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Review

Nanomaterials for electrochemical detection of pollutants in water: A review

The survival of living beings, including humanity, depends on a continuous supply of clean water. However, due to the development of industry, agriculture, and population growth, an increasing number of wastewaters is discarded, and the negative effects of such actions are clear. The first step in solving this situation is the collection and monitoring of pollutants in water bodies to subsequently facilitate their treatment. Nonetheless, traditional sensing techniques are typically laboratory-based, leading to potential diminishment in analysis quality. In this paper, the most recent developments in micro- and nano-electrochemical devices for pollutant detection in wastewater are reviewed. The devices reviewed are based on a variety of electrodes and the sensing of three different categories of pollutants: nutrients and phenolic compounds, heavy metals, and organic matter. From these electrodes, Cu, Co, and Bi showed promise as versatile materials to detect a grand variety of contaminants. Also, the most commonly used material is glassy carbon, present in the detection of all reviewed analytes.

1 Introduction: Water pollution

Water is the most important component of life. The survival of humanity and the rest of the living beings depends on a continuous supply of water. However, due to the development of industry, agriculture, and population growth, an increasing number of wastewaters is discarded. These waters, when poured directly into the water bodies, cause problems of environmental pollution of global concern. The effects of these actions are observed in studies carried out by the World Health Organization. In their latest update published in 2012, this organization determined that in 2003, 80% of illnesses in developing countries was caused by unsafe water, poor sanitation, and lack of hygiene education [1]. This resulted in millions of cases of blindness caused by trachoma in developing countries, while in places with good water supplies the disease is unheard of. Despite all these effects, by 2008, approximately 80% of wastewater worldwide remained uncollected and untreated [2].

The world is at a point where finite water not only impacts human health but also limits future economic growth and development. Urban settlements are the main source of point pollution, and when combined with untreated industrial waste, it becomes a particularly serious problem. In countless fast-growing cities, wastewater treatment infrastructure has been deemed non-existent or outdated, so pollutants have a greater impact [1,2]. The collection, analysis, and treatment of wastewater are essential since even if it is reused as a raw material—as has been the case in some paper-producing plants—the effluent ends up containing higher levels of organic matter and other pollutants [3]. These pollutant-laden waters contribute to increased eutrophication and dead zones (in both oceans and freshwater), affecting more than 245 000 km^2 of marine ecosystems, which show an increase in damage and invasive species [1]. These problems must therefore be controlled urgently. The first step in solving this situation is the collection and monitoring of pollutants in water bodies, due to the impact of water quality on the environment and public health, to subsequently facilitate its treatment.

Wastewater contains different pollutants and features different levels of pollution. Excessive amounts of nutrients have been determined to be the most common source of pollution for surface waters. Similarly, downstream groundwater also contains high levels of nutrients because negatively charged nitrate and phosphorus ions are not held

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Abbreviations: **BOD**, biochemical oxygen demand; **COD**, chemical oxygen demand; **CV**, cyclic voltammetry; **DPASV**, differential pulse anodic stripping voltammetry; **FSCV**, fast-scan cyclic voltammetry; **GCE**, glassy carbon electrode; **GO**, graphene oxide; **LSV**, linear sweep voltammetry; **MWCNTs**, multi-walled carbon nanotubes; **Nf**, Nafion; **NiNP**, nickel nanoparticle; **RGO**, reduced GO; **SCE**, saturated calomel electrode; **SV**, stripping voltammetry; **SWASV**, square wave anodic stripping voltammetry; **SWV**, square wave voltammetry; **UGO**, upright GO

by soil particles and can be leached down through the soil [4,5]. The presence of nitrogenous compounds in wastewater is commonly associated with the fertilization of crops, chemical synthesis, and preservatives of the food industry. It has been noted that nitrogenous compounds in drinking or groundwater are of concern due to their relation to human health effects such as cancer, neural tube effects, and methemoglobinemia [6,7]. Although the presence of phosphorus in water is not considered directly toxic to humans and animals, it is indirectly the first cause of oxygen deficit and harmful algal blooms of coastal and estuarine ecosystems [8].

Heavy metals are pollutants usually found in wastewater due to the mining industry and are of concern because of their ability to persist for long periods of time and their nonbiodegradable nature. The toxicity of the metals regularly involves the interaction between the heavy metal ion and the specific target protein, which results in a change in protein structure and function [9]. Heavy metals such as lead, mercury, copper, zinc, and cadmium are known to be potentially carcinogenic to humans and other organisms and may lead to epilepsy, dysarthria, pneumonia, and damage to the central nervous system [10].

The level of contamination in water bodies because of organic matter is mainly tested by analyzing the biochemical oxygen demand (BOD) or the chemical oxygen demand (COD), which estimate the degree of biological and chemical oxidation, respectively [11]. COD is considered to be a more important measure of organic matter than BOD since BOD generally lacks reproducible results and requires a long time to complete the analysis, which is 5 days in its most common form [12]. COD is strictly controlled by environmental regulatory agencies [13].

In this paper, we review the most recent developments in micro- and nano-electrochemical devices for pollutant detection in wastewater. Reviews in the same area such as the ones by Jang et al. and Kruse demonstrate the importance of the topic of water pollutants and sensors. However, they focus on the lab-on-a-chip and chemiresistors respectively, while this review puts the spotlight on the nanoscale through sensors with nanomaterials and the employment of electrochemistry [14,15]. The review has been limited to the sensing of three different categories of pollutants based on a variety of electrodes. The categories are nutrients and phenolic compounds, heavy metals, and organic matter. In the nutrients and phenolic compounds category, we look into the detection of nitrate, phosphate, phenol, bisphenol A, hydroquinone, and catechol; in the heavy metals, we focus on lead, mercury, copper, zinc, and cadmium; and in the organic matter, we center on the COD. For each of these, we focus on the linear range, the LOD, and the electrodes employed. Nonetheless, when available, other relevant features of the devices are analyzed such as the processing time, type of sample, electrochemical method, and toxic matter discharge.

2 Detection of nutrients and phenolic compounds

Excessive amounts of nutrients in water pose a big threat to public health and animal life; nitrate, phosphate, and ammonia are among the most hazardous pollutants of groundwater across the world. Their use in products such as fertilizers, cosmetics, furniture, paint, and others has caused water pollution over time. These nutrients in high concentration can cause severe consequences in human health, in some cases leading to diseases such as hypertension, diabetes, and in some cases even cancer. Besides human health, excessive amounts of nutrients can cause other problems such as eutrophication, which leads to oxygen depletion in the water body and harming wildlife [16–18]. Additionally, phenolic compounds pollution has become a major concern because they tend to persist in the environment over a long time, which results in an accumulation that then exerts toxic effects on humans and animals. These compounds also tend to dissociate into other, very toxic, moieties upon entering water [19].

2.1 Nitrate and phosphate detection

Nitrate (NO^{3-}) and phosphate (PO_4^{3-}) contamination has increased mainly due to the agricultural and livestock industries, where fertilizers release nitrate and inorganic phosphate ions directly in groundwater [20]. The resulting contamination is a big problem as it harms animals and plants due to its toxicity and, besides being a big threat to public health, can also cause oxygen depletion [21–23]. The detection of these compounds can be classified in indirect and direct methods. Indirect methods, such as reduction of nitrate ions to ammonium, require extra reagents, are time-consuming, and suffer interference by other ions. On the other hand, direct methods (e.g., electrochemical sensors) overcome said disadvantages. Nonetheless, they may still have their disadvantages; for example, poor sensitivity. Gold and platinum had been under investigation as electrodes for nutrient detection for years, but they are too slow and ineffective. This has led to an increase in the use of copper and cobalt for direct methods because of their selectivity and low overpotential for reduction [24–29].

2.1.1 Copper nanowires

A wide variety of electrodes (e.g., Ru, Rh, Ir, Pt, Ag, and Au) have seen use for nitrate ions detection. However, copper has begun to be the most used electrode due to its low overpotential for the reduction of nitrate ions [28]. Patella et al. utilized an array of vertically standing copper nanowires obtained by galvanic deposition into a nanoporous membrane. The deposition was achieved by coupling the copper current

collector with an aluminum tube by a conductive carbon paste. Subsequently, the copper-aluminum couple was immersed in an electrolytic solution containing 0.1 M $CuSO_4$ and 0.05 M H_3BO_3 at pH 2 leading to the dissolution of aluminum, which acts as a sacrificial anode, and the deposition of Cu into the polycarbonate pores. The resulting sensor was then analyzed by cyclic voltammetry (CV), in the potential range of –1.4 to –0.1 V (versus Ag/AgCl) at a scan rate of 50 mV/s, and showed the presence of reduction peaks at –0.97 and –0.42 V and was calibrated for the latter due to higher intensity. Linear sweep voltammetry (LSV) in the potential range from -0.1 to -0.8 V (versus Ag/AgCl) with a scan rate of 10 mV/s was finally employed to determine the LOD of about 9 μM, as well as two linear ranges from 10 to 50 and 50–1500 μM, with a sensitivity of 0.0636 and 0.73 μA/μM cm^2, respectively. This work also shows the value of increasing the surface area of the electrode by increasing deposition time [30].

Similarly, Wu et al. prepared a Cu nanowire array by electrochemical reduction of copper oxide nanowires attained by thermal oxidation. Specifically, Cu wires were annealed in air at 600°C for 4 h with a heating rate of 10°C/min. The Cu nanowire arrays were then developed by electrochemical reduction under -1.4 V (versus RHE) in 0.1 M KOH solution purged with N_2 gas, reaching completion when the cathodic current reached a stable, near-zero horizontal. The sensor was then investigated by LSV under pH of 2 and the peak was found at –0.46 V. Finally, they detected nitrate ions with a LOD of 12.2 μM, along with a linear range of 50–600 μM and a sensitivity of 0.357 μA/μM cm. The authors concluded that it could serve as the platform for electrocatalysis or electrochemical detection after chemical modifications [31].

2.1.2 Cobalt nanomaterials

For phosphate detection, cobalt (Co)—a highly sensitive metal—has gained a lot of attention since the cobalt oxide (CoO) group has demonstrated good selectivity toward different phosphate species such as PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^{-}$ [32]. Pang et al. used a nano-cobalt and iron (Fe^{2+}) alloy on a chip for detecting dihydrogen phosphate ($H_2PO_4^{-}$). The electrodeposition of the alloy, defined as the production of *in situ* metallic coatings by an electric current on a conductive material immersed in a solution containing a salt of the metal to be deposited [33], was made in an acidic environment at room temperature from a solution with the following formula: 31.25 g cobalt sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), 25.75 g ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), 4.25 g sodium chloride (NaCl), and 7.5 g of boric acid (H_3BO_3). Constant current deposition at 36 A/m^2 with a two-electrode system was used for 1200 s. Afterward, to measure the detection of the pollutant, an open circuit potential (OCP) was measured using a three-electrode, activated with a 0.025 M KHP solution, system of the electrode plated with Co/Fe^{2+}, Pt as the auxiliary electrode, and Ag/AgCl as the reference. The produced nano-Co/Fe^{2+} sensor had a LOD of 2.14×10^{-6} M, a

linear range from 1×10^{-6} to 1×10^{-1} M at pH 4.0, and stability for 16 days. It also was unaffected by common anions and cations in aqueous solutions. [34].

Another nano-cobalt sensor was developed by Wang et al. by using a ZnO nanoflake modified wafer. With the wafer acting as the cathode and a Pt mesh as the anode, the electrodes were soaked into 75 mM $CoSO_4$ electrolyte with an applied current of 40 mA/cm^2 for 300 s for cobalt film electroplating. Afterward, for electrode patterning, a photolithography process was carried out, followed by conditioning the microelectrode in DI water for around 24 h to form a CoO layer on the electrode surface. The electrode was subsequently characterized by CV tests from –1.0 to 0.2 V with a scan rate of 50 mV/s. This revealed that the nanostructured cobalt sensor had an oxidation peak at around –0.4 V versus Ag/AgCl, as well as a linear detection range of 1×10^{-6} to 1×10^{-3} M, which they attribute to the increase in reaction sites of the nanostructure compared to planar sensors [35,36].

2.2 Phenolic compounds detection

Phenolic compounds, or phenols, include phenol (Phe), bisphenol A (BPA), hydroquinone (HQ), and catechol (CC) among others. Among other things, they are present in cosmetics, pesticides, antioxidants, plastic bottles, metal cans, and varnishes. Such compounds are emerging as pollutants because regular water treatment processes do not degrade them [37–39]. They can harm animals, the environment, and even humans by disrupting the endocrine and reproductive system, neurological problems, burns, and diabetes [40,41].

2.2.1 Silver NPs/Carbon Nanotubes

Silver nanoparticles (AgNP) have gained interest due to their unique electronic, catalytic, and optical properties, which are different from their bulk counterparts making them attractive for sensing applications [42]. In their work, Goulart et al. developed a sensor based on silver nanoparticles and multi-walled carbon nanotubes (MWCNTs) to simultaneously detect four phenolic compounds (Phe, BPA, HQ, and CC)—in contrast to traditional methods that detect phenols individually or in pairs. To make the sensor, 10 μL of pretreated MWCNTs suspension in dimethylformamide was deposited as a droplet on a glassy carbon electrode (GCE). The solvent was evaporated to form the MWCNT/GCE. Then, an electrodeposition step of AgNP was carried out via CV for 10 scans from -0.2 to 0.4 V at a scan rate of 100 mV/s in 22 mL of a 0.1 M/L KCl solution with 3.0 mL of AgNP. The following conditions were established when performing square wave voltammetry (SWV) to study the electrochemical detection: sample pH of 3.0, frequency of 10 Hz, amplitude of 20 mV, and step potential of 2 mV. The resulting anodic current peaks for HQ, CC, BPA, and Phe were found at +0.28, +0.39, +0.72, and +0.82 V (versus Ag/AgCl), respectively. The produced AgNP/MWCNT/GCE sensor had a LOD of 0.16, 0.2, 0.24, and
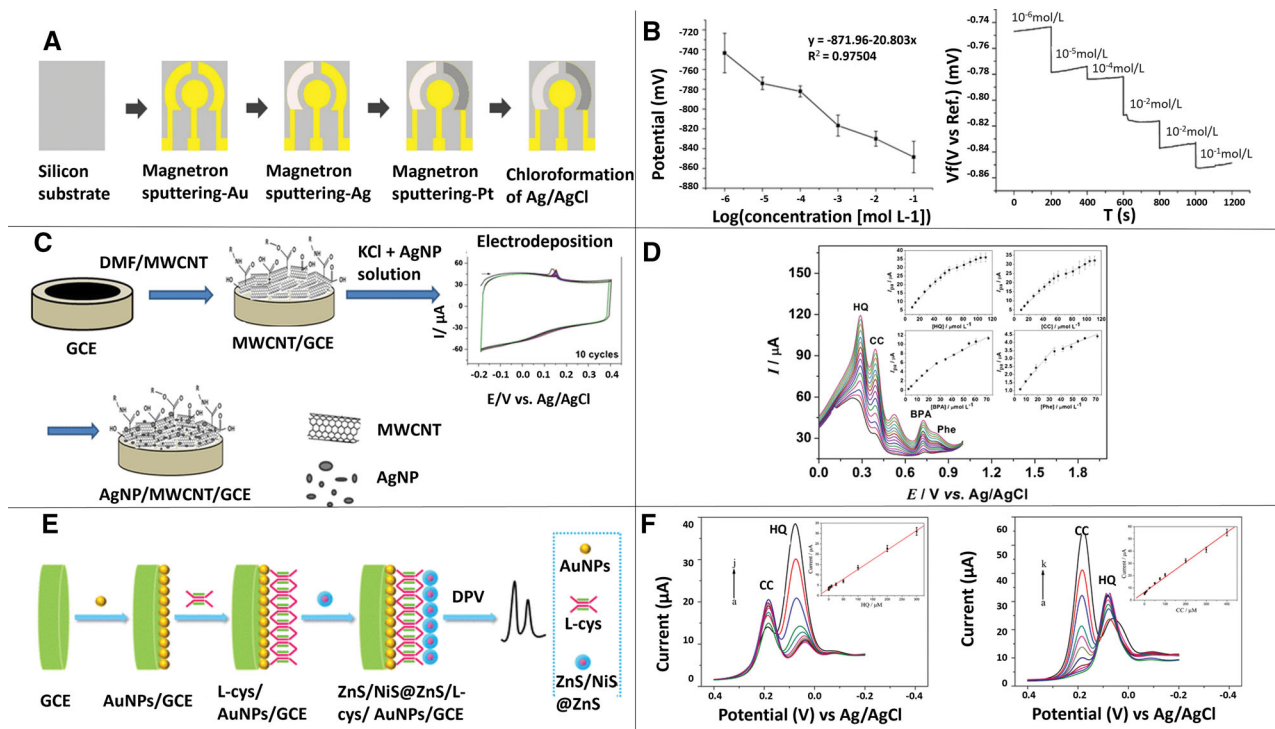
Figure 1. (**A, B**) Schematic diagram of the fabrication of the nano-Co/Fe^{2+} sensor, the potential response curve, and linear fitting curve after annealing of the sensor. (Adapted with permission from [34], © (2021) Elsevier). (**C, D**) Schematic diagram of the fabrication of the AgNP/MWCNT/GCE sensor, square wave voltammetry (SWVs) obtained by the sensor in the presence of different concentrations of hydroquinone (HQ), catechol (CC), bisphenol A (BPA), and phenol (Phe). (Adapted with permission from [43], © (2018) Springer). (**E, F**) Schematic diagram of the fabrication of the ZnS/NiS@ZnS/L-Cys/AuNPs/GCE sensor, differential pulse voltammetry (DPVs) obtained by the sensor in the presence of different concentrations of hydroquinone (HQ), and catechol (CC). (Adapted with permission from [47], © (2015) Springer).

3.0 µM, and a linear range of 2.5 to 260, 20 to 260, 5.0 to 152, and 2.4 to 152 µM for HQ, CC, BPA, and Phe, respectively [43].

2.2.2 Gold NPs/Quantum dots/L-cysteine/Glassy carbon electrode

Gold nanoparticles (AuNPs), also called gold colloids, are the most stable metal nanoparticles and offer great size-related electronic, magnetic, and optical properties [44,45]. Quantum dots are extensively used due to their specific electronic and catalytic properties [46]. Wang et al. presented a sensor for the simultaneous detection of HQ and CC using both previous materials as well as GCE and L-cysteine (L-cys). They started by immersing the GCE into AuNPs and performing electrodeposition at 1.5 V for 40 min. Then, they carried out an electropolymerization of L-Cys on the AuNPs/GCE surface in a 0.1 M phosphate buffer with 5 mM L-Cys by CV for 15 cycles between −0.5 and 2.0 V (versus Ag/AgCl) at 100 mV s^{-1} (L-Cys acts as a connection reagent between carboxyl functionalized QDs and AuNPs). Finally, the L-Cys/AuNPs/GCE was immersed into a 2 mL solution of 0.1 M PB with 6 mg ZnS/NiS@ZnS QDs in a centrifuge tube for 12 h at 4°C. The electrochemical determination of

HQ and CC was done by differential pulse voltammetry in 0.1 M PB (pH 7.5), where the concentration of each phenolic compound increased while the other remained steady. The ZnS/NiS@ZnS/L-Cys/AuNPs/GCE electrode exhibited great results with an anodic peak at 80 and 184 mV, and a LOD of 24 and 71 nM, for HQ and CC, respectively [47]. Figure 1 shows the fabrication and results of nutrient and phenolic compounds sensors.

A summary of the nanosensors used for the detection of nutrients and phenolic compounds is given in Table 1.

3 Detection of heavy metals

Contamination of water by heavy metals poses a big threat to plants, animals, and human health due to its toxicity. Lead poisoning, for example, can lead to problems such as anemia, encephalopathy, Fanconi syndrome, intellectual disability, and interfere in the neural growth of developing brains [48]. Cadmium in high concentrations is one of the most toxic substances causing cancer, renal failure, and osteomalacia [49]. Mercury poisoning causes severe damage to the brain, nervous system, and kidneys [50]. Heavy metals can harm human health through three pathways: inhalation, diet, and dermal contact [51]; their exposure to the environment can cause

Table 1. Summary of nanosensors for the detection of nutrients and phenolic compounds

Analyte	Electrode	Electrodeposition	Electrochemical technique	LOD (μM)	Linear range (μM)	Reference
Nitrate	Cu NWs	Reduction	CV and LSV	$9.00E^{+00}$	$1.00E^{+01}$ to $5.00E^{+01}$ and $5.00E^{+01}$ to $1.50E+03$	[30]
Nitrate	Cu NWs	GD	LSV	$1.22E^{+01}$	$5.00E^{+01}$ to $6.00E^{+02}$	[31]
Dihydrogen phosphate	Nano-Co/Fe^{2+}	Constant current	OCP	$2.14E^{+00}$	$1.00E^{+00}$ to $1.00E^{+05}$	[34]
Phosphate	Nano-cobalt/ZnO nanoflake	Electroplating	CV	–	$1.00E^{+00}$ to $1.00E^{+03}$	[35]
Hydroquinone	AgNP/MWCNT/GCE	CV	SWV	$1.60E^{-01}$	$2.50E^{+00}$ to $2.60E^{+02}$	[43]
Catechol	AgNP/MWCNT/GCE	CV	SWV	$2.00E^{-01}$	$2.00E^{+01}$ to $2.60E^{+02}$	[43]
Bisphenol A	AgNP/MWCNT/GCE	CV	SWV	$2.40E^{-01}$	$5.00E^{+00}$ to $1.52E^{+02}$	[43]
Phenol	AgNP/MWCNT/GCE	CV	SWV	$3.00E^{+00}$	$2.40E^{+00}$ to $1.52E^{+02}$	[43]
Hydroquinone	ZnS/NiS@ZnS/L-Cys/AuNPs/GCE	CV	DPV	$2.40E^{-02}$	–	[47]
Catechol	ZnS/NiS@ZnS/L-Cys/AuNPs/GCE	CV	DPV	$7.10E^{-02}$	–	[47]

CV, cyclic voltammetry; DPV, differential pulse voltammetry; GD, galvanic deposition; LSV, linear sweep voltammetry; OCP, open circuit potential; SWV, square wave voltammetry.

the contamination of water bodies and end up in drinking water, entering the food chain harming animals and humans. On the other hand, heavy metals can also harm plants and soil; when accumulated in the soil can cause fertility problems and plant death. Cadmium and Zinc inhibit photosynthesis and root and shoot growth [52] that can result in browning of root tips, chlorosis, disrupting chlorophyll synthesis, inducing lipid peroxidation, altering membrane permeability, and leading to the death of the plant [53]. The release of heavy metals to the environment has increased over the years through activities such as transportation, agriculture, mining, and heavy use in the chemical industry for products as fertilizers, pigments, catalysts, electric components, etc., increasing the risk of heavy metal poisoning [54]. Several analytical methods have been developed that can detect heavy metals in water. However, these methods are often expensive, and not practical for *in situ* detection [55]. Electrochemical methods have shown the potential to be just that, easy, cost-effective, and precise methods that can eventually be used for *in situ* applications. Different approaches have been taken involving nanomaterials for the detection of heavy metals.

3.1 Carbon nanotubes

Carbon nanotubes have been demonstrated to be useful electrode materials thanks to some of their properties such as high surface area, fast electron transfer rate, great mechanical strength, and chemical stability [56,57]. They have proven to be useful in applications such as heavy metal detection, as Morton et al. showed in their paper. They used l-Cysteine-functionalized carbon nanotubes on a GCE/MWCNT/CO/Cys. L-Cys is an amino acid that has a high binding constant for some heavy metals. The fab-

rication of the electrode consisted of the carboxylation of MWCNTs, which was done by sonicating 0.7 g of the material in a mixture of H_2SO_4 and HNO_3 for 4 h, it was allowed to cool and then filtered through a 0.25 μm pore-size membrane, washed on a deionized membrane, and dried at 110°C. The MWCNT-COOH was then functionalized by suspending them in a solution containing 0.1 M 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and a 0.1 M of *N*-hydroxysuccinimide (NHS) in 0.1 M acetate buffer (pH 5.5) for 1 h. After centrifugation and washing, the nanotubes were suspended in a solution with 0.1 M cysteine for 1 h, they were washed, deionized, and centrifuged to get the resulting MWCNT/CO/Cys. The electrode was prepared by polishing a GCE with 0.05 μm size alumina powder, then a 10 mg/L suspension of MWCNT/CO/Cys in water was sonicated for 10 min. Finally, the suspension was cast on the GCE and left to dry. In this work, the electrode was used to detect lead and copper ions in water. Cyclic voltammograms were applied to cysteine-functionalized carbon nanotubes on GCEs after accumulation in a blank buffer solution and a solution containing Cu^{2+}, it was found that there is a prominent anodic peak and small cathodic peak. The electrode system without cysteine compared to the L-Cys-functionalized carbon nanotubes showed no results. Differential pulse anodic stripping voltammetry (DPASV) was used, with Ag/AgCl as the reference electrode, showing a peak at –0.02 V after accumulation in 20 ppm of Cu^{2+}. For lead, the peak was obtained at –0.6 V after accumulation. These peaks are attributed to the oxidation of the ion. The detection limit was 15 ppb for Cu^{2+} and 1 ppb for Pb^{2+} [58].

Anodic stripping voltammetry (SV) is a very effective method commonly used for the detection of heavy metals in water. This method was used to test and measure lead and cadmium ions in water using a modified GCE

(GO/MWCNTs/Nafion [Nf]/GCE) as the working electrode, in an electrolyte containing metal ions. For the preparation of the electrode, the process of segmentation and carboxylation of MWCNTs was carried out, which consists in mixing the MWCNTs with a 1:3 ratio of concentrated HNO_3 to concentrated H_2SO_4 for 4 h, then they were filtered, rinsed, and dried. Graphene oxide (GO) nanosheets were obtained by ultrasonic exfoliation of graphite oxides. GO/MWCNTs hybrid composites were obtained by mixing 10 mL of GO hydrosol and 10 mL of MWCNTs dispersion followed by a 2 h ultrasonication and a drying process. Then, the graphene/MWCNTs/Nf composite film was fabricated. Ultrasonic agitation was used to disperse GO/MWCNTs nanocomposites into the water to produce a 0.5 mg/mL GO/MWCNTs colloid. A GCE was polished with 1.0, 0.3, and 0.05 mm alumina slurry, respectively, then the GCE was scanned to remove contamination, and finally, an aliquot of 5 μL of the colloid was cast on the GCE as well as a 5 μL of Nf solution to obtain the GO/MWCNTs/Nf/GCE. The range of potentials studied was between –0.9 and –1.5 V with a saturated calomel electrode (SCE) as the reference electrode. Huang et al. found that the more negative the preconcentration potential, the easier the Pb^{2+} and Cd^{2+} were reduced, causing the increase in stripping peak currents. The stripping potential chosen was –1.4 V. An advantage of the MWCNTs over other electrodes is that several heavy metal ions can be determined simultaneously. Using DPASV it was able to simultaneously detect Zn, Pb, Cd, and Cu ions. This method shows clear advantages when trying to detect heavy metal ions in water [59].

A chitosan (CS)/carbon nanotube modified electrode was developed by Wu et al. for the detection of Cu^{2+}, Cd^{2+}, and Pb^{2+}. The good conductivity, high electron transfer rate, and high surface area of carbon nanotubes combined with the high sensitivity and capability of adsorption of the CS film create a good combination for a highly sensitive and selective electrode. For the preparation of the electrode, a screen-printed electrode was washed with water and cleaned by CV. Then, the Chit/CNT solution was electrodeposited. Square wave anodic stripping voltammetry (SWASV) was used for the detection of Cd^{2+}, Pb^{2+}, Cu^{2+}, with a potential range of –1.0 to 1.0 V (versus Ag/AgCl) and a frequency of 50 Hz, an amplitude of 40 mV, and a potential step of 4 mV. The LOD achieved was 0.1 ppm for Cu^{2+}, 0.8 ppm for Cd^{2+}, and 0.6 ppm for Pb^{2+}. The GCE/Chit/CNT was effective when used for the detection of heavy metals in wastewater samples and proved its effectiveness in *in situ* applications [60].

3.2   Bismuth NPs

Bismuth is an environmentally friendly material that has been known to be a great substitute to mercury in mercury-based electrodes for heavy metal analysis. Bismuth-based electrodes offer well-defined, highly reproducible responses, favorable resolution of neighboring peaks, high hydrogen evolution, with good signal-to-background characteristics,

comparable to mercury electrodes [61]. Because of their environmentally friendly characteristics, they represent a very attractive option for making disposable metal detectors. It has been demonstrated that Bi is effective in SV and potentiometry when used in conjunction with carbon paste electrodes, GCEs, and others [62]. They have been used in the detection of a wide variety of heavy metals, including lead [63], cadmium [57], thallium [64], zinc [57], and copper [63].

Niu et al. developed screen-printed electrodes modified with a bismuth nanoparticle porous nanocomposite for the detection of heavy metal ions. For this implementation, they used SWASV. For the fabrication of the electrode, a powder containing the Bi/C nanocomposite was prepared, 15 g of material was ball-milled in quantities of 1 g for 7 min without the addition of any solvent, including 100 mL agate containers together with two agate balls of 12 mm in diameter. The ink used for the screen-printed electrode was composed of 60% of Bi-C material and 40% of the binding agent and additives.

The SWASV signal for determination of Pb^{2+} and Cd^{2+} showed peaks at the potentials of –0.85 and –0.6 V for Cd(II) and Pb(II), respectively versus Ag/AgCl. The LOD was calculated, providing estimated values of 2.2 and 3.8 ppb for Cd(II) and Pb(II), respectively. After studies with tap water and urban wastewater, the Bi/C/SPE proved to be a reliable way of measuring and detecting heavy metals in water [65].

Chen et al. proposed a Bi-based porous screen-printed carbon electrode (Bi/P/SPCE) for detection of heavy metals using SV. The process used for the creation of the electrodes consisted of creating the porous screen-printed carbon electrode and then depositing the Bi film. The results, comparing the proposed Bi/P/SPCE with a Bi-coated screen-printed carbon electrode (Bi/SPCE) and a Bi-coated GCE (Bi/GCE), showed clear advantages with higher peaks with the Bi/P/SPCE at potentials of –0.824 and –0.6 V for cadmium and lead, respectively versus Ag/AgCl. The LOD achieved was 0.03 and 0.34 μg/L for lead(II) and cadmium(II), respectively [66].

Bismuth nanoparticles have been demonstrated to be very useful as electrode materials for heavy metal detection. Sahoo et al. proposed a reduced GO/bismuth nanocomposite (RGO/BI) as electrode material for detection of Cd^{2+}, Pb^{2+}, Zn^{2+}, and Cu^{2+}. An RGO/Bi nanocomposite, previously prepared, was dispersed in a methanol medium (dispersion solution). This dispersion was then drop-casted to form a uniform coating onto the carbon paste electrode surface. Using this modified electrode, and through DPASV versus SCE, they were able to determine the presence of these heavy metals in water solutions with current peaks in potentials of –0.8 and –0.55 V for Cd^{2+} and Pb^{2+}, respectively. The potentials for Zn and Cu were –1.12 and –0.18 V, respectively. The detection of Cu ions in water has been a problem with Bi-based electrodes since the oxidation peak for Bi comes at a potential of –0.3 V which is before the Cu peak at 0.02 V [67], but the RGO/BI solves this problem, interestingly with this electrode, the Cu peak comes first with a potential of –0.18 V versus the Bi peak of –0.09V. LODs obtained were 2.8, 0.055, 17, and 26 mg/L for Cd^{2+}, Pb^{2+}, Zn^{2+}, and Cu^{2+}, respectively. [63]

3.3 Iron oxides

Glassy carbon has been a common electrode material, but it has been demonstrated to be ineffective with heavy metal detection. However, modifications have been made to glassy carbon to achieve this goal. This is the case with iron oxides; they show great benefits when used in GCEs to boost the electrode's response to the presence of heavy metals in a sample. Magnetite, for instance, has been used for the detection of Cr^{3+} due to its large surface area and stability of the RGO [68]. It has been used for a variety of objectives in water treatment, lithium-ion batteries, magnetic switches, among others [69].

Miao et al. developed a DNA modified $Fe_3O_4@Au$ nanoparticles as probes, which can be immobilized onto a magnetic GCE for detection of Ag^+ and Hg^{2+}. The Fe_3O_4 and nanoparticles were synthesized by a hydrothermal method dissolving 1.35 g of $FeCl_3 \cdot 6H_2O$ in 40 mL of ethylene glycol, then adding 3.6 g of NaAc. After cooling and removing the residual matrix, the NPs were obtained. For the synthesis of the $Fe_3O_4@Au$ 15 mg of Fe_3O_4 NPs was dissolved in 150 mL of distilled water, ultrasonication was performed and 3 mL of $HAuCl_4$ with a concentration of 6 mg/mL was added to the solution, then a $NaBH_4$ solution of 0.2 M was prepared, and 0.9 mL slowly added to the mixture of Fe_3O_4 NPs and $HAuCl_4$. The $Fe_3O_4@Au$ NPs were collected using a magnet. A LODs of 0.37 ppb for Ag^+ and 0.34 ppb for Hg^{2+}, respectively, were obtained, meeting the USEPA guidelines. Simultaneous detection of Ag^+ and Hg^{2+} was achieved through SWV. This method showed great results when tested in real water samples from lakes in China. Some of the advantages of $Fe_3O_4@AuNPs$ are great selectivity and it is a simple and cost-effective process for the detection of these heavy metals [70].

Iron oxides have also been used for the detection of other heavy metals; Sun et al. worked on a magnetite RGO modified GCE for the detection of Cd^{2+} through SWASV with Ag/AgCl as a reference electrode. This electrode material has been successful in the detection of Cd^{2+} ions. It showed great selectivity toward Cd^{2+}, and other heavy metal ions did not interfere significantly. The peak for Cd^{2+} appeared at –0.8 V and the LOD was 0.056 μM. Magnetite showed great results and showed potential for further development for use in wastewaters [71].

3.4 Gold NPs/chitosan

CS is another material that has been used in electrodes for heavy metal detection because of its good water permeability and film-forming ability, which, combined with other components, as carbon nanotubes or gold nanoparticles, can achieve great results. Gold nanoparticles have properties that make them attractive for their use in electrodes. They offer a large surface area, high electronic conductivities, and excellent catalytic properties [72]. On the other hand, CS has great film-forming ability and adhesion to heavy metals [73]. There-fore, it has been used in combination with other nanomaterials as gold nanoparticles [74], iron oxides [75], and bismuth nanoparticles [76], to enhance metal detection capabilities.

Lu et al. created a graphene/AuNPs/CS hybrid film on a GCE for the determination of Pb^{2+} in water through DPASV. A solution with GO and CS was prepared by adding CS flakes into a 1 M acetate buffer, stirring, and adding a GO suspension. Then, the solution was ultrasonicated and finally mixed with $NAuCl_4$, followed by CV between –1.6 and +0.6 V (SCE) at 50 mV/s for 10 cycles. After this process, the GR/AuNPs/CS/GCE was obtained.

Different electrodes were compared using DPASVs for 100 mg/L of lead (II) between all electrodes, the GR/AuNPs/CS/GCE had the highest response peak, with 15 μA at a potential of –540 mV. This scheme has the benefits of being a simple method with high sensitivity and low detection limit, found as 0.01 μg/L, one of the lowest published. The optimal working conditions for this electrode are a deposition time of 600 s and a deposition potential of –1.2 V. The modified electrode showed very accurate results when tested in real water samples, proving its reliability. An interference study was made by Lu et al., which found that there is little interference with substances such as Mg(II), Al (III), Ca (II), Zn (II), Co (II), Ni (II), and Ag (I). However, a more significant interference was observed with Cu (II) and Cd (II) [77].

Gold nanoparticles have been proved to improve the detection of heavy metals in water when used in conjunction with GCEs. Besides the detection of lead, evidence suggests that they can be used to improve the detection of Hg^{2+} and even Cu^{2+}, as Ting et al. demonstrated in their work. They used a graphene quantum dot modified GCE with gold nanoparticles (GQD/AuNP) for detection of Hg^{2+} and Cu^{2+}. For the preparation of the electrode, Cysteamine-capped AuNPs were synthesized via chemical reduction of a gold chloride solution, then the solution was mixed with a GQD solution following the addition of 40 mg ethyl(dimethylaminopropyl) carbodiimide (EDC) with shaking for 1 h. The solution was centrifuged to remove excess GDQs. The GCE was polished and 3 μL of the GQD/AuNPs solution was drop-casted on the electrode and left to dry. Finally, 3 μL of 5% Nf solution was drop-coated to obtain the modified electrode.

Low LODs were obtained at 0.02 nM with S/N = 6.25 for Hg^{2+} and 0.05 nM with S/N = 4.81 for Cu^{2+}. Anodic SV of the GQD/AuNPs electrode showed a peak at 0.43 V in the presence of 0.1 μM of Hg^{2+}. When compared to the GQD/AuNPs electrode the AuNPs-coated GCE showed a weak oxidative peak, and the GQD coated GCE showed no peak at all, which indicates there is a great synergistic interaction between the GQD and AuNPs. The deposition time and potential used were 120 s and –0.2 V with SCE as the reference [78]. Figure 2 shows a summary of the fabrication and results of some heavy metals sensors.

A summary of the nanosensors used for the detection of heavy metals is given in Table 2.
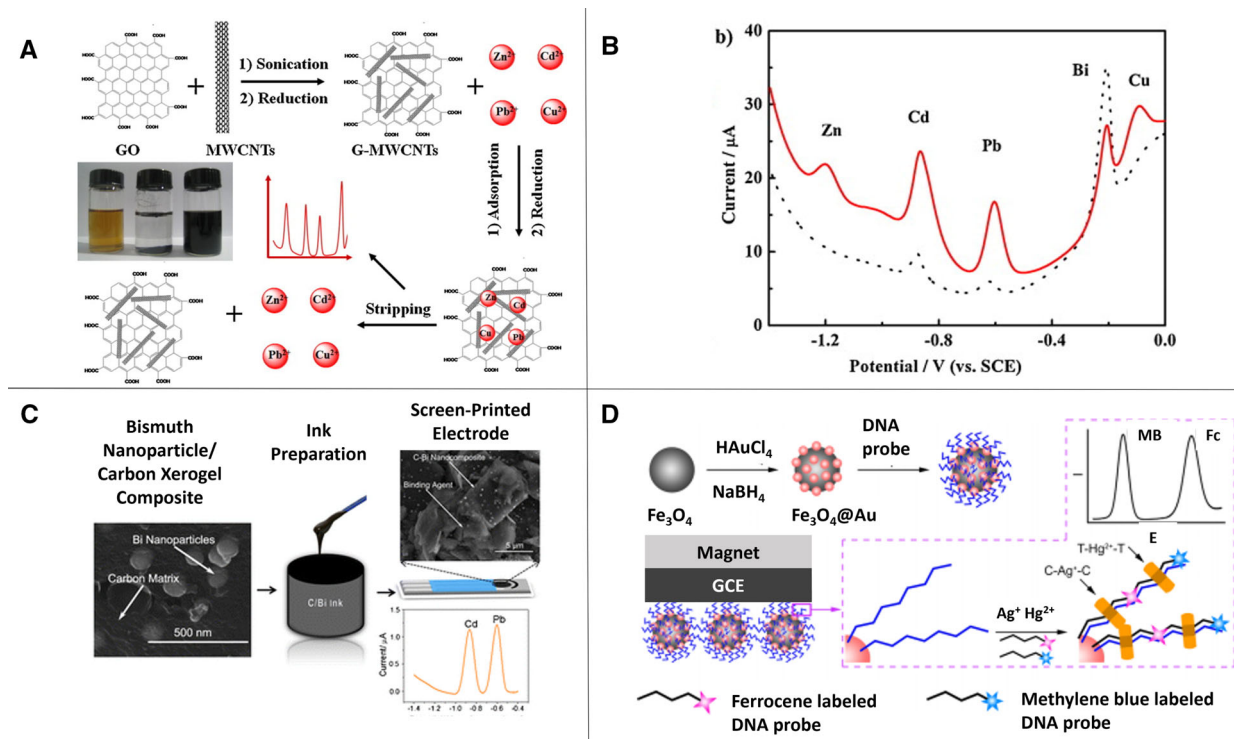
Figure 2. (**A**, **B**) Schematic diagram of the fabrication of the G/MWCNTs/GCE sensor, differential pulse anodic stripping voltammetry (DPASV) stripping signals for Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} ions on the sensor. (Adapted with permission from [59], © (2014) Elsevier). (**C**) Summary of the fabrication of the Bi/C SPE sensor and the square wave anodic stripping voltammetry (SWASV) signals recorded for Pb^{2+} and Cd^{2+}. (Adapted with permission from [65], © (2016) Springer). (**D**) Summary of the fabrication of the DNA modified $Fe_3O_4@Au$ NPs and MGCE sensor and the procedure for the simultaneous detection of Ag^+ and Hg^{2+}. (Adapted with permission from [70], © (2017) American Chemical Society).

4   Detection of organic matter (COD)

COD works as a critical indicator of the pollution levels of water and is crucial for water quality assessment. COD is defined as a measure of the equivalent oxygen content of organic matter in a sample susceptible to oxidation by strong chemical oxidants such as potassium permanganate ($KMnO_4$) and potassium dichromate ($K_2Cr_2O_7$) [79]. Unfortunately, this method, despite its superior oxidizing capacity, exhibits several disadvantages such as low sensitivity, low precision, a large sample volume, and high consumption of high-cost chemicals (for example, Ag_2SO_4), corrosive (H_2SO_4 concentrated), and toxic ($HgSO_4$). Also, the traditional method involves a reflux process that takes 2–4 h, which means that it is not ideal for high throughput detection [80].

4.1   Copper nanomaterials

Copper is a material commonly used for COD as seen in the works by Badr et al. [81], Hassan et al. [82], and Wang et al. [83] due to its high electrocatalytic activity. In their work, Badr et al., potentiostatically electrodeposited copper nanoparticles on the surface of a GCE at –0.6 V versus Ag/AgCl for 60 s in a solution of 50 mM $CuSO_4 \cdot 5H_2O$ containing 0.1 M $NaClO_4$.

The electrochemical behavior analysis was carried out by LSV in 0.075 M NaOH, which showed an anodic peak at 0.6 V similar to bare GCE. The optimized nano-Cu/GCE-based COD sensor exhibited a linear range of 15–629.3 ppm and a LOD of 1.7 ppm. The authors credit the increase in sensitivity of COD detection to the high catalytic activity of nano-Cu and consider that the simplicity and environmentally friendly sensor is promising for real sample analysis [81].

Hassan et al. reported the use of a copper cable and pure copper disk substrates coated with nano-copper films using potentiostatic deposition and fast-scan cyclic voltammetry (FSCV). The potentiostatic deposition was under –1.0 V (versus Ag/AgCl) for 180 and 240 s from 4 mM $CuSO_4 \cdot 5H_2O$ mM H_2SO_4 bath for the cable and the disk electrode, respectively. In the case of FSCV for the Cu-cable electrode, the potential scan window was from –0.10 to –1.30 V (versus Ag/AgCl) for 30 cycles at 100 mV/s. For the Cu-disk electrode the potential scan window was from –0.80 to –1.80 V (versus Ag/AgCl) for 20 cycles at 100 mV/s. The electrochemical detection was analyzed with the use of LSV in 0.075 M NaOH, with peaks in the range of 0.6–0.7 V (versus Ag/AgCl), where the FSCV sensors exhibited the highest oxidation current due to a higher surface area and more uniform distribution. With the potentiostatic deposition, the cable and disk sensors showed a linear range of 2–595 and

Table 2. Summary of nanosensors for the detection of heavy metals

Electrode	Analyte	Electrodeposition	Electrochemical technique	LOD (mg/L)	Tested on real water samples	Reference
GCE/MWCNT/ CO/Cys.	Cu^{2+}	–	DPASV	$1.50E^{-02}$	Yes	[58]
GCE/MWCNT/ CO/Cys.	Pb^{2+}	–	DPASV	$1.00E^{-03}$	Yes	[58]
G/MWCNTs/GCE	Pb^{2+}	–	DPASV	$2.00E^{-04}$	Yes	[59]
G/MWCNTs/GCE	Cd^{2+}	-	DPASV	$1.00E^{-04}$	Yes	[59]
GCE/Chit/CNTs	Cu^{2+}	CV	SWASV	$9.98E^{-02}$	Yes	[60]
GCE/Chit/CNTs	Cd^{2+}	CV	SWASV	$7.99E^{-01}$	Yes	[60]
GCE/Chit/CNTs	Pb^{2+}	CV	SWASV	$5.99E^{-01}$	Yes	[60]
Bi/C/SPE	Pb^{2+}	–	SWASV	$3.80E^{-03}$	Yes	[65]
Bi/C/SPE	Cd^{2+}	–	SWASV	$2.20E^{-03}$	Yes	[65]
Bi/P/SPCE	Pb^{2+}	–	SV	$3.00E^{-05}$	Yes	[66]
Bi/P/SPCE	Cd^{2+}	–	SV	$3.40E^{-04}$	Yes	[66]
RGO/Bi/CPE	Zn^{2+}	–	DPASV	$1.70E^{-02}$	Yes	[63]
RGO/Bi/CPE	Cd^{2+}	–	DPASV	$2.80E^{-03}$	Yes	[63]
RGO/Bi/CPE	Pb^{2+}	–	DPASV	$5.50E^{-04}$	Yes	[63]
RGO/Bi/CPE	Cu^{2+}	–	DPASV	$2.60E^{-02}$	Yes	[63]
DNA modified Fe_3O_4@Au NPs and MGCE	Ag^+	–	SWV	$3.70E^{-04}$	Yes	[70]
DNA modified Fe_3O_4@Au NPs and MGCE	Hg^{2+}	–	SWV	$3.40E^{-04}$	Yes	[70]
Fe_3O_4/RGO/GCE	Cd^{2+}	–	SWASV	$6.20E^{-03}$	No	[71]
GR/AuNPs/CS/GCE	Pb^{2+}	CV	CV	$1.00E^{-06}$	Yes	[77]
GQD/AuNP/GCE	Hg^{2+}	–	ASV	$4.00E^{-06}$	No	[78]

CV, cyclic voltammetry; DPASV, differential pulse anodic stripping voltammetry; SV, stripping voltammetry; SWASV, square wave anodic stripping voltammetry; SWV, square wave voltammetry.

2–369.9 mg/L and a LOD of 2.4 and 1.5 mg/L, respectively. The cable and disk sensors made through FSCV displayed a linear range of 2–595 and 2–280.9 mg/L and a LOD of 2.6 and 1.2 mg/L, respectively. All four were proven useful as COD sensors for surface waters, being the optimal depending on the use, while also having a high tolerance level to Cl^- ion, showing 1.0 M Cl^- minimal influence [82].

Alternatively, Wang et al. worked with a copper/cobalt micro-nano film which was fabricated *in situ* on a gold electrode via electrochemical reduction of $CuCl_2$ and $Co(NO_3)_2$. The electrodeposition of a micro-nano Cu/Co sensing film on a 3 mm gold electrode surface was carried out under $-200\,\mu A$ for 100 s in a 0.1 M, pH 4.0 acetate buffer solution containing 27 mM $CuCl_2$, 3 mM $Co(NO_3)_2$ (versus SCE). The micro-nano Cu/Co sensor was tested by amperometric detection in 0.1 M NaOH and showed a peak at 0.6 V (versus SCE), which is consistent with the other works reviewed in this section. The sensor had a linear range of 1.92–768 mg/L and a LOD of 0.609 mg/L [83].

4.2 Graphene oxide/nickel NPs

In recent years, graphene has become a common material for sensors due to its great optical, electronic, and magnetic properties. GO, a popular modifier of the graphene family,

has reactive oxygen functional groups making it even more popular in the field of biosensors, and it is usually modified with other materials to improve its electrochemical properties [84,85].

In the study performed by Li et al., a magnetic field is first used to orient the GO flakes vertically on the surface of a screen-printed electrode. Afterward, Ni nanoparticles were electrodeposited on the upright GO (UGO) in a 5 mM $Ni(NO_3)_2$ solution (pH4 phosphate buffer) under -1.3 V (versus Ag/AgCl) for 130 s. Later, rinsed by ultrapure water and operated in a 0.5 M NaOH solution by potential cycling between 0.15 and 0.80 V (versus Ag/AgCl) for 20 cycles. Then, chronoamperometry was carried out in 0.5 M of NaOH for 150 s for the detection of COD. The resulting nickel nanoparticles (NiNPs)/UGO sensor displayed a linear detection range of 0.1–400 mg/L and a lower detection limit of 0.02 mg/L. The authors attribute the results to the fact that the UGO electrode had a large effective surface area and good in-plane conductivity in comparison with regular GO, while the NiNPs improved the selectivity [86].

Likewise, in a work by Zhang et al., NiNP/Nf/GO was developed for a rapid determination of COD. The electrodeposition of the NiNPs on the Nf/GO was carried out under -1.2 V (versus Ag/AgCl) for 100 s in a pH 4 phosphate buffer containing 5.0 mM $Ni(NO_3)_2$, posterior to the mixing of 1.0 mg/mL of GO with an equal volume of Nf. After
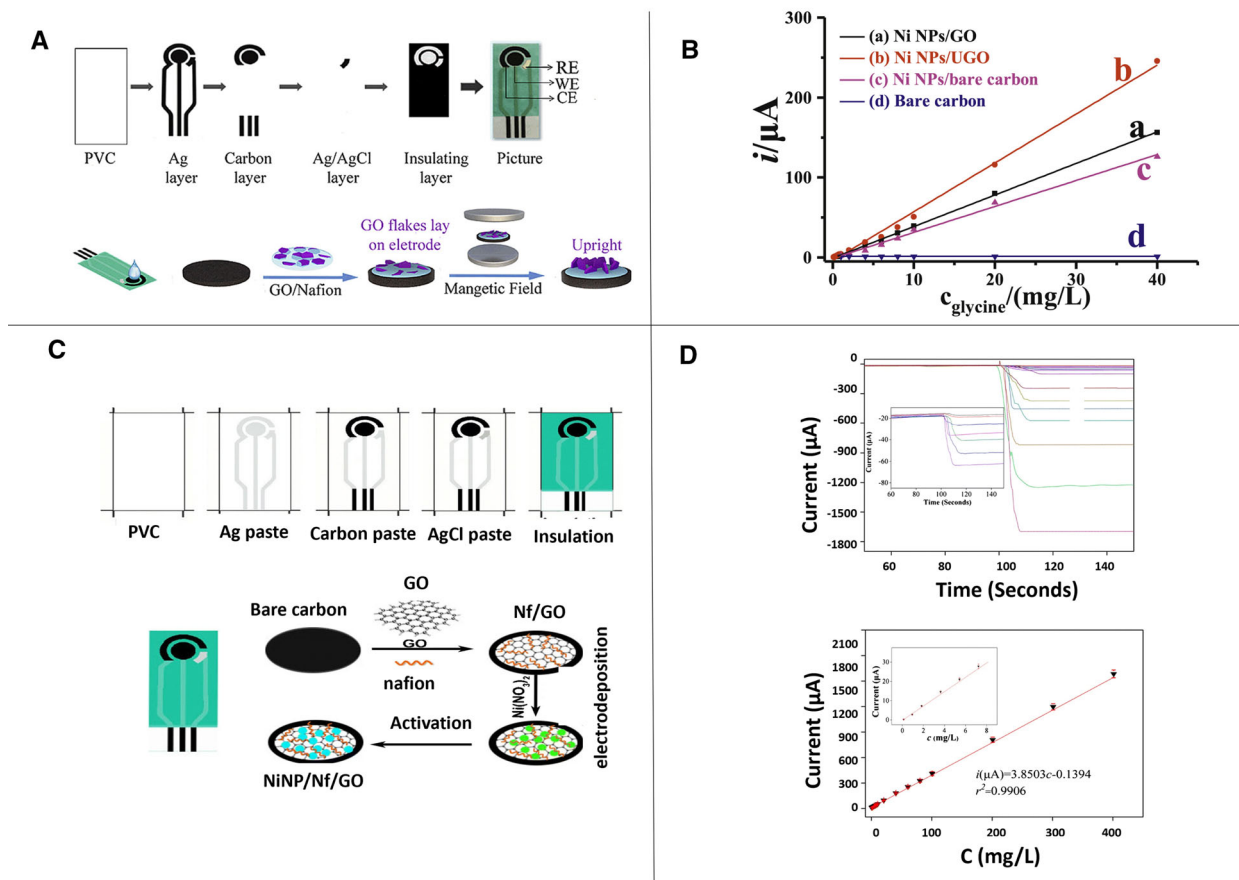
Figure 3. (**A**, **B**) Schematic diagram of the fabrication of the NiNPs/UGO sensor, the relationship between oxidation current and concentration of glycine (COD solution). (Adapted with permission from [86], © (2020) Elsevier). (**C, D**) Schematic diagram of the fabrication of the NiNP/Nf/GO sensor, amperometric i-t, and linear calibration curves of standard COD solutions of glycine. (Adapted with permission from [87], © (2018) Springer).

rinsing with ultrapure water, it was conditioned in a 0.5 M NaOH solution by potential cycling between 0.2 and 0.6 V (versus Ag/AgCl) for 20 cycles to achieve maximum activation of the electrode surface toward electrocatalytic oxidation. With an optimal oxidation potential of 0.45 V (versus Ag/AgCl), the amperometry was performed for 150 s with 0.5 M NaOH. The sensor showed a linear detection range of 0.1–400 mg/L and a LOD of 0.05 mg/L [87]. Both papers give good use to both, NiNPs and GO, by showing the lowest detection limit of COD present in this review because of the enhanced electrical activity and electrocatalytic oxidation ability.

4.3 Titanium oxide/gold NPs

Research has shown that titanium oxide (TiO_2) is an effective material for the photodegradation of organic pollutants in water, it is inexpensive, nontoxic, photosensitive, and environmentally friendly. Nevertheless, TiO_2 based photocatalytic methods have lower photocatalytic activity, which reduces the range and reproducibility of the determination

of COD [88]. Therefore, Liang et al., modified a TiO_2 nanotube array by gold nanoparticles (AuNPs) to improve the sensitivity, stability, and lifetime of the sensor. Their sensor is prepared through the electrodeposition of AuNPs at the TiO_2 NA in 0.05 mol/L H_2SO_4 + 5.0 mmol/L $HAuCl_4$ solution at 0 V under sonicating. The results from the $AuNP/TiO_2$ NA sensor from photoelectrocatalysis, in the presence of L-ferri/ferrocyanide redox couple, at 0.05 V are comparable with those of the standard $K_2Cr_2O_7$ method, having a detection limit of 5 mg/L and a linear range of 5–100 mg/L [89]. Figure 3 represents the fabrication and results of chosen organic matter sensors.

A summary of the nanosensors used for the detection of organica matter is given in Table 3.

5 Discussion

The electrochemical detection of nitrate and phosphate can be carried out using many electrodes, including Ru, Rh, Ir, Pt, Ag, and Au. Nevertheless, copper and cobalt resemble to

Table 3. Summary of nanosensors for detection of organic matter

Electrode	Electrodeposition	Electrochemical technique	LOD (mg/L)	Linear range (mg/L)	Reference
Nano-Cu/GCE	Potentiostatic	LSV	$1.70E^{+00}$	$1.50E^{+01}$ to $6.29E^{+02}$	[81]
Nano-Cu/Cu-cable	Potentiostatic	LSV	$2.40E^{+00}$	$2.00E^{+00}$ to $5.95E^{+02}$	[82]
Nano-Cu/Cu-disk	Potentiostatic	LSV	$1.50E^{+00}$	$2.00E^{+00}$ to $3.69E^{+02}$	[82]
Nano-Cu/Cu-cable	FSCV	LSV	$2.60E^{+00}$	$2.00E^{+00}$ to $5.95E^{+02}$	[82]
Nano-Cu/Cu-disk	FSCV	LSV	$1.20E^{+00}$	$2.00E^{+00}$ to $2.80E^{+02}$	[82]
Micro-nano Cu/Co	Reduction	Amperometric	$6.09E^{-01}$	$1.92E^{+00}$ to $7.68E^{+02}$	[83]
NiNPs/UGO	CV	CA	$2.00E^{-02}$	$1.00E^{-01}$ to $4.00E^{+02}$	[86]
NiNP/Nf/GO	CV	Amperometric	$5.00E^{-02}$	$1.00E^{-01}$ to $4.00E^{+02}$	[87]
AuNP/TiO2NA	Sonication	Photoelectrocatalytic	$5.00E^{+00}$	$5.00E^{+00}$ to $1.00E^{+02}$	[89]

CA, chronoamperometry; CV, cyclic voltammetry; FSCV, fast-scan cyclic voltammetry; LSV, linear sweep voltammetry;

be the main choice of electrodes for nitrate and phosphate detection, respectively. These materials allow the fabrication of an inexpensive sensor with high selectivity and low overpotential for reduction. Specifically, the use of copper nanowires increases the surface area of the sensors compared to bare copper, which is a crucial characteristic for the detection of nitrate. However, more investigation into this electrode is needed to determine other relevant factors to improve the selectivity, as electrodeposition and electrochemical detection methods. In terms of the detection of phenols, both works reviewed showed great promise, with one focusing on the detection of more pollutants while the other focused more on selectivity. The work by Goulart et al. should be used as a stepping stone for future works, due to the innovation of the simultaneous detection of four pollutants, which is two to four times as many pollutants compared to other sensors [43,47,90]. In addition, the synergy of metal nanoparticles with GCE should not be ignored and studied with more detail for optimal pairings for each pollutant.

Among the nanomaterials used, bismuth came out to be one of the most versatile materials in metal detection, it was successfully used to detect lead, cadmium, zinc, copper, and even indium and thallium [67]. Bismuth-based electrodes achieved better results with a lower LOD than the carbon nanotubes and chitosan electrodes. One of the most important benefits of bismuth is that it is environmentally friendly due to its low toxicity and its ability to substitute mercury for metal detection [63], which makes it perfect for many applications. Even though bismuth electrodes have been successfully used to detect copper, many researchers have found it challenging to use them due to the oxidation peak of bismuth interfering with the one of copper.

This is where carbon nanotubes excel; they are primarily used in the detection of lead and copper, where their chemical and mechanical stability promises low interference and clear peaks for both analytes when compared to bismuth. CNTs are usually combined with other materials to enhance selectivity as they have trouble working by themselves. The few functional group on their surface make it highly hydrophobic and they are unable to chelate metal ions in aqueous solutions [59]. This material is perfect to use in combination with bis-

muth, cysteine, chitosan, or other electrode enhancing materials. Their properties make them a very versatile material that can work in countless combinations.

Gold nanoparticles have a great affinity toward mercury, which is a difficult metal to detect with other materials such as bismuth and carbon nanotubes. The benefits of gold nanoparticles include their very low LODs, the lowest of all, they have great sensitivity and versatility, being able to detect mercury, silver, copper, cadmium, and lead [77]. However, the downside of this material is that it has presented some interferences with copper and cadmium.

The analysis of COD through electrochemical sensors has shown great results in vital parameters such as sensitivity, stability, toxicity, analysis time, and cost. The improvement in such parameters is affected by a series of factors, being the electrode material a critical one. Although copper is not the perfect material since it can corrode by water [91], its popularity, which can be also seen in other areas including biosensors [92], can be credited to the abundance of the material as well as its great electrical conductivity, low toxicity, and inexpensiveness. What copper-based sensors lack in LOD, they make up for it in ease of production, scalability, and sensitivity. This could lead to the use of copper as the default electrode for general detection, while other electrodes could be used when more accuracy is needed. There is where electrodes based on NiNPs and GO stand out. They showed the lowest LOD and linear range, among all the sensors reviewed, by taking advantage of a large surface area and high electrocatalytic oxidation ability of their materials. Future studies could focus on the increase on the response signal of COD detection of copper materials by possible pairings with other synergistic metals, such as cobalt, as done by Wang et al. [83]; or on a simplification, and inexpensive, preparation of NiNPs/GO sensors without the loss of accuracy, by using potential supporting materials such as Nf [87], GCE [93], or metallic nanoparticles [94].

There are endless types of pollutants of water that can be further studied and reviewed, and one that will continue to increase in importance—due to its use in electrical components, green technologies, and petroleum refining—is rare earth elements. These elements pose a risk through tailings

(i.e., a mixture of particles, wastewater, and floatation chemicals from the processing stages) and due to the presence of radioactive materials within them. Studies done by Makombe et al. show the use of electrochemistry for the detection of cerium, lanthanum, and praseodymium. Their work, similarly to many of the previously reviewed works, employed GCE. They paired the GCE with alizarin complexone and an antimony film to develop the sensor, which later—with the help of adsorptive differential pulse stripping voltammetry and ICP-optical emission spectroscopy—would determine the presence of rare earth elements [95,96].

6 Concluding remarks and future perspectives

There is a huge necessity for adequate wastewater treatment due to all the pollutants and their effects on the environment, animals, and humans. The first step to solve this situation is the development of cheap and effective sensors that monitor common pollutants such as nutrients, phenols, heavy metals, and organic matter in water bodies, to subsequently facilitate their removal. Traditional sensing techniques present a series of disadvantages, specifically in the cost and analysis quality areas, such as sensitivity, selectivity, and LOD, which provide a demand for improvement in on-site sensors. In this review, we discussed recent progress made in the development of nanosensors, produced with a variety of electrodes, for the detection of nutrients and phenolic compounds, heavy metals, and organic matter. We explicitly describe the reason of use for the electrodes employed, the process of making the sensor, the application of electrochemistry, and the results achieved, as well as a comparison with the other sensors in terms of LOD and linear range, and other parameters when available. These sensors show the great results of current nanosensors for water pollutants and can serve as a guide for forthcoming monitoring technology.

The detection of pollutants in wastewater has evolved from expensive methods to cost-effective, simple, and green electrochemical methods that can, in some cases, be used for *in situ* applications. A variety of nanomaterials have been proven to enhance the detection proficiency of the sensors, achieving very low LODs and capabilities such as being useful for a mixture of pollutants and resistance to interference. The use of nanomaterials as electrodes in electrochemical detection shows the potential they have on their own as well as when being paired with other nanomaterials. The aforementioned sensors show a trend of improvement through the years, overcoming the disadvantages of more traditional methods and paving the way for more positive ecological and economic benefits in the whole process of wastewater treatment.

The works reviewed exhibit the relevance of testing the electrodes under controlled conditions as well as real water samples. However, to ensure the accuracy and precision of the performance under all conditions, we encourage more tests to be taken so that interferences with other substances can be detected and taken into consideration when using the electrodes allowing the user to be certain that their results are as true to life as possible.

Nanomaterials are implemented in the hope of being a quick and easy to use tool in the detection of nutrients, heavy metals, and organic matter, their use has proven to be extremely successful, and is precisely this success that raises new questions. Is it possible to mass-produce nanomaterial using electrodes for their use world-wide? What is the durability of these electrodes? What is their life cycle? What is their environmental impact after they are left unusable? Forthcoming work in the detection of water pollutants will most likely involve a focus on at least one of the following features: cheap nanomaterials (e.g., GCE) to allow mass production and increasing overall testing of wastewaters; the combination of a variety of nanomaterials (e.g., NiNPs with GO) to overcome individual weaknesses; and manipulation of the geometry (such as upright GO) to enhance properties of the materials. A huge variety of nanomaterials enhance the selectivity of different analytes and the only recommendation that we can make is to seek synergistic interactions between them to try and achieve even better results. Nanomaterials are bringing new possibilities to the detection of pollutants, and we can comfortably say that a great future holds for this area of study.

The authors have declared no conflict of interest.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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