Recent progress regarding electrochemical sensors for the detection of typical pollutants in water environments

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Abstract
A variety of organic and inorganic pollutants in water environments pose threats to human health. Therefore, it is critical to develop effective techniques to determine and monitor the levels of water contamination. Compared to traditional detection methods, electrochemical sensors have the advantages of high sensitivity, low detection limits, and good selectivity. In this review, we summarize the progress made from 2000 to 2020 regarding the development of electrochemical sensors capable of detecting typical pollutants in different water environments. Since the concentrations of typical organic contaminants (antibiotics and pesticides) in water environments are often very low (generally at the nmol level), further improvements to the electrode sensitivity and detection limit will be necessary. We also found that more detailed cost analysis of electrode materials is needed to support future production and applications. When we apply the electrode to detect real water samples, the anti-interference and electrochemical sensor componentization need to be further enhanced. Besides, although groundwater serves as the main, or only, source of drinking water in many areas, current studies on the electrochemical detection of groundwater pollutants are limited. We hope that this review will provide new ideas for the future development of electrochemical water contaminant sensors.

Keywords Electrochemical sensor · Pollutant · Water environment · Carbon material

Introduction
Water environment quality plays an extremely important role in sustainable societal development; human lives and production are inseparable from water environments. The quality of water sources directly affects the safety of human drinking water [1]. Due to economic development and the extensive use of various chemicals, a large number of toxic and harmful substances enter the water environment, posing serious threats to human health, production and safety [2, 3]. Approaches for the prevention, control, and measurement of water pollution are becoming increasingly strict worldwide [4].

Generally, pollutants in water environments can be divided into two types: organic pollutants and inorganic pollutants. In this paper, we discuss representative organic pollutants (antibiotics and pesticides) and inorganic pollutants (Pb, Cd, Cr and As ions), selected due to their wide use and high toxicity. Researchers have proposed many removal methods for these pollutants [5–9]. The rapid and accurate detection is critical for efficient pollutant removal. In particular, in situ detection is vital for the early discovery of water pollution accidents and rapid identification of pollution severity.

At present, traditional methods for the detection of the above pollutants include inductively coupled plasma mass spectrometry (ICP-MS) [10], atomic absorption spectroscopy (AAS), gas chromatography mass spectrometry (GCMS) and high-performance liquid chromatography mass spectrometry (HPLC–MS) [11], and others. These methods have good detection sensitivity and accuracy, but...
remain unsuitable for in situ monitoring due to such factors as large size, high cost, prolonged analysis time, and complex operation [12, 13]. Compared to the above methods, electrochemical sensors have the advantages of small size, simple operation, rapid electrical signal response, and lack of necessity for complex pretreatments, while simultaneously maintaining a high detection sensitivity. For these reasons, this approach has good potential for real-time and in situ analysis [14].

Pollutants exist at different concentrations and in different forms in different water environments and water chemical conditions (such as pH value, chemical composition, and interference factors) can also vary. Overall, these differences between water environments can significantly influence electrode sensitivity, anti-interference performance, stability, and service life. However, existing reviews regarding the detection of pollutants by electrochemical sensors in different types of water environments are very limited.

Here, we summarize literature regarding the detection of selected water contaminants by electrochemical sensors over the past 20 years. We discuss electrode applications in different water samples, perform statistical analysis on published data of selected pollutants and electrochemical sensors, and analyze research hotspots. Furthermore, we also summarize relevant challenges, opportunities, and potential directions for future development. We hope that this review will provide useful information that inspires people to further advance the practical applications of this research.

Development of electrochemical sensors

Principles of electrochemical sensor detection

The principle underlying the use of electrochemical sensors (or, electrodes) to detect pollutants is that a certain concentration of pollutants is first adsorbed on the electrode interface, after which an electro-catalysis-based redox reaction occurs at the electrode surface. Since redox reactions involve the gain and loss of electrons, the number of electrons gained and lost during a chemical reaction can be accurately evaluated by assessing the current value at the macro level. Simply put, a quantitative relationship is established between the pollutant concentration and the electrical signal (current value) [15]. At the same time, the electrode can qualitatively and quantitatively identify different pollutants based on differences in oxidized or reduced peaks between pollutants. Figure 1 illustrates the basic principle of the electrochemical sensor system. A complete electrochemical analysis system includes electrochemical sensing equipment, an electrochemical detection instrument and an electrolyte. The electrochemical detection instrument typically has a three-electrode structure composed of a working electrode (WE), a reference electrode (RE) and a counter electrode (CE).

Development of the working electrode

Since the working electrode plays a very significant role in the electrochemical sensor as a whole, many studies have concentrated on improvements to the working electrode.

Initially, electrochemical detection was typically performed using mercury electrodes, such as suspended mercury electrodes, mercury drop electrodes, and mercury film electrodes. These options were selected due to the advantages of cleanliness, ease of renewal, and good reproducibility [16–18]. However, mercury is a volatile and toxic heavy metal, which has limited its electrochemical applications. Currently, mercury electrodes are rarely used in the field of electrochemical analysis.

Since the 1970s, researchers have avoided electrode toxicity by using solid electrodes (such as gold and platinum electrodes), which exhibit high conductivity and good stability. However, heavy metals are non-renewable and expensive. Following these developments, increasing attention was drawn to carbon-based solid electrodes. Carbon electrodes have the advantages of good conductivity, low cost, small background current, wide potential windows, and ease of modification [19]. Therefore, electrodes made of carbon (nano-) materials have become widely used by researchers to detect various pollutants. However, bare solid electrodes still have several obvious disadvantages. Compared with mercury electrodes, they exhibit inferior repeatability and stability. Compared with modified electrodes, they have smaller specific surface areas and fewer surface functional groups, which is not optimal for target adsorption and catalytic oxidation on the electrode surface. For these reasons, current research focuses primarily on modified carbon electrodes.
For modified carbon electrodes, various methods have been used to modify the chemical composition and microstructure of the electrode surface to improve the performance. Generally, electrode modification strategies can be divided into two types: top-down and bottom-up. Top-down modifications typically employ lasers, plasma, ozone or other etching methods to etch the electrode surface, achieving satisfactory surface roughness and adding required surface functional groups to improve adsorption performance and electrochemical activity [20–22]. As shown in Fig. 2a, b, we modified the glassy carbon electrode (GCE) with nitrogen plasma and laser, and obtained the required oxygen-containing functional groups and nitrogen functional groups, then successfully detected ciprofloxacin (CFX) and ofloxacin (OFL). Figure 2c shows that through UV/Ozone modification, a satisfactory electrode structure and oxygen functional group are obtained, and effective direct electron transfer (DET) is obtained at the modified electrode. In contrast, bottom-up modifications introduce active materials onto the electrode surface through methods, such as self-assembly [23, 24], coating [25], electrochemical polymerization [26, 27], and electrochemical deposition [28]. These modified materials are versatile and include carbon nanomaterials, quantum dots, metal (oxide) nanoparticles, conductive organics, enzymes and antibodies [23, 29–33].

**Application of electrochemical sensors to detect common water pollutants**

**Common organic pollutants: antibiotics**

Antibiotics are widely used in the prevention and treatment of human, animal and plant diseases, in addition to serving as effective additives to promote livestock and poultry growth [34–36]. However, most antibiotics consumed by humans and animals are excreted, either in the form of the original drug or as metabolites. This means that antibiotics are mainly discharged into the environment through human or livestock excreta, aquaculture industry medicines, and production wastewater [37–42]. Antibiotics have been detected in a wide variety of water environments, including surface water, groundwater, and wastewater, among others [43, 44]. For human health and ecological safety, it is very important to accurately and easily determine the concentration of antibiotics present in various water environments [45].

At present, a variety of techniques have been established to detect antibiotics, including liquid chromatography-mass spectrometry (LC–MS) [11, 46], fluorescence photometry [47, 48], capillary electrophoresis [49], and fluorescent labeling [50]. These technologies are highly sensitive and selective. However, they require relatively expensive instruments, complicated operating procedures, and long detection times. In contrast, the advantages of electrochemical methods include low cost, rapid response, high sensitivity, easy operation, and suitability for on-site monitoring [51].

In recent years, there have been many reports on the electrochemical detection of antibiotics. We have identified key papers published in the previous 20 years by searching the Web of Science using “antibiotic,” “water,” and “electrochemical sensor” as keywords. The trend chart in Fig. S1. (A) shows the number of identified core papers published between 2000 to 2020, with the electrochemical detection of water contaminants illustrated at each stage. Based on our findings, trends regarding the use of electrochemical sensors to detect antibiotics can be divided into three stages. During Stage 1 (2000–2012), no articles were published regarding the electrochemical detection of antibiotics in water environments. During Stage 2 (2012–2018), the number of relevant papers published increased gradually. During this period, antibiotics pollution drew increasing attention [43], and people began to realize the importance of sensor-based antibiotic detection in water. In Stage 3 (2018–2020), the number of studies on electrochemical sensor detection of antibiotics sharply increased, indicating that electrochemical sensor detection of antibiotics in various water environments has attracted increasing attention, as has the requirement for environmental protection.

Between Stages 2 and 3, there were no obvious differences in the proportion of articles related to the detection of antibiotics in various water environments. The fewest articles were published regarding the detection of antibiotics in groundwater. However, antibiotic pollution in groundwater has been widely reported [44, 52]. The limited number of studies regarding the detection of antibiotics in groundwater suggests that this research area may not yet have received sufficient attention. The present linear concentration range of antibiotic detection is mainly at the μg/L level, but the concentrations of antibiotics found in actual water environments (especially surface water and groundwater environments) are typically at the ng/L level [44]. Therefore, the sensitivity of electrochemical sensor detection requires further improvement in the future.

**Common organic pollutants: pesticides**

Pesticides play an important role in agriculture. Since the utilization efficiency of pesticides is low, only a small amount of pesticide is left on the surface of plants to be used. Instead, most pesticides enter the soil, water, or atmosphere, before entering the water environment through surface run-off (rainfall, leaching, field drainage, etc.) and causing pollution [53]. Recent studies have shown that pesticides can be widely detected in surface water [54] and groundwater [52, 55]. Previous studies have also shown that long-term
human exposure to pesticides can cause endocrine disorders, damage the central nervous system, and seriously threaten human health [56]. Therefore, the topic of residual pesticides in the water environment has attracted increasing attention.

Common methods for detecting pesticides include GCMS and HPLC–MS. Although chromatography is accurate and selective, these techniques usually involve complex sample preparation, including pre-analysis and other steps, making them expensive, time-consuming, and technically challenging [57]. Therefore, electrochemical sensors have become a promising rapid detection method. Here, we summarize published papers from the previous two decades related to the electrochemical detection of pesticides in water environments.

The trend chart in Fig. S1(B) shows the number of core papers published between 2000 and 2020 and available through Web of Science, with the electrochemical detection of water contaminants illustrated at each stage. Research into the detection of pesticides using electrochemical sensors can be divided into three stages. During Stage 1 (2000–2005), there were no published articles, indicating that electrochemical sensors had not yet been used to detect pesticides in water environments. The number of papers published during Stage 2 (2006–2013) increased gradually, indicating that researchers had started to realize the importance of sensor detection of pesticides in water. In Stage 3 (2014–2020), the number of studies regarding electrochemical sensor detection of pesticides greatly increased, indicating that electrochemical sensor detection of pesticides in various water environments had achieved increasing attention. Though analysis, we determined that studies on surface water (lake water, river water, etc.) account for around two-thirds of the total articles published, indicating that the majority of research attention has been paid to surface water pesticide pollution. Of note, studies on the detection of organophosphorus pesticides (OPPs) in water account for 35% of total studies, probably because OPPs have been widely used in agriculture across the world since organochlorine pesticides were banned.

The electrochemical detection of OPPs mainly includes the detection of enzyme-free electrochemical sensors and enzyme bioelectrochemical sensors. Enzyme-free electrochemical sensors mainly include the use of graphene or graphene composite materials to modify electrodes in water environments. The number of papers published during Stage 2 (2006–2013) increased gradually, indicating that researchers had started to realize the importance of sensor detection of pesticides in water. In Stage 3 (2014–2020), the number of studies regarding electrochemical sensor detection of pesticides greatly increased, indicating that electrochemical sensor detection of pesticides in various water environments had achieved increasing attention. Though analysis, we determined that studies on surface water (lake water, river water, etc.) account for around two-thirds of the total articles published, indicating that the majority of research attention has been paid to surface water pesticide pollution. Of note, studies on the detection of organophosphorus pesticides (OPPs) in water account for 35% of total studies, probably because OPPs have been widely used in agriculture across the world since organochlorine pesticides were banned.

![Fig. 2 Examples of top-down modifications](image-url)

- **A** GCE was modified using a nitrogen plasma for Ciprofloxacin (CFX) detection. Copied with permission from Ref. [21]
- **B** GCE was directly modified using a picosecond laser for ofloxacin (OFL) detection. Copied with permission from Ref. [20], and
- **C** UV/Ozone modification for efficient direct electron transfer (DET). Copied with permission from Ref. [22]
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Common inorganic pollutants: heavy metal cadmium, lead, and chromium ions

Detection of heavy metal cations (Cd and Pb ions)

Cadmium (Cd) and lead (Pb) are two of the most common heavy metal cations with high toxicity in water. In natural environments, Cd often co-exists with lead. Cd is widely used in the electroplating, chemical, electronics, and nuclear industries. Primary pollution sources include lead–zinc ores, non-ferrous metal smelting, electroplating, and industrial use of Cd compounds as catalysts or raw materials [65]. Cd ions readily accumulate in the kidneys, where they impair filtering function, and can also enter the human body through the digestive and respiratory tracts. In addition, it can cause health effects, such as fractures, reproductive disorders, and damage to the central nervous system and immune system [66, 67]. The International Agency for Research on Cancer has classified Cd(II) ions as carcinogens [68]. In the 1950s, a serious Cd pollution incident occurred in Toyama Prefecture, Japan. Lead ions are also highly toxic, and excessive lead exposure can cause a variety of diseases, including memory loss, anemia, and muscle paralysis, among others [69]. According to the standards of the World Health Organization (WHO), the concentration of Cd(II) and Pb ions in drinking water should not exceed 5 and 50 μg/L, respectively. Therefore, the determination of Cd(II) and Pb concentrations in water is critical to human and environmental health. Various conventional analysis methods have been used for heavy metal detection, including AAS, inductively coupled plasma optical emission spectroscopy (ICP-OES), ICP-MS, and electrochemical analysis. Among these approaches, the electrochemical detection method has high sensitivity, high chemical stability and high thermal stability, in addition to good selectivity, fast detection speed, and simple operation [70, 71]. Electrochemical sensors have gradually become an alternative tool for the rapid detection of heavy metals. Therefore, we identified and analyzed studies from the past 20 years that used electrochemical sensors to detect Cd(II) and Pb ions in water environments.

Figure S1(C) shows trends from 2000 to 2020 in the publication of core papers involving the electrochemical detection of Cd ions in water environments, as found through Web of Science. We divided these trends into three stages. The first stage (2000–2011) represents the early stages of the development of electrochemical sensors for the detection of Cd(II) ions in water environments. The average number of articles published each year was fewer than ten. The second stage lasted from 2011 to 2015, and the number of papers published in this stage increased to 112 over five years. Researchers had realized the importance of rapidly detecting Cd ions in water environments, leading more researchers to study this issue. The third stage occurred from 2016 to 2020. The number of papers published during this stage increased sharply, reaching 431 in 5 years, with more than 80 relevant papers published each year. This increase is likely due to the rapid development of carbon materials in recent years, resulting in various new materials that could be used for electrode modification [72–74]. In addition, the majority of studies concerned the detection of Cd in surface water. Here, surface water refers to dynamic and static water sources on the land surface, including rivers, lakes, ponds, and reservoirs. This was particularly evident during the third stage, where both the number and proportion of papers on surface water increased rapidly, indicating increased attention paid to the monitoring of Cd in surface water. The number of articles regarding groundwater (primarily include well water and spring water) detection also gradually increased, but papers related to the detection of Cd in groundwater only accounted for 21.70% of total papers, indicating limited attention paid to the detection of Cd in groundwater compared to surface water. Although articles related to Cd detection in wastewater have also increased, they represent the lowest proportion overall. This lack of research interest...
may be because the detection of Cd in wastewater has not received sufficient attention or because complicated water environments make it more difficult to achieve good detection response.

Figure S1(D) shows trends in the number of articles regarding the electrochemical detection of lead in water environments published to Web of Science between 2000 and 2020. During Stage 1 (2000–2010), the overall number of articles involving electrochemical detection of lead remained small (fewer than ten articles per year). During Stage 2 (2010–2015), the number of articles increased slightly. During the third stage (2016–2020), the number of relevant papers increased sharply, reaching 309. This trend of Pb ions detection is similar to that of Cd(II) ions detection. It is clear that studies on the detection of lead ions in groundwater environments are limited; such papers account for only 8.2% of total papers published over the past twenty years, indicating insufficient research interest in the detection of Pb ions in groundwater. The proportion of studies related to the detection of lead ions in wastewater increased from 16.67% (2000–2010) to 23.08% (2015–2020), suggesting that increased attention is being paid to wastewater, an important pollution source for both surface water and groundwater.

Various materials including graphene, graphene oxide (GO), and metal (oxide) nanoparticles are widely used as electrode modification materials for the detection of Cd and Pb ions in water environment [12, 75–78]. Among all electrode modification materials, bismuth (Bi) has achieved the most attention in the electrochemical detection of Cd and Pb ions. As an environmentally friendly material, Bi can form binary or multiple alloys with a variety of heavy metals. Most Bi modification on the electrode is in situ Bi plating method [79–82]. This means adding certain concentration of Bi ions into the test solution, and the Bi and target ions are simultaneously pre-enriched in the electrode. Figure 4A shows a typical in situ Bi plating method for obtaining a highly efficient detection of Cd$^{2+}$ and Pb$^{2+}$ ions in water [80]. Although the in situ Bi plating method can achieve a good detection limit, they need an extra addition of Bi ions into the detection solution, which is not suitable to in situ monitor Cd and Pb ions (Especially when the sensor needs to be placed in the groundwater monitoring wells or drinking water environment) for long-term online monitoring). Currently, there are limited studies on the out situ Bi plating method. Hwang et al developed a Bi-biopolymer (chitosan) nanocomposite screen-printed carbon electrode using a Bi and chitosan co-electrodepositing technique (shown in Fig. 4B) [83]. They also used the modified electrode to successfully detect Cd$^{2+}$ and Pb$^{2+}$ ions in real wastewater samples collected from a mining site and soil leachate. Besides, as shown in Fig. 4C, Zou et al. developed a sensor chip consisting of a microfabricated Bi working electrode, an integrated Ag/AgCl reference electrode, a gold counter electrode, and microfluidic channels [84]. The Pb(II) and Cd(II) concentration ranges are 25–400 ppb and 28–280 ppb, respectively. They also applied this sensor chip to detect the Cd (II) concentration in groundwater. Generally, out situ Bi plating methods often require complicated fabrication process and comparatively higher detection limit than in situ Bi plating method. However, it can be better applied to the detection of actual water samples, because there is no need to add a solution containing Bi ions in the detection environment. Therefore, out situ Bi plating with simple fabrication methods deserves more expectations in the future. Besides, some simple instrument was also developed for the real application. Li et al. developed a portable, low-cost detection instrument. As shown in Fig. 5, the instrument has a disposable electrode printed chip for heavy metal determination [85]. The design of disposable plastic pipettes can avoid cross-contamination. This detection instrument is expected to be applied in the on-site detection of heavy metal pollutants in the supernatant of groundwater and tap water.

Chromium ion detection

The heavy metal chromium exists in a variety of valence states, including Cr(0), Cr(II), Cr(III), Cr(IV), Cr(V) and Cr(VI), with different toxicities. The majority of environmental chromium pollution is Cr(VI), primarily through chromium-containing wastewater and industrial sewage discharge (including the electroplating, tanning, printing, and dyeing industries) [86, 87]. Cr(VI) has high mobility in water environments, as well as strong toxicity and carcinogenicity, making it a serious threat to human health [88]. The WHO recommends a maximum acceptable concentration of hexavalent chromium of 0.05 mg/L for drinking water. At present, common traditional methods include the diphenylcarbazide method (DCC), AAS, and ion chromatography based on spectroscopic technology [89, 90]. Although these methods can provide accurate results with lower detection limits, they also require cumbersome pretreatment processes, bulky instruments, and sophisticated operational procedures, in addition to being restricted by site. Electrochemical sensors, with the advantages of simple equipment, low cost, a short measurement time, and a satisfactory detection limit, can empower in situ monitoring of Cr(VI) ions in water [91].

The trend chart in Fig. S1(E) shows the number of core papers published to Web of Science between 2000 and...
ion pollution in groundwater is a widespread and serious global problem [92, 93], meaning that rapid in situ detection of Cr(VI) ions in groundwater is extremely important and requires further attention. At present, the electrodes for detecting Cr(VI) ion are mainly GC and graphene based electrodes [94–96]. Among the modified materials, Au and Ag metal nanometers are widely used to modify carbon electrodes due to their excellent chemical stability and catalytic properties [97, 98]. Studies have shown that Cr(VI) has better activity in acidic media, because its reduction depends on the concentration of H+ to a certain extent [91]. Peng et al. synthesized polyethyleneimine (PEI) functionalized multi-walled carbon nanotubes (SWCNTs) and loaded them on GCE, and detected trace amounts of Cr(VI) in actual surface water samples by amperometric method [99]. Hu et al. developed a one-step electrochemical synthesis of AuPdNPs/rGO nanocomposites, and deposited them on...
GCE electrodes by cyclic voltammetry [100]. Except for the two modified electrodes mentioned above, when detecting actual water samples, HCl is used to adjust the pH of the water sample to be tested to strong acidity. In most other literature, HNO₃, H₂SO₄ or HClO₄ are also used to adjust the pH of the solution. Recently, Niu et al. synthesized two hetero-metal center modified and reduced phosphomolybdate hybrids as electrocatalysts (shown in Fig. 6). Among them, the combination of the reduced phosphomolybdate \([\text{P}_4\text{Mo}^{\text{V}}\text{O}_{\text{67}}\text{O}_{\text{31}}]^{\text{12}}\) clusters and different kinds of dissimilar metal centers (Cu⁺, Cu²⁺, and Mn²⁺) is the first to realize the use of electrochemical sensors in a relatively wide pH range (0–5) to detect ultra-trace Cr(VI) has significant electrochemical performance, due to the synergistic effect of reduced clusters and hybrid metal centers at the molecular level [101]. It provides a new working idea for the detection of Cr(VI) in a wide pH range, which is beneficial to further realize the field application of electrochemical sensors.

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**Fig. 5** The photo of a the heavy metal detection instrument and the schematic for b the principle of pipetting sample into the instrument and how to detect the target heavy metal ions by electrochemical sensor. c The schematic and the photo of the six-electrode chip. W working electrode, R reference electrode, C counting electrode. Copied with permission from Ref. [85]
ability to detect actual water samples in a wider pH range or without adjusting the pH is an important research direction that is worth continuing to explore in the future.

**Common inorganic pollutants: non-metallic As ions**

Arsenic is a non-metallic element that exists widely in nature, and has noted industrial value [102]. While arsenic can exist in several chemical forms in nature (−3, 0, +3, +5), natural water typically contains the inorganic form, with arsenate [As(V)] and sub Arsenate [As(III)] as the most common ions. As(III) and As(V) can be interconverted, but the toxicity of As(III) is much higher than that of As(V). Therefore, detection of As(III) is a perennial research hotspot [103]. As(III) is very harmful to human and animal health. Prolonged environmental exposure has been linked to a variety of serious diseases, including lung cancer, skin cancer, bladder cancer and kidney cancer [104]. Therefore, it is necessary to develop technologies to rapidly and effectively detect As(III) ions in water environments. In recent years, electrochemical sensors have attracted widespread attention for their high sensitivity, high selectivity, simple operation, low detection limit, and low cost [105–107]. To explore research into the electrochemical detection of As in water bodies (groundwater, sewage, surface water, and others), we identified relevant core papers from the past 20 years through Web of Science by using “As,” “water,” and “electrochemical sensor” as keywords.

Figure S1(F) shows that the research history regarding electrochemical sensor-based detection of As(III) can be divided into three stages. During Stage 1 (2000–2005), there were only a few published articles involving the electrochemical detection of As(III) ions in water environments. The number of published papers increased gradually during Stage 2 (2006–2011) as more researchers began to appreciate the importance of detecting As(III) in water environments. During Stage 3 (2012–2020), the number of studies involving electrochemical sensor detection of As(III) ions rapidly increased, indicating that electrochemical sensor detection of As(III) ions in various water environments has gained additional interest. In this context, groundwater primarily includes spring water and well water. In recent years, only 15.52% of published studies focused on the electrochemical detection of As ions in groundwater. Sewage refers primarily to arsenic-containing wastewater discharged from industries such as electroplating, smelting, tanning, and pesticides, and papers on this topic are the least common (8.62%). Studies of surface water, referring mainly to lakes, rivers, ponds and reservoirs, account for 20% of total published papers, more than both groundwater and wastewater. Studies of other water bodies, including tap water, seawater, drinking water, and a number of lab-prepared solutions (including deionized water and ultrapure water) make up the clear majority of relevant studies, with studies of standard-spiked tap water (which exhibits weak interference) predominating.

Among all electrode materials, gold nanomaterials have attracted increasing attention in the electrical analysis of As(III) due to their excellent electrocatalytic activity, high hydrogen overvoltage and more sensitive anodic current response. Kato et al. developed an AuNPs-embedded carbon film electrode. The cosputtering of Au and carbon were controlled by regulating individual target powers to form fine AuNPs with high electrocatalytic activity embedded in the chemically stable carbon film (Fig. 7A–E). They also successfully detected the tap water samples by using the developed electrode [108]. Yang et al. used AuNPs/ CeO2–ZrO2 nanocomposite modified GCE to analyze As(III) by square wave anodic stripping voltammetry (SWASV) in real groundwater samples from Guandiying Village, Togtoh County. High sensitivity and low detection limit of 20.674 μA ppb−1 cm−2 and 0.137 ppb were obtained, respectively [109]. Liu et al. electrodeposited electroreduced graphene oxide (ERGO)–Au nanoparticles (AuNPs) composite films on GCE by cyclic voltammetry (CV). The detection limit is 0.20 PPB by linear sweep voltammetry [110]. Recently, Nunez et al. developed an electrochemical biosensor for the determination of As(III) by implanting faecal alkali-producing bacteria (AF) on a AuNPs modified screen printed carbon (AUNps–SPCE), achieving a low detection limit [111]. Gold nanoclusters (less than 2.0 nm) are the most attractive materials in the most studied nanocluster (NC) systems. They are very stable and show unique size-dependent optical, electrochemical and catalytic properties [112]. Figure 7F shows the electrochemical environmental sensors for As(III) detection based on various Au nanomaterials [113]. According to WHO standards, the concentration of As(III) ions in drinking water should not exceed 10 μg/L (10 ppb). As shown in Table 1, all prepared electrodes can detect values in this range [114–119], indicating that detection limit does not pose a significant problem for As detection.
Conclusions and prospects

In this review, we primarily describe recent progress regarding the use of electrochemical sensors to detect typical pollutants found in different water environments. Since the current research only includes the Web of Science core collection literature and some references on unrelated topics were excluded from the collection results, bias may still exist. Based on our findings, we present the following a summary and prospects.

Electrode material

At present, electrochemical detection of water environmental pollutants is primarily performed using carbon material-based solid electrodes, with GCEs and graphene electrodes used most widely. Metal (metal oxide) nanoparticles/quantum dots are the materials most commonly used for electrode modification.

Sensitivity

Common inorganic pollutants (Pb, Cd, Cr, and As ions) are typically found in water environments at concentrations in the μg/L to mg/L range, and the reported electrodes satisfy associated requirements regarding the detection limit and sensitivity. However, the concentrations of antibiotics and pesticides in water environments are very low, generally at the nmol level, and further improvements to electrode sensitivity and detection limit will be necessary.

Cost

While many researchers reported a low cost for prepared electrode materials, the majority failed to provide a detailed cost accounting list. Therefore, more detailed cost analysis and comparison remain needed to support future production and applications.
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Currently, most studies are performed on water samples taken back to the laboratory for sensor detection, often requiring spiked standards and the optimization of various conditions. Difficulties arise when translating laboratory detection techniques to real-time monitoring in the field, primarily as a result of high levels of interference in complex environments. For example, some enzymes and aptamers used in electrochemical biosensors are easily affected by the environment conditions, and lose their activity, reducing both reproducibility and stability. In addition, electrochemical sensor componentization remains underdeveloped, particularly with regard to automatic sampling and analysis systems for in situ monitoring.

Prospects

Overall, studies into the electrochemical detection of groundwater pollutants are limited. However, groundwater serves as the main, or only, source of drinking water in many areas. Groundwater pollution is difficult to find, and groundwater flow rate is generally slow. Once groundwater is contaminated, the contaminants can exist for a long time, and the water sources are not easily remediated, leading to a significant threat to drinking water safety. Therefore, it is critical to develop methods for the detection of groundwater pollutants by electrochemical sensors, and researchers should increase future efforts in these directions.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.2116/analsci.21SAR12.

Table 1 Comparison of electrochemical studies of As(III) detection by sensing material

| Analytes | Electrode | Technique | Linear range (μg L⁻¹) | LOD (μg L⁻¹) | Sample | References |
|----------|-----------|-----------|-----------------------|--------------|--------|------------|
| As(III)  | AuNPs/CoO₂-ZrO₂/GCE | SWASV | 0.5–15 | 0.137 | Groundwater | [109] |
| Ibu–AuNSs/Nafion/GCE | CV | 0.1–1800 | 0.018 | Drinking water, tap water, river water, groundwater | [120] |
| EDTA/AuNps/GCE | SWASV | 0.1–15.0 | 0.0025 | Groundwater, drinking water | [115] |
| Fe₃O₄–RTIL/GCE | SWASV | 1–10 | 8×10⁻⁴ | Groundwater | [114] |
| ERGO-AuNPs/GCE | LSV | 0.75–375 | 0.20 | Tap water, mountain spring water, river water | [110] |
| Au@Fe₃O₄–RTIL/GCE | SWASV | 0.4–1 | 0.0022 | Tap water, reservoir water | [121] |
| Ag/Au HPNSs@FO/GCE | LASV | 0.05–16 | 0.01 | Tap water | [119] |
| HCR/RecJ exonuclease/Au | SWV | 0.1–500 | 0.02 | Tap water, lake water, sea water | [118] |
| SWCNTs/ssDNA/Au | DPV | 0.5–10 | 0.5 | Drinking water | [116] |
| rGO/MnO₂ NH/GCE | SWASV | 0.1–50 | 0.05 | Ultra-pure water | [117] |

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Recent progress regarding electrochemical sensors for the detection of typical pollutants...
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