath with ultra-pure water after each measurement. That step was used to reduce the passivation effect at the surface of the electrode. In anodic DPV studies, the oxidation peak was shown at 1.2 V in BR buffer pH 2.4-NP peak shifts towards less positive potential with increasing pH. It was related to the involvement of protons in protonation and deprotonation of electrochemically oxidized species. The linear range of anodic DPV was 2-100 μM with a detection limit was 1.29 μM. Therefore, for cathodic DPV studies, the reduction peak was shown at around -0.6 V in BR buffer pH 2. The reduction peak shifts towards more negative potentials with increasing pH. The linear range was obtained at 2-100 μM with a detection limit was 0.17 μM [27].

Carbon-based electrodes for 4-NP detection had been modified with graphene, polymer, and metal oxide nanoparticles. Graphene is an attractive material due to its extraordinary properties, such as large surface area, high electrical conductivity, good mechanical strength, and biocompatibility [21]. Graphene has a layer structure of sp2 hybridized carbon atom layer that forms hexagonal lattices. Graphene has high conductivity due to the full delocalization of electrons in its geometry structure [28]. Devasenathipathy *et al.* developed a 4-NP electrochemistry sensor using iron phthalocyanine decorated graphene nanosheet composite (GNS-FePc) modified GCE. FePc was used because those materials have excellent electrocatalytic properties and have been used as electrocatalysts for various electrochemical reactions. However, FePc is unstable on the electrode surface and has poor conductivity. Therefore, graphene is used to stabilize FePc. The preparation of the composite used a simple solution-based chemical reduction method. This

method successfully synthesized GNS-FePc composite with highly stable FePc. FePc/GCE has shown a reduction peak at the potential of -0.85 V with a low peak current. Therefore, GNS/GCE and GNS-FePc/GCE show reduction peaks at -0.65 and -0.75 with high and sharp peak currents. Those results indicated that it has good electrocatalytic ability for the reduction of 4-NP. GNS-FePc/CGE has a wide linear range at 100 μM-0.7 mM. Therefore, the detection limit was calculated to be 10 μM. The sensor has good repeatability and reproducibility with RSD of 2.58% and 2.14%. The sensor could measure 4-NP in water samples [29]. The detection limit of this sensor was not too low when compared with other sensors.

To obtain a better performance of GO-modified electrode, Nehru *et al.* developed a 4-NP electrochemical sensor based on graphene oxide-TiO_2 composite (GO/TiO_2) modified GCE. Both materials give a synergic effect to increase the adsorption and electron transfer ability of the surface electrode due to the high surface active area. TiO_2 nanoparticles were prepared using a sol-gel method. The results showed that GO/GCE has low conductivity, but the opposite was shown with GO/TiO_2/GCE. The small peak-to-peak separation at cyclic voltammetry measurement indicated the low conductivity of GO/GCE. GO showed insulating behavior because of its functional group, including OH- and -COOH groups which blocked the diffusion of the redox probe and increased the internal resistance at the electrode interfaces. The electrode has a linear response in the range of 0.02 μM to 370.57 μM. The low detection limit was obtained at 0.0039 μM. The electrode has good reproducibility with an RSD value of 2.35%. The sensor performance was evaluated in a water sample. The recovery results were obtained in 98.4-101.3% [30].

GO has a conjugated area that can increase the conductivity of the materials. However, the absence of percolating pathways between sp2 carbon clusters caused obstructed the long-range conductivity. Consequently, synthesized GO generally has insulating properties. For recovery of the conductivity and other properties of the GO, GO was reduced to remove the oxygen functional group in the surface of graphene and the other atomic-scale lattice defects. It can restore the conjugated network of the graphene [31]. That process is carried out to produce reduced graphene oxide (RGO). Due to the conductivity of RGO, it has been proposed to improve sensor sensitivity. Tang et al. developed an electrochemical sensor for 4-NP based on reduced graphene oxide (rGO) and Au nanoparticles composite modified GCE. RGO and Au nanoparticles have electrocatalytic properties and could provide a synergic effect. RGO/AuNPs coated on the surface of GCE by electrodepositing methods. Their synergic effect was indicated by the characterization of electrodes that have better current response than bare GCE and RGO/GCE toward $Fe(CN)_6^{3-/4-}$. Furthermore, AuNP/RGO/GCE showed the highest electrocatalytic activity to 4-NP because of the synergic effect of AuNPs and RGO as co-catalysts. The electrochemical behavior of 4-NP with AuNP/RGO/GCE showed the main redox peak (O1/R1) at 0.2 V, two pairs of weak redox peaks (O2/R2 and O3/R3), and two reduction peaks at -0.4 V and -0.6 (marked with R). The two reduction peaks were caused by the irreversible reduction of the nitro group to produce hydroxylamine species. Therefore, the main dan two pairs of weak redox peaks are due to the reversible two-electron oxidation-reduction reaction of 4-aminophenol produced via hydroxylamine. The reaction scheme is shown in Fig. 3. The measurement of 4-NP obtained RSD within 3% which indicated good reproducibility. Using DPV methods, the linear concentration range was 0.05-2.00 μM and 4.00-100 μM, with the detection limit being 0.02 μM. Therefore, using SWV methods, the linear concentration range was 0.05-2.00 μM and the detection limit was 0.02 μM. The recovery of the analysis of the water samples was in the range of 98.0% to 104.0% in both DPV and SWV methods [32].

In another work, Yang used GCE modified by reduced graphene oxide/Ag nanocomposite (RGO-Ag). RGO-Ag was prepared with the simple one-pot hydrothermal method using graphene oxide and $AgNO_3$ as starting materials. The electrochemical behavior of the sensor for 4-NP detection was evaluated using CV in pH 4 PBS solution. Based on the CV result, reduction peaks are shown at bare RGO and RGO-Ag electrodes. RGO sheets promote electron transfer between the 4-NP molecules to the electrode surface. The result was a potential reduction peak at -0.507 V, less positive than bare GCE. At the same time, the Ag particles could increase the sensitivity of the sensor. Both modifiers provided the synergic effect. It is indicated from the peak current of RGO-Ag four times greater than bare-GCE. The sensor has a more wide linear range in the range of 1-500 μM.

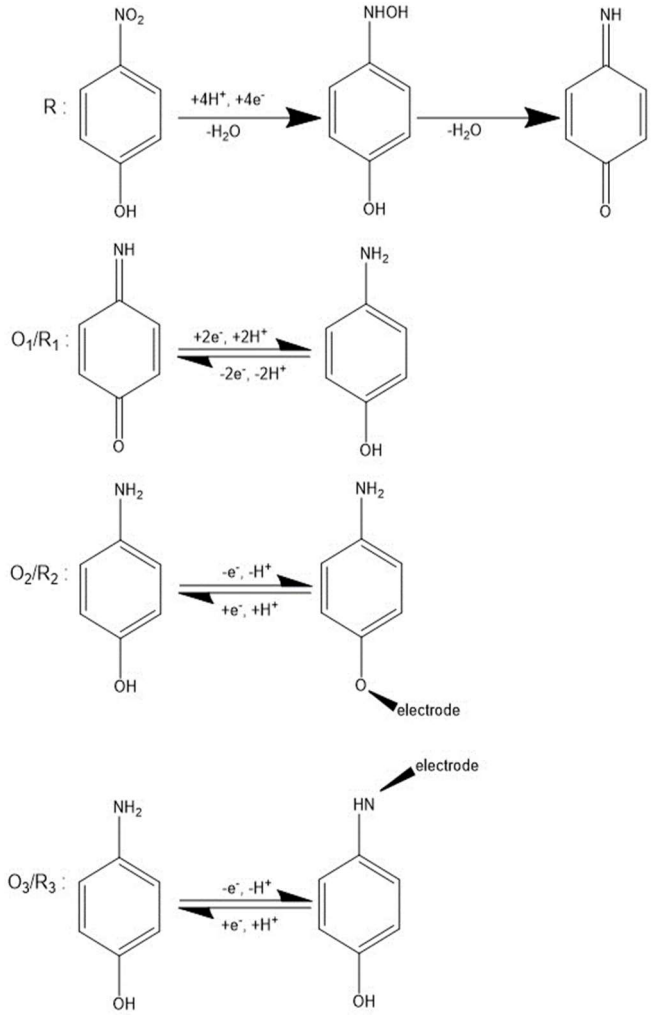

Fig. 3. Possible electrochemical redox reaction of 4-NP on the electrode.

The detection limit was estimated to be 0.114 μM. The sensor has good reproducibility with an RSD was 3.25%. It could measure 4-NP in water samples [33].

The electrochemical sensor also can be modified with conducting polymer to improve the conductivity of the electrode due to electron transfer enhancement through conjugated π structure [34]. The other work from Giribabu et al. also modified GCE with another polymer, poly(methyl orange) (PMO), for the determination of 4-NP. PMO-modified GCE was developed by electropolymerization MO on the surface of GCE using cyclic voltammetry. In the electrochemical sensing of 4-NP, the oxidation peak of 4-NP appeared clearly at 0.98 V using PMO/GCE. That results due to various interactions, such as hydrogen bonding, electrostatic, dipole, and π-π interaction between PMO/GCE and 4-NP. PMO/GCE also has a better electrocatalytic activity than bare GCE based on a higher oxidation peak current. The electrooxidation of 4-NP involved two electrons and three protons in forming p-quinonimine. PMO/GCE has a linear range of 0.6-10 μM with a low detection limit of 170 nM. The results showed a lower detection limit than previous work. PMO/GCE is suitable for water samples with recoveries values in the range of 99.2%-100.9% [35].

Furthermore, Poly(safranine) film (PSN) modified GCE was developed by Liu for voltammetric determination of 4-NP. Electropolymerization of safranine on the GCE was synthesized by CV in PBS pH 6 containing 2.0×10^{-5} M safranine. A poly(safranine) film was made on the surface of GCE by electropolymerization process. Electrochemical behavior studies of the 4-NP on the sensor showed a reduction peak at about -1.5 V. The reduction peak was due to an initial $4e^-/4H^+$ reduction of the nitro group to the hydroxylamine species continued with the reduction to the NO group by releasing $2e^-$ and $2H^+$. The reduction peak produced by poly(safranine) modified GCE is higher than bare GCE. That result indicated the excellent properties of the polymer film, such as its three-dimensional distribution mediators and strong adsorption ability. Therefore, the adsorptive ability might be shown during the pre-concentration process in which 4-NP can be accumulated in the electrode surface via π-π hydrophobic interaction and/or hydrogen bonding caused by the current response enhancement. The peak current was linear to the 4-NP concentration over the range of 8.0×10^{-8} to 4.0×10^{-5} M, with the detection limit being 3.0×10^{-8} M. The sensor has acceptable repeatability and reproducibility with 2.03% and 3.14% RSD values. The sensor was used for water and fruit samples. Analytical results were obtained recovery values in the range of 94.0%-107.1% [36].

Zeng *et al.* modified the GCE surface with molecularly imprinted poly(methacrylic acid) (MIP MAA) to obtain specific cavities for the molecules' target structure [37,38]. MIP was combined with reduced graphene oxide (RGO) to improve the adsorption ability of the electrode surface due to the excellent affinity of RGO with 4-NP. Modified GCE with MIP showed a higher peak signal than modified GCE with NIP. The results indicated that specific cavities on

RGO/MIP/GCE could improve the sensor's ability to detect 4-NP. Furthermore, the selectivity was evaluated with the presence of nitrobenzene, 2,4,6-trinitrotoluene, 2.4-dinitrotoluene, 1,3-dinitrobenzene, and some metal ions. The results showed that the 4-NP signal was not affected significantly by interference. The sensor showed a linear response in the range of 0.01 to 100.0 μM. The detection limit was obtained at 0.005 μM. The sensor had good reproducibility with an RSD value of 4.39%. The sensor performance was evaluated in water samples. The recoveries value was obtained in the range 97.3%-102.8% [23].

Metal oxide nanoparticles (MO NPs) were used as supporting materials in the electrochemical sensor due to various properties, such as their size, stability, conductivity, electrocatalytic, and high surface area. The nanosize, structure and electronic properties of MO NPs provided the fast electron transfer between electrodes and the target molecule. Cu_2O was a widely used MO NPs for electrochemical analysis [39]. Yin *et al*. developed a 4-NP sensor based on Cu_2O nanoparticles modified GCE. Cu_2O nanoparticles could generate a sensitive electrocatalytic response for various molecules. The result of the experiment indicated that Cu_2O nanoparticles increased the sensitivity of the GCE due to the increasing ability of the sensor to adsorb 4-NP onto the electrode surface. However, the oxidation peak of 4-NP in CV measurement decreased significantly during consecutive sweeps until the peak almost disappeared completely in the third sweep. It might be due to the oxidative products of 4-NP or the polymers formed by the oxidative product on the electrode surface and blocking the access of 4-NP. The electrochemistry effective surface areas of the electrodes were also studied by chronocoulometry using 0.1 mM $K_3(Fe(CN)_6)$ as a model complex based on the Anson equation. The result showed that the electrode effective surface area of the modified GCE was higher than that for bar GCE. The sensor has a wide linear range from 1.0 to 400 μM and the detection limit was approximated to be 5.0×10^{-7} M. The sensor has acceptable reproducibility with the RSD values was 3.72%. The sensor was used to determine 4-NP in water samples. The results of the recovery of 4-NP are in the range from 94.60% to 105.5% [40].

Zaidi and Shin developed an electrochemical sensor for 4-NP detection based on MnO_2 NPs and reduced graphene oxide (RGO). MnO_2 NPs ware electrodeposition on the surface of RGO-modified GCE to obtain a synergic effect and improve the redox peak signal of 4-NP determination. The synergic effect was indicated by a cathodic peak shift less negative due to the high electron transfer rate, excellent electrocatalytic activity, and conductivity of the modified electrode. In the analytical performance evaluation, the linear range was obtained at 0.02-0.5 μM and 2-180 μM. The limit of detection was estimated to be 10 nM. The results of selectivity evaluation indicated that the 4-NP signal does not strongly affect the presence of phenol molecules, including 2,4-dinitrophenol, 4-aminophenol, nonylphenol, bisphenol, and phenol at 2 times higher concentration than 4-NP. The sensor had excellent reproducibility with a low-value RSD of 0.5%. The sensor was applied in various water samples with recoveries at the range of 93.50%-98.20% [41].

The electrocatalytic properties of metal oxide nanoparticles, including CeO_2 nanoparticles, were due to the availability of space for oxygen or ionic species in the lattice structure. That species can be switched with species that act as impurities in lattice to increase conductivity properties. Transition metal ions can be dopped in metal oxide crystals to obtain excellent catalytic properties [42-44] Ansari *et al.* modified GCE with CeO_2 nanoparticles (CeO_2 NPs). CeO_2 NPs were doped with Ag to increase the electrocatalytic and conductivity properties of the electrode. The results indicated that measurement 4-NP with a modified electrode obtained an anodic peak signal at 0.5 V, but the signal was not obtained in the bare electrode. The signal has a linear response in the range of 7.81-1000 μM. The detection limit was estimated at 7.8 μM [44]. Another work from Ansari *et al.* is the development of the electrochemical sensor-based GCE coated by Cu-doped CeO_2 NPs. The sensor has more excellent performance than previous work with Ag-doped CeO_2 NPs. The sensor has a more wide linear range at 7.81 to 5000 μM. The detection limit was obtained at 7.18 μM. The sensor also has good stability and reproducibility performance [45].

Electrochemical Sensors for Tetracycline Detection

The use of antibiotics for human health and veterinary has increased in recent years. Tetracycline (TC) is one of the most common antibiotics applied for human therapy, aquaculture, animal medicine, and agriculture materials. TC was widely used due to its advantages, such as economic cost

production and excellent quality. However, the increase in antibiotic consumption is followed by increasing compound discharge to the environment, especially water. TC is difficult to be metabolized by humans and animals, so that excreated through urine and feces into the environment. It can cause an accumulation in the environment in the long term [46-49]. Some authorities have determined the maximum residue limits (MRLs) of the TC in food-producing animals to protect human health and the environment. European Union estimated the MRL of TC in the range of 100-300 μg kg^{-1} in poultry products [50]. Accordingly, analytical methods are needed for monitoring TC in the environment.

In recent years, electrochemical sensors for TC detection was developed with various modification, such as metallic nanoparticles, polymer, carbon nanoparticles, and graphene. Development of the sensor using carbon-polymer composite was reported by Calixto *et al.* In that work, Calixto *et al.* fabricated a simple electrochemical sensor based on a graphite-polyurethane composite electrode. The electrode was prepared by mixing 60% of graphite (m/m) with polyurethane homogeneously. Two oxidation peaks were obtained at 960 and 1100 mV for TC measurement in an electrochemical study. The sensor also has well enough performance. The linear range of the electrode was at the range 4.00 μM-40.0 μM for the first peak and 4.00 μM-20.0 μM for the second peak. The detection limit of the peaks was 2.30 μM and 2.60 μM. Then, the sensor was evaluated in water samples. The recovery value was obtained at 96% [51]. However, the performance of the sensor can be increased due to other supporting materials used.

Metallic nanoparticles can be used as supporting material on carbon-based electrodes. Metallic nanoparticles increased the electrode surface for analyte detection. Kushikawa *et al.* constructed an electrochemical sensor based on GCE modified by platinum nanoparticles supported on carbon (PtNPs/C). PtNPs/C on the GCE surface increased the electroactive area ten times larger. Consequently, the peak currents of TC at the PtNPs/C/GCE significantly increased than at the bare GCE. The pH influence in the electro-oxidation of TC was evaluated in CV. The Nernstian slope of 60 mV pH^{-1} in this study indicated that the oxidation of TC involved the same number of electrons and protons. The second anodic peak of TC's first oxidation produced slopes of 29 mV pH^{-1} at pH 2.0-4.0 and 71 mV pH^{-1} at pH 4.0-7.0. The results were related to the mechanisms involved of one electron and two electrons (pH 2.0-4.0) and both two electrons and protons (pH 4.0-7.0). The first mechanism was the direct oxidation of the phenolic substituents. Therefore, the second mechanism was the oxidation reaction sequence involving two steps of electron transfer coupled with the output of a proton (Fig. 4). Two anodic peaks appeared that has a linear range of 9.99 μM to 44.0 μM. The detection limit of the peaks was 4.28 μM and 6.12 μM. The performance of the sensor was evaluated in urine samples. The recovery value of the TC spike was 102.60% [52].

Metallic nanoparticles, such as AuNPs, can also be combined with other materials to provide a synergic effect and improve the performance of the sensor. Devkota *et al.* developed a sensitive and selective electrochemical sensor for tetracycline determination. Screen printed carbon electrode (SPCE) was modified with gold nanoparticles (AuNP) to increase the sensitivity and molecularly imprinted overoxidized polypyrrole (MIOPPy) to improve the sensor stability. Both modifiers gave the synergic effect to improve the current signal at the oxidation peak of tetracycline. In the study, sodium dodecyl sulfate (SDS) was added to the test solution for facilitated oxidation of TC. The measurement of TC showed a sharp, high peak current and a negative shift in peak potential. SDS that was absorbed onto the electrode and had a negative charge promoted the mass transfer and pre-concentration of TC molecules that have positively charged in acidic conditions. It explained the increase of the oxidation peak of TC with the presence of SDS in a particular concentration. The sensor also has more sensitivity with a low detection limit. The sensor has a linear range from 1 to 20 μmol dm^{-3}. The limit of detection was estimated at 0.65 μmol dm^{-3}. The oxidation peak does not change significantly after the addition of chloramphenicol and amoxicillin. However, after the addition of oxytetracycline which has a similar structure and electrochemical behavior, the oxidation peak of TC was affected significantly. The sensor had an RSD value of 3.43%. The sensor was evaluated in shrimp samples and had percentage recovery values in the range of 92.2 to 105.0% [53]. Another sensor was fabricated by Osikoya *et al.* The electrochemical sensor was based on GCE modified by graphene (Gr) and gold nanoparticles (AuNP) to form Gr-AuNP nanointerfaces. Gr-AuNP/GCE has a linear response in 2.90×10^{-2} mM to 1.53 mM. The

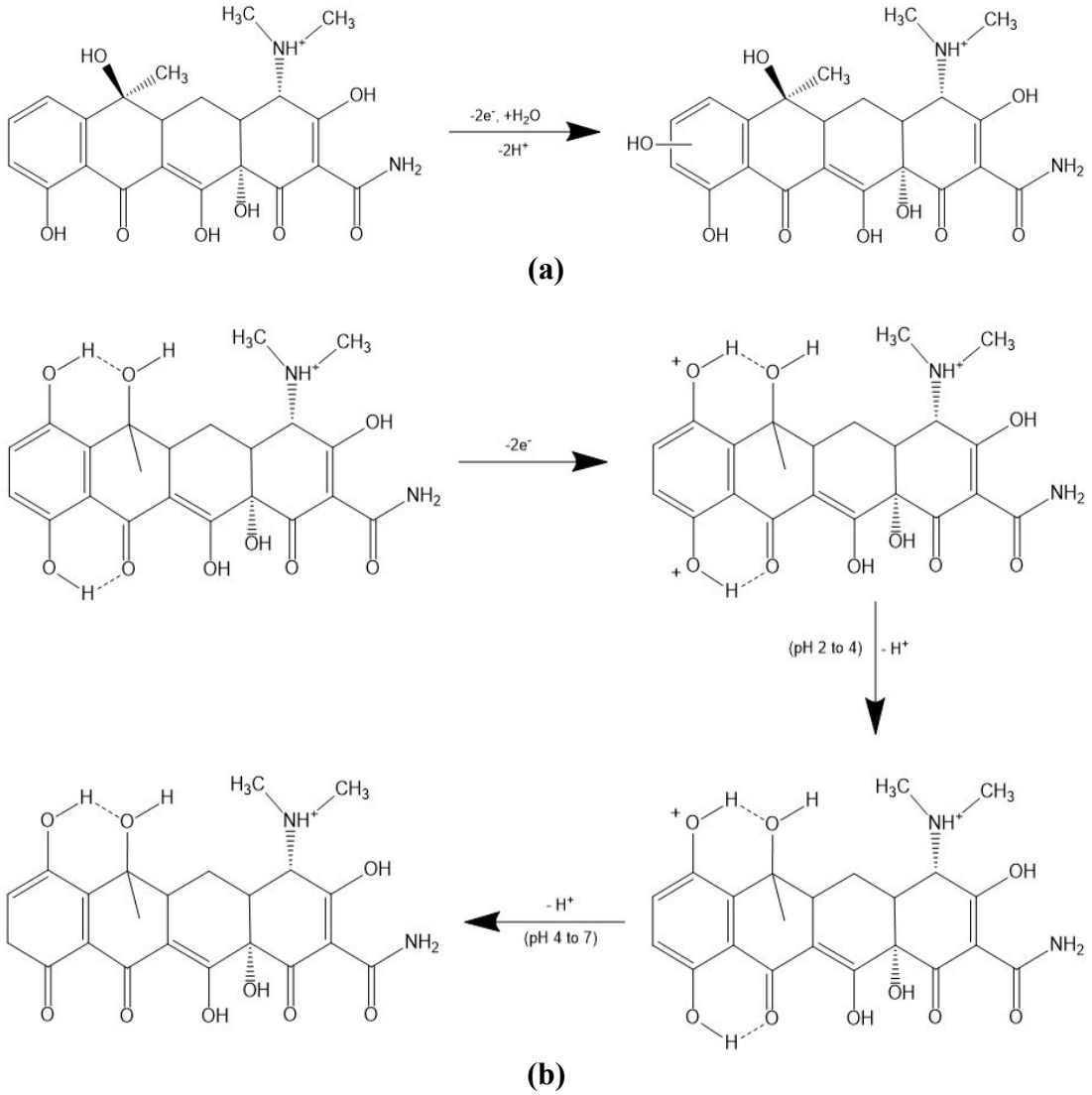

Fig. 4. The proposed mechanism of TC oxidation. (a) direct oxidation I phenolic substituent, (b) sequence of the oxidation reaction.

detection limit of the sensor was obtained at 1.62×10^{-2} mM [54]. However, this work did not obtain the wide linear range and low detection limit like the previous study of Devkota *et al.* that also used AuNPs to modify the electrode.

Recently, carbon-based nanoparticles, such as carbon nanotubes, have been developed for electrochemical analysis of TC [38,55,56]. Carbon nanotubes were used as electrode materials because of their excellent properties, such as mechanical stability, large surface area, and high electrical conductivity. Carbon nanotubes have two types of structure; single-walled and multi-walled [57,58]. Carbon nanotubes can be functionalized with certain functional groups and other materials to improve the electrocatalytic properties, selectivity, and sensitivity. Wong et al. modified carbon paste electrodes with multi-walled carbon nanotubes functionalized carboxyl group (MWCNT-COOH) and graphene oxide (GO). The electrode was prepared with homogeneous graphite powder, MWCNT-COOH, GO, and phosphate buffer solution to improve the conductivity of the carbon paste electrode (CPE). It showed that MWCNT-COOH/GO/CPE had excellent electrocatalytic properties for the determination of TC. The modified CPE had a low redox

potential at 270 mV for anodic peak current. However, the bare CPE had an anodic peak current at 750 mV with CV. The result indicated that CPE modification produced a high electronic transfer and enhanced response of the MWCNT-COOH/GO/CPE. That result can also promote the high selectivity of the sensor because the anodic peak current was obtained in the low potential compared with the anodic peak of the interferences. The sensor was evaluated by adding six pharmaceutical compounds, such as amocillin, clindamycin, lidocaine, hydrochlorothiazide, ranitidine, and piroxicam. The sensor not detected the interferences compounds in the same concentration with TC. The sensor has a linear response range of 2.0×10^{-5} to 3.1×10^{-4} M. The detection limit was estimated at 3.6×10^{-7} M. The sensor was used to determine TC in river water and artificial urine samples. The recoveries of the sample analysis were obtained in the range of 92% to 101%. [55].

Another development of functionalized MWCNT was reported by Wang *et al.* The electrochemical sensor-based GCE was modified by gold nanoparticles-multiwall carbon nanotubes functionalized carbonyl group (MWCNTs-GNPs). MWCNTs-GNPs were coated with MIP methacrylic acid. The number of carboxy groups significantly increased because of MIP coated. It can improve the surface area which interacts with TC. It also stabilized the gold nanoparticles in the electrode surface. The electrochemical behavior of TC on the imprinted electrode was evaluated using CV. No oxidation peak was observed in the GCE and GCE/MWCNTs electrodes. However, an oxidation peak was observed at 1.10 V on the GCE/ MWCNTs-GNPs electrode due to the electrocatalytic oxidation of TC caused by GNPs. GNPs with catalytic properties oxidized TC molecules via phenolic and di-(methyl)amino substituents. The imprinted polymer also provided the specific binding ability for TC molecules, which improved the electrocatalysis of TC on the electrode surface. The selectivity of the sensor was evaluated with oxytetracycline, nafcillin, and chloramphenicol. oxytetracycline has a higher effect than nafcillin and chloramphenicol in the determination of TC because of their similar structure and chemical properties. However, the effect does not significantly interfere TC signal. In the analysis performance evaluation, the peak current was linear at a concentration of 0.1 to 40 mg l^{-1}. The limit of the detection was obtained at 0.04 mg l^{-1} [38].

Palisoc *et al.* coated the GCE surface with gold nanoparticles (AuNPs) and then electrodeposition multi-walled carbon nanotubes (MWCNTs). For the determination of TC, Palisoc *et al.* used the approach $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ as the mediator. The detection limit was obtained at a low concentration. The peak was decreased along with the increase of the TC concentration and had a linear response at 5-140 ppm, but it has a low Pearson coefficient of 0.9159 [56]. With that approach, the sensor did not directly measure the electro-oxidation of TC.

Graphene is a carbon allotrope with excellent features, such as large surface area, high electrical conductivity, electrocatalytic properties, and high adsorption ability. Due to those features, Lorenzetti *et al.* developed a selective and sensitive electrochemical sensor-based SPE modified by reduced graphene oxide (RGO) for tetracycline determination. Based on the high adsorption capacity of the graphene, Lorenzetti et al. applied adsorptive transfer stripping differential pulse voltammetry (AdTDPV) to improve the selectivity and sensitivity of the sensor. The result of AdTDPV was compared with the DPV technique. The current signal obtained by bare SPE is higher than RGO-SPE in the DPV technique. However, the current signal obtained by AdTDPV is higher using RGO-SPE than using bare SPE. The results indicated that AdTDPV improved the determination of TC using RGO-SPE due to the higher adsorption capacity of the RGO-SPE and the low affinity of TC on a bare SPE surface. Consequently, the sensor has a short linear range of 20 μM to 80 μM because limited of the adsorptive capacity of RGO-SPE. The sensor also has low reproducibility with RSD values of 18%. The selectivity was evaluated by the addition of ascorbic acid, phenol, and uric acid. The sensor adsorbed selectively to TC with the presence of phenol and ascorbic acid. However, the signal of TC was influenced by the presence of uric acid in high concentrations. This is due to the strong absorption ability of uric acid in the RGO-SPE surface [59].

Sun *et al.* modified GCE with graphene(Gr)/L-cysteine (L-Cys) composite film to determine TC. The measurement of TC with L-Cys/Gr/GCE has the highest peak current and less negative potential. It indicates that composite film on the surface of GCE has significant electrocatalytic ability. L-Cys could reduce the hydroxyl from the carboxyl group in TC molecules. Meanwhile, the hydroxyl group of the carbon

chains on TC loses electrons and the proton becomes an unstable oxygen-free radical that will rapidly lose electrons and form a double oxygen bond. The limit of detection was estimated at a low concentration. The sensor also has better performance in the presence of the interferences, such as Mg^{2+}, Ca^{2+} (1000-fold), K^{+}, NO^{3-} (500-fold), Na^{+}, Cl^{-} (400-fold), Cu^{2+}, SO_4^{2-} (200-fold), roxithromycin, and norfloxacin (100-fold). The linear range of the sensor is at concentrations 8 µM to 140 µM. The limit of detection was estimated at 0.12 µM. GCE modified by L-Cys-GR generated good reproducibility of the sensor with RSD values at 4.03%. The sensor was evaluated in water samples. The recovery value was obtained in the range of 89.60% to 105.20% [60].

Graphene can be combined with polymer to increase the stability of the sensor and electrocatalytic properties. Kesavan et al. developed the electrochemical sensor with A-polymelamine (p-Mel) film and reduced graphene oxide (RGO) on GCE (p-Mel@RGO/GCE) for TC determination. Melamine is one of the conducting polymers that can improve the electrical conductivity of the GCE. Furthermore, p-Mel can stabilize and increase the active site on RGO [61,62]. The oxidation peak of TC was observed at +0.92 V, which has less positive potential and a higher current than the other electrode in the study. Amine group and positively charged nitrogen from the p-Mel caused π-π interaction with TC and provided electrocatalytic properties. TC redox reaction involved one proton and one electron (proposed by Kezavan *et al*.). Furthermore, the p-Mel film also indicated the redox behavior *via* a proton and electron elimination/addiction reaction at -NH sites on the p-Mel film. The peak current has a linear response in the range of 5.0×10^{-6} M to 2.25×10^{-4} M. The limit of detection was estimated at 2.2×10^{-6} M. The sensor was evaluated in urine samples and had excellent accuracy with recovery values of 99.0 to 99.7% [63].

Benvidi *et al.* developed the aptasensor that used artificial DNA or RNA for TC detection for improved sensor sensitivity. GCE was modified with graphene oxide nanosheets. The aptasensor was fabricated using an amino-modified anti-TC aptamer containing a 76-base sequence with a high affinity for binding to the analyte. Electrochemical impedance spectroscopy (EIS) and DPV were used to investigate the sensor's sensitivity. EIS signals indicated a wide range of linear responses and low and low detection limit, which was 1.0×10^{-13} M to 1.0×10^{-5} M and 2.9×10^{-14} M. The sensor was applied to the blood serum samples with recovery values of 95% and 97% [64]. Benvidi *et al.* also fabricated an aptasensor with poly (L-glutamic acid) and MWCNT modifying GCE. MWCNT was coated in the surface of the electrode and followed by electropolymerization of glutamic acid in the MWCNT/GCE surface. In this work, the same anti-TC aptamer with the previous study was also used in the aptasensor. With EIS, the aptasensor has excellent performance, indicated by the wider linear range and lower detection limit than the graphene oxide nanosheet/GCE aptasensor [65].

Electrochemical Sensors for Diazinon Detection

Organophosphates are commonly used as pesticides, insecticides, and chemical warfare agents because of their effectiveness. However, this compound has toxic properties [66,67]. The pesticide residues can also enter the food chain and cause diverse problems [68]. Diazinon (O, O-Diethyl O-{4-methyl-6-(propane-2-yl)pyrimidin-2-yl] phosphorothioate) is a nonsystemic organophosphate pesticide that is generally used to eradicate insects in agriculture and also for controlling cockroaches, silverfish, and ants in commercial and residential buildings. Diazinon (DZN) acts as an acetylcholinesterase (AChE) inhibitor that can lead to an abnormal accumulation of AChE in the synaptic cleft at muscarinic, nicotinic, and central sites. It can cause toxic effects such as headaches, dizziness, convulsions, delirium, and depression [69]. MRLs of DZN in water was 0.1 µg l^{-1} based on WHO [70]. Therefore, electrochemical methods have been developed for environmental and biological monitoring of diazinon.

Topsoy *et al*. developed an electrochemical sensor for DZN determination based on SPCE coated by polycaprolactone (PCL) and chitosan nanofiber (CS) coated using an electrospinning technique. The electrospinning time corresponded with the thickness of PCL/CHS on the electrode surface. The thick polymeric film could decrease the electrochemical response of the DZN due to the insulating electrode surface. However, the polymeric film structure might improve the sensor selectivity and reduce the effect of interfering molecules. In this study, the electrospinning time was evaluated and had the optimum time of 3 min. Increasing the electrospinning times caused the denser polymeric layer,

more frequently stacked, and the difficulty of DZN molecules to reach the electrochemically active area on the electrode surface. The sensor had a linear signal at 3-100 nM. The sensor had a detection limit of 2.888 nM. The sensor was used for DZN determination in fruit juice samples. The recovery value was obtained at 93.27%-108.30% [71].

Zahirifar *et al.* developed a voltammetric detection of diazinon (DZN) with carbon nanotubes modified carbon paste electrode. Modified with CNT have been chosen because high conductivity of the material, the capability to improve electron transfer, and excellent electrocatalytic ability as electrode materials. CNT was added to the carbon paste and then homogenized to prepare CNT/CPE. Based on the reduction peak current, CNT/CPE increased the peak current approximately four times higher than bare CPE in response to the $Fe(CN)_6^{3-/4-}$ solution. The results indicated that CNT could improve the sensitivity and conductivity of the CPE. CNT/CPE also increased the electrochemical response of DZN at the peak of 0.1 V. The peak exhibited an increase and had a positive reduction potential with pH until it reached the optimum value of 5.25. The lack of proton can be a difficulty for DZN reduction in the high pH. Moreover, DZN represented the clear peak at 0.1 V. CNT/CPE performs a linear detection range in the range of 1×10^{-10} to 6×10^{-8} M with a detection limit of 4.5×10^{-10} M. the sensor was used to detect DZN in fruits and vegetables that diluted in acetate buffer [66].

The electrochemical sensor based on molecularly imprinted polymer (MIP) nanoparticles was developed by Motaharian *et al.* for the determination of DZN. MIP can provide the recognition sites as the modifier agents of the electrode. This study modified CPE with MIP nanoparticles of methacrylic acid (MAA) and ethylene glycol dimethacrylate (EDMA) as crosslinker. MIP nanoparticles were synthesized by the suspension polymerization method in silicon oil. In the preparation step of MIP nanoparticles, the sonication was done to the mixture for 10 min to obtain smaller polymerization droplets. Then, MIP nanoparticles were homogenized with carbon paste to prepare the modified electrode. SEM images of the MIP nanoparticles showed a particle size of less than 100 nm. In the electrochemical study of DZN, the reduction peak signal appeared at -1.24 V in the B.R buffer solution pH 4.4. The linear range was in the range 2.5×10^{-9} to 1.0×10^{-7} M and 1.0×10^{-7} to 2.0×10^{-6} M. The limit of detection was estimated at 7.90×10^{-10} M. The RSD of the sensor was 2.66%. This sensor was used to analyze DZN in well water and apple fruit. The recovery values were in the range of 92.53-100.86% [72].

A similar work was also conducted by Khadem *et al.* In this work, carbon paste was modified with MWCNT and MIP methacrylic acid for DZN detection. MWCNT was added to the paste to improve the sensor conductivity and accelerate the chemical to electric signal transduction. The sensor showed good selectivity due to MIP which provides the recognition site for DZN molecules. The results indicated that the interference including coumachlor, dicloran, dichlrofention, and dimethoate not affect the peak signal of DZN until 1000-fold excess of concentration. Several ions were also evaluated, and the result did not show a significant change in the DZN signal. The linear response of DZN was obtained in the range of 5×10^{-10} to 1×10^{-6} M. The limit of detection was estimated to be 4.1×10^{-10} M. The reproducibility of the sensor was evaluated, and the RSD value was obtained at 3.16%. The sensor was applied to urine and water samples and obtained RSD values in the range of 92.4%-97.50% [73]

To improve the sensor performance, Tadayon *et al.* constructed the electrochemical sensor based on bimetallic Au and Pd nanoparticles coated on the mixture of reduced graphene oxide (RGO) and multiwall carbon nanotube (MWCNTs) nanocomposite modified GCE for determination of DZN. The modification with nanoparticles and nanocomposites are special choices for the construction of a sensing layer in electrochemical sensors. The RGO/MWCNTs hybrids were prepared by sonicating suspension of synthesized GO and acidic treatment MWCNTs and then adding $NaBH_4$ as a reduction agent of GO/acidic MWCNTs mixture. Therefore, Au-PD/RGO/MWCNTs nanocomposite was prepared by chemical reduction method. The modification was done by dropping the suspension of Au-PD/RGO/MWCNTs nanocomposite in DMF solvent onto the surface of activated GCE. In the electrochemical investigation of DZN, the electro-oxidation peak is observed at approximately 0.45 V with modified GCE. In contrast, no peak was observed with bare GCE. With the SWASV method, the electro-oxidation peak was measured linearly in the range of 0.0009 to 11.3 μM. Then, the LOD for determination DZN was

0.002 μM. Also, with an amperometric method, the linear range of DZN determination is 0.003 to 9.5 μM. The LOD was estimated to be 0.0014 μM. The RSD values for measuring various concentrations of DZN were 2.9-3.8%. This method was applied to analysis in water, fruit, and vegetable samples. The recoveries result of the analysis of the samples was in the range of 96% to 105% [74].

Ghodsi *et al.* developed a voltammetric sensor based on MWCNTs/TiO_2NPs modified GCE. TiO_2 nanoparticles have a high affinity to phosphate groups, which can be used in electrochemical sensor development to determine organophosphate pesticides. The preparation of the modified GCE was done by dropping the MWCNTs/TiO_2NPs/acetone mixture on the GCE surface. Moreover, for comparison, MWCNTs/TiO_2NPs were coated in the GCE surface by electrodepositing method. In the study, the electrochemical behavior of DZN indicated two successive reductions (Fig. 5), and the reduction peak current was exhibited at about -0.78 V ad -0.97 V. This study used the first reduction peak to determine DZN due to the more significant peak produced than the second reduction peak. The reduction peak also appeared at -1.2 V due to the reduction of Ti^{4+} to Ti^{3+} corresponding to TiO_2NPs deposited on the electrode surface. The result of the calibration curve was linear in the concentration range of 11 nm-836 nm. The detection limit was estimated at 3 nM. The RSD of the determination of DZN was 3.8%. This sensor was used to analyze water samples. The result of recovery value was in the range of 97.5% to 105.5% [75].

Carbon nanomaterial that is widely developed for many applications is graphene quantum dots (GQDs). The size of GDQs is less than 10 nm, which can provide more active sites due to the oxygen-containing functional group. GQDs also contain a mixture of sp^2 and sp^3 carbon [76,77]. GDQs have excellent properties derived from graphene and carbon dots, including large surface area and diameter, conductivity, electrocatalytic activity, biocompatibility, water-soluble, and simple synthesis [78,79]. Due to their properties, Ghiasi *et al.* used GQDs for developing electrochemical sensors. Ghiasi et al fabricated an electrochemical sensor for DZ determination based on activated GCE (GCEox) modified by graphene quantum dots (GQDs), chitosan (CS), and nickel molybdate nanocomposites ($NiMoO_4$, NMO). The GCE was activated with applied 30 cycles of CV in H_2SO_4 solution at a certain potential. The electrode surface became negatively charged because of the activated process. Then, the modifier was immobilized in the GCEox surface. The sensor had a linear response in the range of 0.1-300 μM. The limit of detection was obtained at 30 nM. The reproducibility was evaluated, and the RSD value was less than 4%. The sensor was applied to the fruit and vegetable samples. The recovery value was obtained in the range of 101.0%-106.0% [80].

The electrochemical sensor for DZ determination was developed by Yola. The determination of DZ was carried out simultaneously with methyl parathion and chlorpyrifos using boron nitride quantum dots (BNQDs)/graphene oxide composite modified GCE. The sensor has an excellent performance. The results showed that the sensor had a linear response in the concentration range of 1.0×10^{-12} M to 1.0×10^{-9} M. The sensor has a low detection limit. The detection limit was estimated to be 6.7×10^{-14} M. The sensor also had excellent reproducibility with an RSD of 0.24%. The sensor was evaluated in water and fruit juice samples. The recovery value was in the range of 97.06-103.23% [81].

Electrochemical Sensors for Heavy Metal Detection

Heavy metal pollutants could cause damage to human health and the environment. These pollutants enter organisms via the alimentary canal and biosphere [82]. Metal ions exist in various environments, including soil, drinking water,

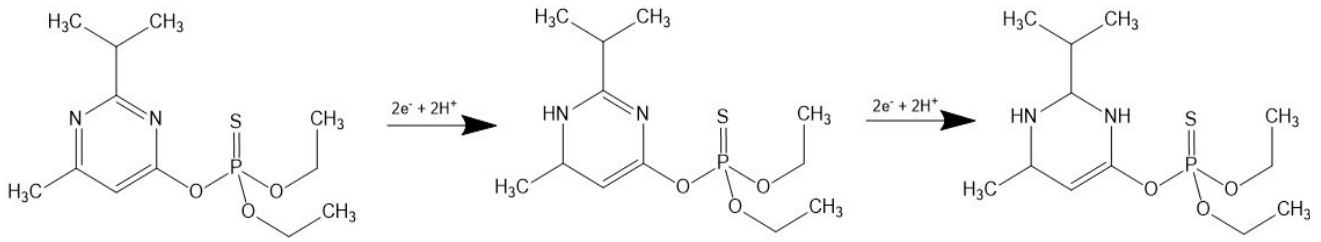

Fig. 5. Proposed mechanism of successive reduction of diazinon.

industrial waste, and food. In humans, excessive Cd^{2+} in the body can produce renal and navicular bone, lung loss, damage to the kidney system, and skeletal deformation. Therefore, excessive Pb^{2+} will cause various symptoms, such as memory loss, irritability, anemia, and muscle paralysis [83]. WHO determined that the limit of lead and cadmium in drinking water are 3 μg l^{-1} and 10 μg l^{-1}, respectively [84]. The analytical methods for monitoring heavy metal pollutants have been developed with various methods and instrumentation, including the electrochemical method.

Previously, mercury was used extensively in electrochemical analysis, especially as a working electrode, because of its unique electrochemical properties. Mercury electrodes have a wide negative potential range, so various reduction reactions can occur for reducible species. One of the mercury electrode designs is the hanging mercury drop electrode (HDME). Constant surface area can minimize charging current to increase the detection limit. In addition, HDME can adsorb and accumulate analytes on the surface of mercury [85]. Therefore, the voltammetry stripping method allows it to be used in the analysis, including for heavy metals. Anodic stripping voltammetry (ASV) is a popular and sensitive voltammetric method for measuring heavy metals. The sensitivity of the ASV technique is due to an effective pre-concentration step followed by an electrochemical analysis stripping step of accumulated analytes. Metal ions are reduced, deposited on the metal surface at the pre-concentration stage, and oxidized again so that the oxidation peak is proportional to the analyzed metal concentration [86]. Ensafi *et al.* used a mercury drop electrode and xylenol orange, which form a ligand complex with several metal ions to detect Cd^{2+} and Zn^{2+}. Using the adsorptive stripping voltammetry technique, the linear range was 10 – 580 ng mL^{-1} for Cd^{2+} and 7-260 ng ml^{-1} for Zn^{2+}. The detection limit was 1.7 ng ml^{-1} and 1.8 ng ml^{-1} for Cd^{2+} and Zn^{2+}, respectively. The sensor was evaluated in water and alloy samples with a recovery value of 97.2-104.6% [87]. In another work, Ensafi et al. used HDME and xylenol orange to determine Cu^{2+}, Pb^{2+}, and Cd^{2+} simultaneously. The linear response range was obtained at 5-150 ng ml^{-1} for Pb^{2+} and Cd^{2+}. The detection limit was estimated at 0.98 ng ml^{-1} for Pb^{2+} and 1.18 ng ml^{-1} for Cd^{2+}. The sensor was used in the water sample with a recovery value of 98-106% [88]. Determining metal ions with mercury electrodes has good sensitivity, especially with the ASV technique. However, the use of mercury in electrodes has a potential risk of poisoning, contamination, and disposal of mercury, so several countries have banned the use of mercury. In addition, HDMEs are easily dislodged, making them relatively unsuitable for on-site analysis [89]. Carbon electrodes can substitute for electrochemical analysis because they are stable, non-toxic, and more suitable for on-field analysis.

Recently, bismuth-coated electrodes were used as an alternative to mercury-based electrodes due to low toxicity and insensitivity to dissolved oxygen in the electrochemical analysis [90,91]. Bismuth can form fused alloys with heavy metal that generate the nucleation process during the deposition step and improve the sensitivity of heavy metal determination [92]. Bismuth nanoparticles have been developed with carbon materials, including graphitic nitride (g-C_3N_4), as potential carbon-like material to produce nanocomposites due to its stable allotrope structures with tri s-triazine units at ambient conditions. Based on their potential, Zheng *et al.* fabricated screen-printed sensors modified with bismuth nanoparticles and g-C_3N_4 material *via* the drop coating method for electrochemical detection of Cd^{2+} and Pb^{2+}. The results showed that the modified electrode showed a lower current density than the unmodified electrode due to the reduced conductivity of bismuth and g-C_3N_4 material on the electrode. However, the modifier improved the electron transfer kinetics. It was shown in the negatively shifting potential of the modified electrode in $Fe(CN)_6^{3-/4-}$ solution. Cd^{2+} and Pb^{2+} were analyzed individually and had the linear range of 30 to 120 μg l^{-1} and 30 to 110 μg l^{-1} for Cd^{2+} and Pb^{2+}, respectively. The Bi/g-C_3N_4 modified electrode has a detection limit of 17.5 μg l^{-1} (Cd^{2+}) and 8.1 μg l^{-1} (Pb^{2+}). The detection limit was lower than the Bi nanoparticles-modified electrode. It indicated that g-C_3N_4 improved the sensitivity for Cd^{2+} and Pb^{2+} detection. The sensor was evaluated in the water sample [91].

Akanji *et al*. developed the carbon paste electrode modified with sodium dodecyl sulfate (SDS) intercalated kaolin clay for Pb^{2+} detection. Clay has properties that are compatible as a modifier for electrochemical detection applications, such as its cation exchange capacity, large surface area, good catalytic properties, and mechanical stability [93]. In the study, kaolinite was modified with SDS *via* direct intercalation in the presence of heat. The results

showed that the modification of CPE with kaolinite and SDS increased the peak currents corresponding to an increase in the electroactive area of kaolinite-CPE (PKC-CPE). The high current of the modified electrode is due to the sulfur group (S^{2-}) present in the SDS molecule, which has an affinity for Pb^{2+}. The sensor has linearity in the range of 1.00-100 ppb with a low detection limit of 2.48 ppb which is still below the permissible limit set by the WHO standard for Pb(II) in drinking water. However, the electrode was not selective in the presence of other metal ions, such as Cu^{2+}, Cd^{2+}, and Hg^{2+}, in the same concentration. The presence of other metal ions caused the decreased Pb^{2+} signal due to the high competition of ions for S^{2-} as modified material at the electrode surface. The sensor was also tested in the water sample and had a recovery value of 94.5% [94].

Zhou *et al.* also designed the electrochemical sensor with bismuth that modified the Fe_3O_4/RTIL (room temperature ion liquid) electrode. The Fe_3O_4 was synthesized with two methods, resulting in the large and small sizes of Fe_3O_4 particles (LFe_3O_4 and SFe_3O_4). Bismuth was modified by in situ modification *via* electrodeposition in the SFe_3O_4/RTIL/GCE surface. The results showed that SFe_3O_4 has better properties and electrochemical behavior than LFe_3O_4. SFe_3O_4 has a large surface and could be easy to transfer the electron. It caused significant improvement in the effective surface area and active site, which resulted in capturing metal ions effectively. SFe_3O_4/RTIL/GCE has excellent electrochemical properties, including increased ΔI, reduced ΔE, and high conductivity. SFe_3O_4/RTIL/GCE also has low charge transfer resistance in the measurement with electrochemical impedance spectroscopy (EIS). Bismuth in the form of Bi^{3+} has an important role in the accumulation of metal ions. The optimation of Bi^{3+} concentration results indicated that an increase in Bi^{3+} concentration could electrodeposit more Bi particles and pre-concentrate more metal ions in the electrode surface. However, the current response was reduced in a particular concentration due to the saturation adsorption of Bi^{3+}. In the study by Zhou *et al*., Cd^{2+} and Pb^{2+} detection was evaluated simultaneously and individually for each metal ion. SFe_3O_4 indicated the enhancement in the electrochemical response and low detection limit towards Cd^{2+} and Pb^{2+}. In the simultaneous detection, Bi/SFe_3O_4.RTIL/GCE has a wider linear range than other modified electrodes in the concentration range from 0.01 to 0.8 μM and has a detection limit of 3 and 4 nM for Cd^{2+} and Pb^{2+}, respectively. Therefore, in individual detection, the linear concentration range was 0.006 to 0.8 μM for Cd^{2+} and Pb^{2+}. The detection limit was estimated at 1.6 and 2.4 nM, respectively. The results indicated a two times lower detection limit and wider linear concentration range than simultaneous detection. The sensor has good selectivity in the presence of other metal ions, such as Cu^{2+}, Hg^{2+}, Fe^{3+}, Ag^{+}, K^{+}, Ni^{2+}, As^{3+}, Ca^{2+}, Cr^{6+}, and Cr^{3+}. The other metal ions were not detected using Bi/SFe_3O_4/RTIL/GCE. The sensor was evaluated in a soil sample with a recovery value of 98.9 -101.4% [83].

Celik *et al.* fabricated the electrochemical sensor from GCE-modified 3,8-diaminobenzo(c)cinnoline (3,8-DABCC) and GO for Cd^{2+} and Pb^{2+} detection. The sensor has a linear range of 0.5-25 μg l^{-1} for Cd^{2+} and Pb^{2+}. Therefore, the detection limit of Cd^{2+} and Pb^{2+} was estimated at 0.12 and 0.21 μg l^{-1}, respectively. The selectivity was evaluated with interferences ions, such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}, in a 300-fold mass ratio to analytes. The results showed that the signal deviation of Cd^{2+} and Pb^{2+} do not change more significantly than 4%. The sensor was evaluated in the milk sample extract and had a recovery value of up to 95% [95].

CONCLUSION

Water environment monitoring can be carried out by developing electrochemical sensors based on carbon electrodes. Carbon electrodes provide excellent performance in determining a water environment pollutant due to the supporting material used for modification. Carbon electrodes have been WIDELY applied in environmental analysis due to compatibility with various supporting materials such as carbon nanoparticles (carbon nanotubes, graphene, graphene oxide, reduced graphene oxide, graphene quantum dots), metallic nanoparticles, metal oxide nanoparticles, and conducting polymer. Supporting material that has specific properties, including large surface area, remarkable electrocatalytic activity, excellent conductivity, good stability, adsorption ability, high active sites, and recognition cavities, lead to improved sensor performance. The

Table 1. Application of Carbon-based Electrodes for Electrochemical Sensors in Various Analytes

Analytes	Electrode	Modifier	Technique	Linear range (μM)	LOD (μM)	Sample	Ref.
4-Nitrophenol	GCE	RGO-Ag	Amperometric	1-500	0.114	Water	[33]
	GCE	GNS-FePc	CV	100-700	10	Water	[29]
	GCE	-	DPV	2-100	1.29 (Ipa) 0.17 (Ipc)	-	[27]
	GCE	PMO	DPV	0.6-10	0.170	Water	[35]
	GCE	PMB	DPV	0.015-0.25	0.09	Water	[26]
	GCE	PSN	LSV	0.08-40	0.03	Water, Fruit	[36]
	GCE	Cu_2O NPs	DPV	1.0-400	0.5	Water	[40]
	GCE	GO	LSV	0.1-120	0.02	Water	[25]
	GCE	RGO	DPV SWV	4.00-100, 0.05-2.00	0.02	Water	[32]
	GCE	Ag-Ce_2ONPs	CV	7.81-1000	7.8	-	[44]
	GCE	Cu-Ce_2ONPs	CV	7.18-5000	7.18	-	[45]
	GCE	GO-TiO_2	DPV	0.02-370.57	0.0039	Water	[30]
	GCE	MnO_2-RGO	LSV	0.02-0.5 2-180	0.01	Water	[41]
	GCE	MIP MAA-RGO	DPV	0.01-100.0	0.005	Water	[23]
Diazinon	CPE	CNT	DPV	0.0001-0.06	0.00045	Fruit, Vegetable	[66]
	CPE	MIP MAA NPs	SWV	0.0025-0.1, 0.1-2.0	0.00079	Water Water, Fruit	[72]
	GCE	Au-Pd/rGO/MWCNTs	SWAV Amperometric	0.0009-11.3, 0.003-9.5	0.002, 0.0014	Water, Fruit, Vegetable	[74]
	GCE	MWCNTs/TiO_2 NPs	SWV	0.011-0.836	0.003	Water	[75]
	GCE	GQDs/CS/NiMoO4 NMO	DPV	0.1-300	0.03	Fruit Vegetable	[80]
	GCE	BNQDs/GO	DPV	1.0 × 10-6-1.0 × 10-3	6.7 × 10-8	Fruit	[81]
	SPCE	PCL/CS	DPV	0.003-0.1	0.0028	Fruit	[71]

Table 1. Continued

	CPE	MWCNT/ MIP MAA	SWV	0.0005-1	0.00041	Water Urine	[73]
Tetracycline	SPCE	MIPOPPy/ AuNP	DPV	1-20	0.65	Shrimp	[53]
	CPE	MWCNT-COOH/GO	AdsDPV	20-310	0.36	Water Urine	[55]
	GCE	Gr/AuNP	Chronoamperometric	29-1530	16.2	-	[54]
	SPCE	ERGO	AdTDPV	20- 80	12	Water Milk	[59]
	GCE	Gr/L-Cys	DPV	8-140	0.12	Water	[60]
	GCE	MWCNTs-GNPs/MIP MAA	CV	0.22-90.01	0.09	-	[38]
	GCE	PtNPs/C	CV	9.99-44	4.28 6.12	Urine	[52]
	Graphite	Polyurethane	DPV	4.00-20.0	2.30 2.60	Water	[51]
	GCE	MWCNTs/AuNPs	DPV	11.25-315	0.09	Chicken egg	[56]
	GCE	p-Mel/ERGO	DPV	5.0-225	2.2	Urine	[63]
	GCE	Graphene nanosheets/anti-TC	EIS	1.0×10^{-7}-0.1	2.9×10^{-8}	Blood serum	[64]
			DPV	1.0×10^{-4}-100	3.1×10^{-11}		
	GCE	MWCNT/ poly(L-glutamic)/anti-TC	EIS	1.0×10^{-10}-1.0	3.7×10^{-11}	Honey	[65]
			DPV	1.0×10^{-9}-1.0	3.1×10^{-10}		
Pb^{2+}	CPE	Kaolinite clay	SWV	0.0048-0.48	0.012	Water	[94]
Cd^{2+}, Pb^{2+}	SPE	Bi/g-C_3N_4	SWASV	0.27-1.06 (Cd^{2+}) 0.14-0.53 (Pb^{2+})	0.15 (Cd^{2+}) 0.04 (Pb^{2+})	Water	[91]
	GCE	Bi/SFe_3O_4/ RTIL	SWASV	0.006-0.8 (Cd^{2+}, Pb^{2+})	0.0016 (Cd^{2+}) 0.0024 (Pb^{2+})	Soil	[83]
	GCE	3,8-DABCC/GO	DPASV	0.0044-0.22 (Cd^{2+}) 0.0024-0.12 (Pb^{2+})	0.11 (Cd^{2+}) 0.10 (Pb^{2+})	Milk	[95]

combination of several supporting materials can provide a synergic effect that fabricates electrochemical sensors with excellent sensitivity, selectivity, reproducibility, and accuracy in sample analysis.

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