

Sensing Technology for Rapid Detection of Phosphorus in Water: A Review

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Abstract

Purpose: Phosphorus is an essential element for water quality control. Excessive amounts of phosphorus causes algal bloom in water, which leads to eutrophication and a decline in water quality. It is necessary to maintain the optimum amount of phosphorus present. During the last decades, various studies have been conducted to determine phosphorus content in water. In this study, we present a comprehensive overview of colorimetric, electrochemical, fluorescence, microfluidic, and remote sensing technologies for the measurement of phosphorus in water, along with their working principles and limitations. **Results:** The colorimetric techniques determine the concentration of phosphorus through the use of color-generating reagents. This is specific to a single chemical species and inexpensive to use. The electrochemical techniques operate by using a reaction of the analyte of interest to generate an electrical signal that is proportional to the sample analyte concentration. They show a good linear output, good repeatability, and a high detection capacity. The fluorescence technique is a kind of spectroscopic analysis method. The particles in the sample are excited by irradiation at a specific wavelength, emitting radiation of a different wavelength. It is possible to use this for quantitative and qualitative analysis of the target analyte. The microfluidic techniques incorporate several features to control chemical reactions in a micro device of low sample volume and reagent consumption. They are cheap and rapid methods for the detection of phosphorus in water. The remote sensing technique analyzes the sample for the target analyte using an optical technique, but without direct contact. It can cover a wider area than the other techniques mentioned in this review. **Conclusion:** It is concluded that the sensing technologies reviewed in this study are promising for rapid detection of phosphorus in water. The measurement range and sensitivity of the sensors have been greatly improved recently.

Keywords: Eutrophication, Phosphorus, Rapid detection, Sensor, Water quality

Introduction

Phosphorus is an essential nutrient that can be utilized by plants and microorganisms (Xie et al., 2013). It is generally present in one of three forms: orthophosphates, condensed phosphates (pyro-, meta- and poly-), and organic phosphorus (Korostynska et al., 2012). Orthophosphate especially is a leading nutrient for plant growth and energy supply. Major natural sources of phosphorus are phosphate rocks (Aydin et al., 2010), and artificial sources

are fertilizers and detergents (Law al and Adeloju, 2012). This phosphorus can be conveyed from the mainland to water sources by surface run-off, leaching, and rainfall. The content of phosphorus dissolved in water is one of the major factors to determine water quality. For drinking water, the World Health Organization set an allowable phosphorus concentration of 1 mg L⁻¹ (Law al and Adeloju, 2013). The phosphorus limits are 0.2 and 10 mg L⁻¹ for natural and wastewater, respectively (Berchmans et al., 2012).

Over the past decades, the effects of phosphorus on eutrophication have become more serious. Eutrophication occurs when the amount of nutrients in water increases. With the over-enrichment of phosphorus, the dissolved

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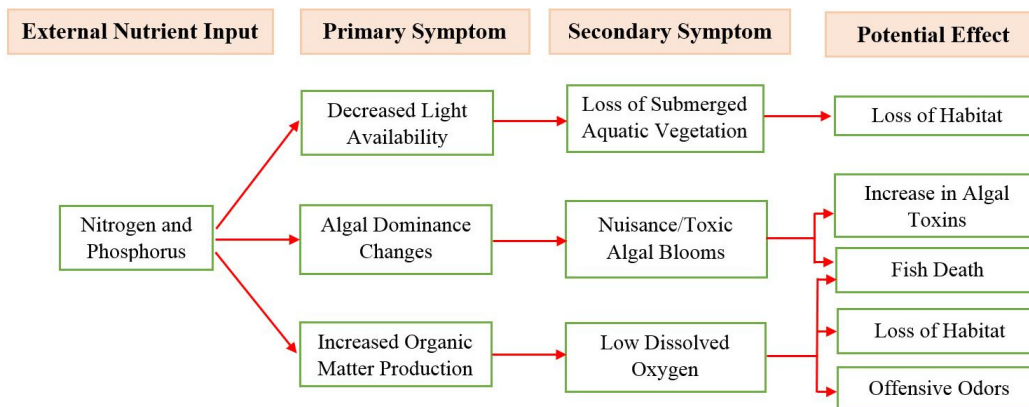


Figure 1. Eutrophication in water (modification from Bricker et al., 1999).

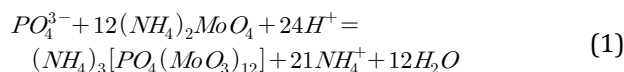
oxygen level in the water decreases. This leads to hypoxia or anoxia, resulting in algal blooms and thus eutrophication occurs (Chang et al., 2013). Eutrophication also reduces water clarity and thus decreases the aesthetic value of water. The consequences of eutrophication in water are shown in Figure 1.

The phosphorus content in surface water is a vital indicator in environmental monitoring. To keep the quality of the aquatic environment and water good, it is important to monitor the phosphorus content. For phosphorus detection, researchers have developed inexpensive and convenient techniques with fast responses, high selectivity, and high sensitivity over a wide concentration range. Many attractive techniques have been introduced. In this review, we present a comprehensive overview of the colorimetric, electrochemical, fluorescence spectroscopic, microfluidic, and remote sensing technologies for phosphorus measurement in water, along with their working principles and limitations.

Colorimetric Techniques

A colorimetric method is commonly used to determine the concentration of a chemical element or compound in solution by using a color-generating reagent. Color change occurs when the target analyte reacts with a specific reagent. The absorbance may increase in proportion to the concentration of colored species formed, or due to increased light scattering through the aggregation of smaller particles. The main advantages of this technique are that it is specific to one chemical species and is inexpensive for analysis. Murphy and Riley (1962) developed a colorimetric approach for the determination

of soluble phosphate in seawater. It was established as a standard procedure for colorimetric measurement of phosphorus. In this method (Figure 2) an ammonium molybdate reagent solution, containing ascorbic acid and antimony (III), reacts with phosphate ions to produce a blue-colored phosphomolybdate complex (Equation 1). However, this method suffers from interference by turbidity.



Following the standard method, Ganesh et al. (2012) proposed a colorimetric method using hydrazine sulfate as the reductant at a concentration of 0.5–5 $\mu\text{g mL}^{-1}$ instead of ascorbic acid. In this method, the phosphorus concentration was measured by the color intensity at a visible wavelength with relatively high sensitivity, but there was potential for interference from foreign materials. Recently, Moonrungee et al. (2015) also studied the blue phosphomolybdate colorimetric method, and achieved a detection limit of 0.01 mg L^{-1} from measuring the intensity of the blue-colored complex: the color intensity was proportional to the phosphorus concentration. A continuous flow analysis method, followed by a traditional colorimetric method, was also demonstrated by Kjaer et al. (2013), and used to determine dissolved reactive phosphate in ice cores. However, this experimental system was complex and meant its field use was limited.

A colorimetric method based on gold nanoparticles (AuNPs) has been described that was also attractive in allowing the detection of metal ions by their surface plasmon resonance absorption properties. He et al. (2013) measured phosphate anions in aqueous solution using a

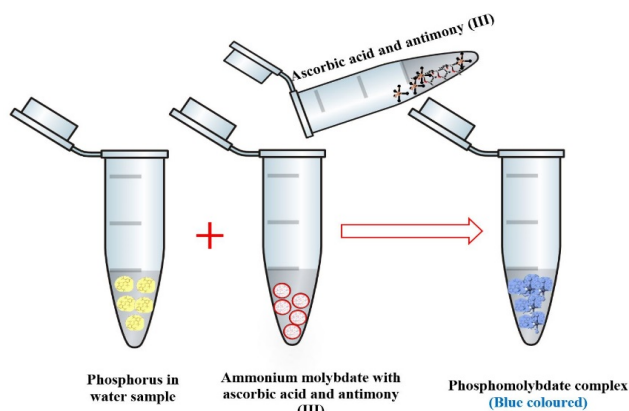


Figure 2. Standard colorimetric method to detect phosphorus.

terpyridine-zinc complex that functionalized AuNPs to bind phosphate. On reaction of mercaptophenyl terpyridine zinc-AuNPs with phosphate ions, the color changed from wine red to blue-gray. Liu et al. (2013) demonstrated another colorimetric method. When AuNPs reacted with europium ions, the color changed from wine red to blue. The color changed back to wine red when phosphate was added to the mixture of AuNPs and europium ions. The linear range of this colorimetric method for the measurement of phosphate was from 5.0×10^{-7} M to 3.0×10^{-5} M, with a low detection limit of 76 nM. The response time of the sensor was within 5 min.

In recent years, paper-based devices for the colorimetric determination of chemicals have attracted a great deal of attention because they offer an easy detection procedure. Jayawardane et al. (2012) produced a paper-based phosphomolybdate blue method for the detection of phosphorous in water. The measurement range was $0.2\text{--}10$ mg L⁻¹ with a detection limit of 0.05 mg L⁻¹. Again, the color intensity was proportional to the phosphorus concentration. It was a simple cheap platform, but its sensitivity was not high.

In colorimetric methods, some foreign substances can form similarly colored species to the target moiety. This can cause detection errors. Using a narrow wavelength band for the measurement of the color intensity may help to reduce the errors caused by foreign materials.

Electrochemical Techniques

Electrochemical methods rely on the chemical response of an analyte generated on electrical stimulation. It deals with the loss of electrons (oxidation), or the gain of

electrons (reduction), that a material experiences during the electrical process. These redox reactions can provide information about the analyte concentration, kinetics and reaction mechanisms, chemical status, and other aspects of the behavior of a species in solution. Electrochemical sensors operate by reacting with the samples of interest to generate an electrical signal proportional to the analyte concentration in the sample. A typical electrochemical sensor consists of a sensing/working electrode, a reference electrode, and a counter electrode. A variety of electrodes and electrochemical methods has been used to detect phosphorus in water.

Kolliopoulos et al. (2015) proposed a fast and portable electrochemical device to detect dissolved phosphorus by using screen-printed graphite electrodes. This work focused on the alteration of a colorimetric method to an electrochemical one in order to increase the measurement range. This modification lowered the detection limit to 0.3 $\mu\text{g L}^{-1}$. It also decreased the measurement time, and the number of reagents required to detect phosphorus. However, this sensor needed sample pretreatment and a complicated fabrication procedure.

Wang and Bishop (2010) introduced an ion-selective microelectrode to detect different forms of phosphate ions. The microelectrode was made of cobalt. The detection range was between 10^{-5} M and 10^{-1} M. The response time of this sensor was less than two minutes. The sensor had a good selectivity to phosphate ions and gave good reproducibility. However, the electrode had to be calibrated under controlled conditions. A solid state phosphate ion-selective electrode framed by a crystal disk was used by Tafesse and Enemchukwu (2011). The electrode was made of aluminum (Al), aluminum phosphate (AlPO₄), and copper (Cu). The analytical range was between 10^{-6} and 10^{-1} mol L⁻¹. The life time of the sensor was relatively long, but the response time varied with ion concentration.

Bai et al. (2013) developed an electrochemical microsensor to detect total phosphorus in water based on the reduction of the phosphomolybdate complex. The sensitivity was found to be -0.657 nA per ($\mu\text{mol L}^{-1}$), which is not particularly high. Bai et al. (2014) modified the electrochemical microsensor using microelectromechanical systems (MEMS) technology and AuNPs to improve the sensor performance. The detection limit of the sensor was 1.2×10^{-7} mol L⁻¹ and the linear range was 3×10^{-7} to 3×10^{-4} mol L⁻¹. This electrode could be integrated in microfluidic systems.

Wang et al. (2014) measured phosphorus in fresh water using a gold microband array electrode. They used a linear sweep voltammetric method to reduce the phosphomolybdate complex. The detection range was from 0.02 to 0.50 mg L⁻¹. Jonca et al. (2011) introduced an autonomous in situ electrochemical sensor to detect phosphate in seawater. Molybdate and sulfuric acid were added to a sample of seawater to yield the phosphomolybdate complex. This complex was detected electrochemically without adding any other reagents. The detection limit was 0.12 μM. However, this sensor could be affected by the presence of silicate and the mixing ratio of molybdate to sulfuric acid.

To detect monohydrogenphosphate, an ion-selective polyvinyl chloride membrane electrode was developed by Modi et al. (2011). The electrode used phenylurea-modified calixarene as an ion carrier. The detection limit was 2 × 10⁻⁸ mol L⁻¹ and the lifetime was 15 days. Norouzi et al. (2012) developed a nano-composite carbon paste electrode, and Ejhieh and Masoudipour (2010) introduced a potential surfactant-modified zeolite (SMZ) carbon paste electrode to detect phosphorus.

In electrochemical techniques, various metal electrodes and ion-selective membranes have been used to measure phosphate ions. These electrochemical sensors show good linear output, good repeatability, and high detection capacity, but the sensitivity depends on the material used for the electrode.

Fluorescence Techniques

The fluorescence technique is a spectroscopic analysis method in which the analyte is excited electronically by irradiation with a specific wavelength, and then emits radiation of a different wavelength. The emission spectrum provides information for the quantitative and qualitative characterization of the target analyte.

Krockel et al. (2014) proposed a miniaturized fluorescence detector to measure the concentration of phosphate. The measurement range and detection limit were 0–40 μg L⁻¹ and 0.22 μg L⁻¹, respectively. The detector could collect large amounts of isotropically emitted light, thus suppressing interference from the excitation light. Hosseini et al. (2011) developed a novel and simple fluorescence enhancement method for a selective pyrophosphate sensor through the use of new aluminum complex to get

significant enhancement of the fluorescence intensity. The analytical range of the sensor was 1.6 × 10⁻⁷ to 1.0 × 10⁻⁵ mol L⁻¹. The detection limit was 2.3 × 10⁻⁸ mol L⁻¹. Ganjali et al. (2012) also proposed a similar fluorescence enhancement sensor to detect pyrophosphate. This method used a thulium complex instead of an aluminum complex to get greater fluorescence enhancement. Zhao et al. (2011) presented an easy process for phosphate detection using an on-off fluorescence probe. The probe was made of europium-adjusted carbon dots. Zhang et al. (2012) also proposed a fluorescence chemosensor to detect inorganic phosphate.

Fluorescence methods are simple and rapid analytical techniques. The fluorescence intensity is sensitive to changes in natural light intensity, temperature, sample turbidity, pH, photochemical decay, etc. It also can be affected by compounds, which can absorb a portion of either the excitation or emission energy.

Microfluidic Techniques

Since microfluidic technology was introduced in the 1990s, it has developed rapidly and been widely used in areas of chemical, medical, and environmental monitoring. A microfluidic system incorporates several features to control chemical reactions with low sample and reagent consumption. It is a set of micro-channels etched or molded into a biocompatible material like glass and silicon or a polymer like polydimethylsiloxane. The controlled microenvironment for handling fluids and particles is the main advantage of this technique in chemical analysis (Ren et al., 2012). For this reason, a low-cost, portable, and rapid microfluidic device was developed to detect phosphorus in water.

Cleary et al. (2008) developed a microfluidic sensor for on-site detection of phosphate in wastewater. The microfluidic device made of polymethyl methacrylate (PMMA) was designed with a T-junction shape to mix phosphate sample and reagent. The phosphate concentration was then estimated using optical absorbance. The detection limit was in the order of a few mg L⁻¹. Legiret et al. (2013) proposed an integrated micro-analyzer to measure phosphate in seawater. They transferred a vanadomolybdate colorimetric method into “lab-on-a-chip” analytical system. The measurement range was 0.1–60 M and it could measure up to 20 samples per hour. Tong et al. (2010)

also introduced a microfluidic chip to measure phosphorus. It consisted of microfluidic channels with sensing and heating electrodes. When the phosphorus solution reached a micro-digestion well, the heating electrode increased the sample temperature to 120°C. A cobalt sensing electrode measured the electrical signal to estimate the phosphorus content.

Remote Sensing Techniques

Remote sensing is a technique to identify, observe, and measure an object from a distance, typically from an aircraft or a satellite. It is mostly done using optical techniques. Some researchers have estimated the phosphorus concentration in a lake using remote sensing.

Gao et al. (2015) measured total phosphorus concentration in a lake by analyzing multi-spectral satellite images. The band ratio method and multivariate statistical modeling were used to estimate the total phosphorus concentration. The total phosphorus concentration measured ranged from 0.0397 to 1.89 mg L⁻¹, with an average of 0.195 mg L⁻¹ and a standard deviation of 0.314 mg L⁻¹ for the whole lake. Chen and Quan (2012) determined nitrogen and phosphorus concentrations in a lake using a hyperspectral data set. The determination of coefficient (R²) for the prediction models of nitrogen and phosphorus were 0.24 and 0.63, respectively. The average nitrogen and phosphorus concentrations were 1.99 and 0.09 mg L⁻¹, respectively.

Conclusions

Phosphorus is one of the key elements for water quality control. The presence of large amounts of phosphorus in water greatly decreases water quality and leads to eutrophication. Thus, it is essential to measure the amount of phosphorus in water, and for this reason many researchers have turned their attention to the detection of phosphorus in water using different techniques. This paper reviewed some key technologies that have shown good selectivity and sensitivity in measuring phosphorus in water. Colorimetric techniques measure phosphorus by detecting color change in a simple way. It is specific for a single chemical species and inexpensive for use in analysis. Electrochemical techniques operate by reacting with the sample and generating an electrical signal proportional

to the sample analyte concentration. They showed good linear output, good repeatability, and high detection capacities. The fluorescence techniques detected phosphorus by the spectroscopic emission properties of the target analyte after irradiation with an excitation wavelength, and gave quantitative and qualitative results. Microfluidic techniques incorporate several features to control chemical reactions in a micro device. For the measurement of phosphorus in a wide area such as a lake, remote sensing methods can be used. All of these techniques show great potential for detecting phosphorus in water. The measurement range and sensitivity of the sensors have recently been greatly improved.

Conflict of Interest

The authors have no conflicting financial or other interests.

Acknowledgments

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