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Detection and Monitoring of Algal Toxins: Advances in Analytical Techniques and Biosensors

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Abstract Algal toxins pose significant threats to ecology, public health, and the economy. They exist in aquatic ecosystems and are toxic to both humans and animals. This study mainly discusses the development of biosensors. The optical and electrochemical sensors, nanosensors, and lab-on-a-chip equipment involved in the research can all be used to detect toxins. The research focuses on how to make these sensors more sensitive, accurate, and capable of real-time monitoring. These technologies can be used for environmental and public health monitoring. For example, they can detect toxins in freshwater and marine ecosystems, as well as toxins in drinking water. These advanced technologies can also be used in harmful algal blooms (HABs) warning systems. Research has shown that a comprehensive approach is crucial for managing algal toxins. The research also provides direction for future work, including further research, development of new technologies, and implementation of better detection systems. These works can reduce the harm of algal toxins to public health and the environment, and promote the continuous development of this field.
Keywords: Algal toxins; Biosensors; Harmful algal blooms (HABs); Real-time monitoring; Environmental and public health

1 Introduction

Algal toxins (also known as cyanotoxins) are harmful substances produced by certain algae and cyanobacteria, typically occurring during harmful algal blooms (HABs). These toxins can contaminate water sources and pose a threat to human health, aquatic life, and the environment. Common algal toxins include microcystin, saxitoxin, toxoids, and chondroitin sulfate (Zhang et al., 2018; Tran et al., 2020). Their chemical structures and toxicity are different. These toxins mainly come from freshwater and marine environments. Ecological factors such as nutrient pollution and climate change can promote the massive proliferation of toxin producing algae (Bickman et al., 2018).

Algal toxins in water can cause many problems, affecting the environment, human health, and economy. Firstly, they can disrupt the ecosystem in the water, causing massive death of fish and other aquatic organisms, resulting in a decrease in the variety of organisms in the water (McPartlin et al., 2017; Gosset et et al., 2018). The harm to human health is also significant. If exposed to these toxins through drinking water, swimming, or eating contaminated seafood, it may cause diarrhea, damage the nervous system, and even be fatal in severe cases (Chuong et al., 2022). The economic losses are not small either, as it requires spending money to treat polluted water, provide medical treatment for people, and the tourism and fishing industries will also be affected.

This study aims to introduce the latest technology for detecting algal toxins. We will focus on three methods: electrochemical biosensors, portable detection devices, and precision instrument analysis (such as UPLC-MS/MS and LC-MS/MS). These new technologies can quickly and accurately detect various algal toxins in water. By summarizing existing technologies and pointing out areas for improvement in the future, we hope to help researchers, government officials, and relevant practitioners better address the issue of algal toxins and protect everyone's health and environmental safety.

2 Types and Characteristics of Algal Toxins

2.1 Classification of algal toxins

Algal toxins can be classified into several different types, mainly based on their chemical structure and toxicity characteristics. The first type is neurotoxins, such as type A toxins and saxitoxin (Zervou et al., 2017; Cevallos Cede ñ o et al., 2022). These toxins can damage the nervous system, causing serious neurological problems in both humans and animals (Figure 1). The second type is hepatotoxins, including various microcystin toxins and chlorella toxins, which mainly damage the liver and may cause liver disease or even liver failure. There is also a type of toxin such as cylindrical algae toxin and chondroitin sulfate, which have complex effects and may damage cells as well as affect the nervous system.

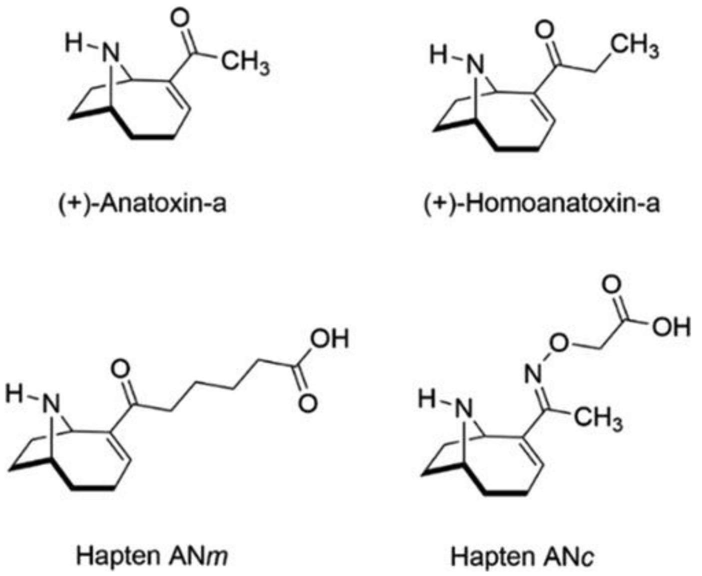

Figure 1 Chemical structure of (+)-anatoxin-a, (+)-homoanatoxin-a, and haptens AN*m* and AN*c* (Adopted from Cevallos-Cedeño et al., 2022)

2.2 Toxicological effects on humans and animals

Algal toxins pose great harm to humans and livestock, and can be fatal in severe cases. Neurotoxins, such as toxin-a, can cause muscle spasms, difficulty breathing, and in severe cases, respiratory arrest leading to death. Hepatotoxins (such as microcystins) can damage the liver, causing symptoms such as abdominal pain and vomiting, and in severe cases, may lead to liver failure (Greer et al., 2016; Massey et al., 2020). Even long-term exposure to small amounts of toxins may lead to chronic diseases such as cancer. Toxins such as diatom toxins can also damage the kidneys and cells, further increasing health risks.

2.3 Environmental factors influencing algal toxin production

The production of algal toxins is influenced by various environmental factors. Among them, nutrients such as nitrogen and phosphorus are particularly important as they promote the growth of harmful algal blooms (HABs) and toxin production (Vogiazi et al., 2019). Temperature and sunlight can also affect algal growth, with harmful algal blooms occurring more easily at higher temperatures (Medlin et al., 2020). The acidity and saltiness of water are different, and the types and quantities of toxins produced will also vary. With the intensification of climate change and eutrophication of water bodies, there may be more and more severe red tide phenomena in the future (McPartlin et al., 2016).

3 Traditional Methods for Algal Toxin Detection

3.1 Bioassays and their limitations

The traditional method for detecting algal toxins is bioassay. This method can measure the biological activity of toxins. For example, conducting experiments on mice is a common method for detecting microcystin toxins. However, biometric methods have many drawbacks. Firstly, conducting experiments on animals raises ethical concerns. Secondly, this method requires specialized laboratories and equipment. Most importantly, it cannot accurately distinguish the specific types of toxins. In addition, biometric methods are time-consuming and require professional personnel to operate, so they are not suitable for daily monitoring (Massey et al., 2020; Rossignoli et al., 2021).

3.2 Chromatographic techniques

Scientists often use chromatographic techniques to detect algal toxins in water, such as high-performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS). These methods are very effective in accurately identifying different types of toxins in water. There is a new technology called UPLC-MS/MS that is particularly useful now. It can detect multiple algal toxins at once and is very sensitive, even detecting very few toxins (less than 2.0 ng/L) (Tran et al., 2020). The LC-MS/MS method is also good, and after improvement, it can detect various blue-green algae toxins with stable data (Zervou et al., 2017). However, there is a big problem with these methods, which is that the required instruments are too expensive and must be operated by professional personnel, making it inconvenient to use in field testing.

3.3 Immunoassays for algal toxins

Immunoassay methods such as enzyme-linked immunosorbent assay (ELISA) are commonly used for detecting algal toxins. This method is easy to operate, highly sensitive, and relatively inexpensive. There are now specialized ELISA kits available to detect toxins such as microcystin, chlorella toxin, and saxitoxin, with the lowest detectable level being ng/mL (Petropoulos et al., 2019; Carmona Molero et al., 2022). This detection method is very suitable for daily monitoring and can also achieve automated large-scale detection. However, it has a drawback that cross reactions and matrix effects may occur, which can affect the accuracy of the detection results. Recently, researchers have developed improved versions of immunoassay methods, such as ELIMC (enzyme-linked immunosorbent assay) assay, which incorporates magnetic particles to make the detection more sensitive and accurate.

4 Advances in Analytical Techniques

4.1 Liquid chromatography coupled with mass spectrometry (LC-MS/MS)

The most reliable method for detecting algal toxins is liquid chromatography tandem mass spectrometry (LC-MS/MS). This method is particularly sensitive and the results are also very accurate. Since 2011, the European Union has been using it to detect lipophilic toxins in seawater. Now this method has become more advanced, incorporating high-resolution mass spectrometry (HRMS) technology, which can not only detect known toxins but also discover new types of toxins (Zendong et al., 2015). Scientists have also improved this method by incorporating automatic online solid-phase extraction (SPE) technology, which enables faster and more accurate detection of lipophilic marine algal toxins (LMAT) in seawater (Wang et al., 2021). Nowadays, many coastal farms use this method for daily inspections to ensure the safety of shellfish and other seafood.

4.2 Capillary electrophoresis for rapid toxin analysis

Capillary electrophoresis (CE) is a good method for detecting algal toxins, with fast analysis speed and particularly suitable for examining large quantities of samples. Although CE is not as commonly used as LC-MS/MS, it can serve as a supplement to other detection methods. This method has many advantages: it has good separation efficiency, requires a small amount of sample, and can quickly screen for toxins in various environmental samples.

4.3 High-throughput screening methods for environmental samples

Scientists have developed a new efficient detection method that can quickly detect algal toxins in large quantities of environmental samples. They combined two chromatographic techniques (reverse phase liquid chromatography (RPLC) and hydrophilic interaction chromatography (HILIC)) with high-resolution mass spectrometry (HRMS). This combination method is very powerful, as multiple types of toxins can be identified in one test, whether they are easily soluble in oil or water (Chen et al., 2016). This method is particularly useful for monitoring harmful algal blooms (HAB). In addition, they also use ultrasound to help extract toxins from algae samples, which results in more complete extraction and more accurate and reliable detection results.

4.4 Portable analytical tools for field applications

Now with portable detection tools, algal toxins can be monitored anytime and anywhere, and problems can be dealt with immediately. Among them, electrochemical biosensors are particularly useful (Zhang et al., 2018). This small device is very convenient to carry, easy to use, and the detection results are also very accurate. Its working principle is very clever: using biometric elements to find toxins in water, and then reading the results using electrochemical methods. Recently, scientists have improved the design of sensors and enhanced the signal amplification effect, making these biosensors more user-friendly and particularly suitable for on-site detection.

5 Development of Biosensors for Algal Toxin Detection

5.1 Principles and types of biosensors

There are mainly two types of biosensors for detecting algal toxins. One type is optical biosensors, such as planar waveguide optical sensors (Bickman et al., 2018). It uses fluorescence immunoassay to detect toxins, such as microcystin and cytotoxin, with accurate and sensitive results. Another type is electrochemical biosensors, which are particularly popular now because they can quickly detect in situ (Vogiazi et al., 2019). This type of sensor has three key components: a biological element specifically designed to identify toxins, an electrochemical detection device, and electrodes capable of amplifying signals. The sensor designed in this way has a very low detection limit and good repeatability.

5.2 Nanosensors for enhanced sensitivity and specificity

Scientists are now combining nanomaterials with biosensors, and the results are particularly good. Nanomaterials are small, but have a large surface area and are very friendly to organisms (Cunha et al., 2018). Using them in sensors can amplify the detection signal, make the sensor more sensitive, detect fewer toxins, and have a wider measurement range. For example, there is an electrochemical gene sensor for detecting algal toxins. After adding nanomaterials (Orozco et al., 2016), the RNA of toxic algae in water can be accurately found, and the performance of the entire sensor has been greatly improved.

5.3 Lab-on-a-chip devices for real-time monitoring

There is now a powerful detection technology called "chip laboratory", which can monitor algal toxins in real time. This technology integrates multiple laboratory functions onto a small chip, making testing fast and easy to carry. For example, scientists have invented a digital microfluidic diluter (Han et al., 2019) that can be used to monitor marine pollution, quickly locate toxic substances in water, and provide accurate and stable detection results. There is also a microfluidic sensor based on Xurography technology (Abbas et al., 2020), which has been used in urban pollution monitoring with good results and can reliably detect toxic substances.

5.4 Integration of biosensors with IoT for remote monitoring

Now, scientists have combined biosensors with Internet of Things (IoT) technology to create a new method for remote monitoring of algal toxins. This method can continuously collect data and transmit it in real-time, allowing us to detect and respond to harmful algal blooms (HABs) more quickly. These biosensors placed in the wild can measure the content of algae and toxins at any time, which is both cost-effective and efficient (McPartlin et al., 2017; Wang and Chen, 2024). The recently developed portable biosensor systems, such as the MBio system, are particularly useful, proving that IoT technology can indeed enable biosensors to play a greater role in on-site detection of blue-green algae toxins.

6 Applications in Environmental and Public Health Monitoring

6.1 Use of advanced techniques in freshwater and marine ecosystems

The technology for detecting algal toxins is becoming increasingly advanced nowadays. Portable biosensor systems, such as MBio, are particularly useful and can quickly detect various blue-green algae toxins in freshwater with accurate and reliable results (Bickman et al., 2018). Electrochemical biosensors are also very good, with stable detection results and suitable for direct on-site use. For toxins in seawater, scientists have also developed specialized biosensors that can quickly and accurately identify toxins produced by harmful algal blooms (HABs), and are convenient and cost-effective to use (McPartlin et al., 2016). These new technologies have made toxin detection in freshwater and seawater simpler and more effective.

6.2 Algal toxin monitoring in drinking water supplies

Effective detection of algal toxins is necessary to ensure the safety of drinking water. There are currently two main methods: one is UPLC-MS/MS technology combined with solid phase extraction (SPE), which can accurately detect various toxins in freshwater with high sensitivity and fully meet the requirements of drinking water monitoring (Tran et al., 2020; Wang, 2024). Another method is ELISA immunoassay, which is effective in detecting toxoid A and has simple and fast operation (Cevallos Cade ñ o et al., 2022). These new methods can detect trace amounts of toxins in water, greatly improving the level of drinking water safety management.

6.3 Early warning systems for harmful algal blooms (HABs)

6.3.1 Integration of real-time monitoring data into early warning systems

The key to timely warning of harmful algal blooms lies in the use of real-time monitoring data. The newly developed biosensors can continuously detect the levels of algae and toxins in water, solving the shortcomings of traditional methods (McPartlin et al., 2017; Panda et al., 2021). These sensors can provide the latest data at any time, which is particularly important for early detection and response to harmful algal blooms.

6.3.2 Regional toxin dispersion prediction using sensor networks

Sensor networks can effectively predict the diffusion of toxins in water. Solid phase adsorption toxin tracking (SPATT) technology is one of the methods, which collects toxins in water for a long time through specially designed adsorption materials (such as porous synthetic resins) (Rou é et al., 2018). By networking these sensors, it is possible to simultaneously monitor large areas of water, not only for a more detailed view, but also for real-time data transmission (Figure 2). Once toxin contamination is detected, immediate action can be taken. This networked monitoring system collects a large and comprehensive amount of data, which can help us better predict and respond to red tide.

6.3.3 Application of artificial intelligence and machine learning in algal bloom early warning systems

More and more artificial intelligence (AI) and machine learning (ML) are being used to enhance algal bloom warning systems. These intelligent technologies can quickly analyze massive amounts of data collected by biosensors and other monitoring devices, identify patterns, and predict when harmful algal blooms (HABs) will appear (Gosset et al., 2018; Han et al., 2019). Combining AI, ML, and real-time monitoring data can make warning systems more accurate and reliable, allowing us to respond to harmful algal blooms earlier and better.

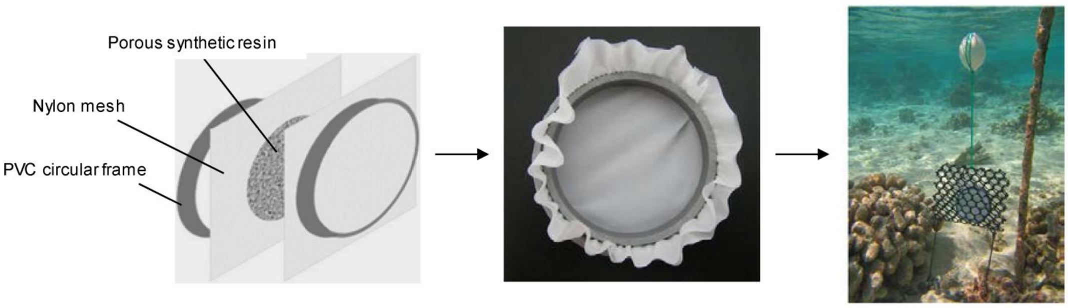

Figure 2 Example of one design used for the deployment of SPATT device in the field. Left: mode of assembly of SPATT device; Middle: SPATT device; Right: SPATT device deployed in the field (Adopted from Roué et al., 2018)

7 Challenges and Limitations

7.1 Sensitivity and specificity issues in complex matrices

The biggest challenge in detecting algal toxins is to achieve both sensitivity and accuracy in complex water environments. There are many other substances in the water that can interfere with the detection results and affect the accuracy of biosensors. For example, although electrochemical biosensors are very useful, if there are other organic or inorganic substances in the water, false alarms or missed detections may occur (Maguire et al., 2018; Chuong et al., 2022). Although the detection capabilities of some biosensors have improved, further improvement is needed in detecting trace toxins under different environmental conditions (Medlin et al., 2020).

7.2 High costs and accessibility of advanced analytical tools

The main problem with using high-tech equipment to detect algal toxins is that it is too expensive. Although devices such as planar waveguide optical sensors and electrochemical sensors are useful, they are expensive and require expensive materials to support them (Gosset et al., 2018). In addition, operating these devices requires specialized training, which is difficult to achieve in places with limited funds. Due to high costs, many projects that require long-term monitoring cannot afford these devices, and continuous monitoring is precisely the key to timely detection and treatment of harmful algal blooms (HABs).

7.3 Regulatory and standardization barriers for biosensor deployment

The use of biosensors to monitor algal toxins still faces regulatory challenges. The biggest problem currently is the lack of unified standards to validate and certify these new detection devices (Vogiazi et al., 2019). There are two main difficulties due to the lack of clear regulations: first, it is difficult to obtain approval for the use of new technologies, and second, relevant units are afraid to try them easily. To incorporate biosensors into the existing monitoring system, it is necessary to comply with current regulatory standards, and this docking process is often complex and time-consuming. Even more troublesome is that due to the lack of clear approval processes, many innovative biosensor technologies are stuck in the final step and cannot be widely applied in the market (Wu et al., 2019). These regulatory barriers make it difficult for good technology to truly work.

8 Conclusion

The recent new technologies in algal toxin detection have enabled us to better address the issue of harmful algal blooms (HAB). Electrochemical biosensors are a very useful tool that can quickly detect toxins on site, and the results are accurate and reliable. These sensors mainly rely on three parts of work: biological components specialized in identifying toxins, electrochemical devices for detecting signals, and systems for amplifying signals. After adding nanomaterials, the sensor becomes more sensitive, able to detect smaller amounts of toxins, and has a wider measurement range. There is now a portable detection system (such as the MBio system) that can quickly detect various blue-green algae toxins in freshwater, making it very suitable for on-site use. The new methods used in the laboratory, such as UPLC-MS/MS, are also very powerful and can accurately measure the content of multiple algal toxins in environmental samples at the same time.

The key to effectively managing algal toxins is to combine different detection methods. Traditional methods and new biosensors each have their own advantages and disadvantages, and their combined use yields the best results. For example, although old methods such as microscopic examination and molecular testing are accurate, they are time-consuming and laborious. And biosensors can quickly produce results on site, which is particularly important for timely treatment of harmful algal blooms (HABs). By integrating various methods, a better monitoring and early warning system can be established. This is the only way to protect public health, aquatic environment, and avoid economic losses caused by algal toxins.

Future research will focus on improving the performance of biosensors to make them more sensitive, accurate, and stable in detecting algal toxins. Specifically, we can start from these aspects: developing new biometric components and signal amplification methods that can detect trace amounts of toxins while reducing false alarms. We also need to develop unified standards to validate biosensors and ensure stable operation in different environments. In addition, it is possible to combine biosensors with remote sensing technology, automatic sampling equipment, and other monitoring methods to form a more comprehensive real-time monitoring network. The most important thing is to develop cheap and easy-to-use biosensors that are convenient for on-site deployment and use, so that more places can use this technology.

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Conflict of Interest Disclosure

The authors affirm that this research was conducted without any commercial or financial relationships that could be construed as a potential conflict of interest.

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