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Utilização de tecnologias alternativas *in situ* como *prescreening* para o monitoramento e avaliação da qualidade da água

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Utilização de tecnologias alternativas *in situ* como *prescreening* para o monitoramento e avaliação da qualidade da água

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“For me, I am driven by two main philosophies: know more today about the world
than I knew yesterday and lessen the suffering of others.
You'd be surprised how far that gets you.”
- Neil deGrasse Tyson

RESUMO

SILVA, G. M. (2022). **Utilização de tecnologias alternativas *in situ* como *prescreening* para o monitoramento e avaliação da qualidade da água**. Dissertação. Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos.

O monitoramento da qualidade das águas é uma ferramenta chave para os tomadores de decisões na gestão hídrica, uma vez que auxilia a minimização da poluição das águas e, consequentemente, os danos relacionados ao meio ambiente e à saúde humana. Deste modo, esta pesquisa teve, como objetivo, um debate sobre o uso de novas tecnologias alternativas aos métodos convencionais, presentes na literatura científica, para o monitoramento da qualidade da água, com aplicação *in situ* e *online*, bem como o desenvolvimento de um espectrofotômetro portátil, integrado com *smartphones*, para análise de metais em amostras de água. No artigo de revisão sobre o uso de novas tecnologias para o monitoramento da qualidade da água, com características de portabilidade, baixo custo e monitoramento *online*, foi possível identificar um aumento do número de trabalhos relacionados ao tema, principalmente a partir de 2012, sendo publicados 641 estudos em 2021. Os trabalhos citados contemplam os principais parâmetros físicos, químicos e biológicos da água e são baseadas principalmente no uso de sensores ópticos e eletroquímicos. Entretanto, devido ao recente desenvolvimento desses dispositivos, análises mais robustas são necessárias para garantir a precisão, repetitividade e acurácia dos resultados. Já no desenvolvimento do sistema portátil de espectrofotometria (*Smartphone Handheld System of Spectrophotometry*, na sigla SHSS), os resultados mostraram que o dispositivo apresentou desempenho semelhante a um espectrofotômetro de bancada convencional, com LOD e LOQ do SHSS para análise de Cobre iguais a 0,589 e 1,784 mg.L^{-1}, respectivamente; e o LOD e LOQ do SHSS para análise de Ferro igual a 0,479 e 1,450 mg.L^{-1}, respectivamente. Além do mais, o SHSS foi capaz de mensurar concentrações de Cobre e Ferro em amostras com concentrações desconhecidas semelhantes ao equipamento comercial utilizado, sendo uma alternativa potencial para experimentação em *in situ* e obtenção de resultados rápidos. Finalmente, novos estudos podem ser realizados para o aprimoramento do sistema e na identificação de novas substâncias pela mesma técnica.

Palavras chaves: qualidade das águas; *in situ*; s*martphone*; tempo real; tecnologias verdes; monitoramento das águas.

ABSTRACT

SILVA, G. M. (2022). **Use of alternative *in situ* technologies as prescreening for water quality monitoring and assessment**. Dissertation. São Carlos School of Engineering, University of São Paulo, São Carlos.

Monitoring water quality is a key tool for decision makers in water management, as it helps to minimize water pollution and, consequently, damage related to the environment and human health. Thus, this research aimed the debate on the use of new technologies, present in the scientific literature, alternative to conventional methods for monitoring water quality with *in situ* and online application, as well as the development of a portable spectrophotometer integrated with smartphones for analyzing metals in water samples. In the review article on the use of new technologies for monitoring water quality, with characteristics of portability, low-cost and online monitoring, it was possible to identify an increase in the number of works related to the topic, mainly from 2012, being published 641 studies in 2021. The cited works cover the main physical, chemical and biological parameters of water monitoring and are based mainly on the use of optical and electrochemical sensors. However, due to the recent development of these devices, more robust analyzes are necessary to guarantee the precision, repeatability and accuracy of the results. In the development of the portable spectrophotometry system (Smartphone Handheld System of Spectrophotometry, acronym SHSS), the results showed that the device performed similarly to a conventional benchtop spectrophotometer, with LOD and LOQ of SHSS for copper analysis equal to 0.589 and 1.784 mg.L^{-1}, respectively; and the LOD and LOQ of the SHSS for Iron analysis equal to 0.479 and 1.450 mg.L^{-1}, respectively. Furthermore, the SHSS was able to measure copper and iron concentrations in samples with unknown concentrations similar to the commercial equipment used, being a potential alternative for *in situ* experimentation and obtaining rapid results. Finally, new studies can be carried out to improve the system and identify new substances using the same technique.

Keywords: water quality; *in situ*; smartphone; real-time; green technologies; water monitoring.

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1 INTRODUCTION

Water is an important element for maintaining life on Earth and essential for meeting human needs. Although abundant, about 97.5% of the planet's water is salty and only 2.5% is fresh, in which 0.3% of this percentage are in rivers and lakes forms (BADRAN, 2017). According to Bicudo, Tundisi and Scheuenstuhl (2010), Brazil has the largest freshwater reserve in the world (approximately 12% of the total reserves) and, on the report of Brazilian Water Resources Conjuncture Report, about 255 thousand $m^{-3}.s^{-1}$ of water flow through the Brazilian territory, of which 80% is in the Amazon basin (ANA, 2017). However, polluted water may have limited consumption, even in locations with a large amount of this resource and, for this reason, it is necessary to consider the use of water whenever we think about the water pollution problem (WEINER; MATTHEWS, 2003).

The deteriorated water quality may, for example, hold a low level of biodiversity and contain agents that are harmful to human health, which generate an increase in the costs of water treatment for public supply (BASSEM, 2020; PLAPPALLY; LIENHARD V, 2013). However, this type of water quality is not limited for less noble uses, such as for landscape harmonization, vessel navigation and power generation (ADEJUMOKE. *et al.*, 2018). According to Von Sperling (2014), the superficial water quality is a consequence of natural conditions (such as geology, vegetation, climate, etc.) and the different types of land use in the hydrographic basin area.

Studies on the correlation between land use and water quality shown changes in water quality as a result of urban areas and agricultural activities, such as the increase in nitrogen, by Tsegaye *et al.* (2006), and the increase in phosphorus, by Pratt and Chang (2012) and Wan *et al.* (2014). Ngoye and Machiwa (2004), for example, concluded that agriculture made a significant contribution to nutrient uplift in the Ruvu River, Tanzania. However, Baker (2003) emphasizes that these relationships are complex and that, generally, any observed correlation between the polluting source and water quality can be a characteristic of a specific locality.

A way of synthesizing and making water quality information more easily interpretable, according to Kachroud *et al.* (2019), is by the “Índice de Qualidade das Águas” (IQA), used in Brazil since 1975 based on the National Sanitation Foundation (NSF) Water Quality Index. The IQA is able to categorize the water quality from “very poor” to “excellent” conditions. In addition, based on the IQA, the Agência Nacional de Águas (2012) revealed that 75% of the

1,988 monitoring points of Brazilian rivers had a “good” quality condition. However, in urban areas, the report showed that this percentage dropped to 26% and that 32% of the points were categorized as “poor quality”.

The IQA is obtained from nine monitoring parameters, such as, for example, Dissolved Oxygen (DO), Total Coliforms, pH and Biochemical Oxygen Demand ($BOD_{5,20}$). However, since it was first introduced, different studies have adapted the NSF model in different water bodies, adjusting weights and removing or incorporating new parameters for each specific location (BENOUARA; LARABA; RACHEDI, 2016; CUDE, 2001; HOSEINZADEH *et al.*, 2015; MISAGHI *et al.*, 2017). Furthermore, due to the presence of emerging contaminants (or toxic contaminants), many studies have applied different index that allow a better representation of water quality, such as the HEI/HPI (Heavy Metal Evaluation Index or Heavy Metal Pollution Index) (GIRI; SINGH, 2014; JAHAN; STREZOV, 2017; KHOSHNAM *et al.*, 2017; MADZIN *et al.*, 2017).

The presence of heavy metals in the environment has been the subject of several studies, mainly due to their ability to dissolve in water and cause harmful effects on living beings (GHEORGHE *et al.*, 2012). The heavy metal term refers to any metal and metalloid that has a relatively high density (between 3.5 and 7.0 $g.cm^{-3}$) and which can be toxic at low concentrations (on the order of $\mu g.L^{-1}$), such as mercury (Hg), arsenic (As), and cobalt (Co) (GAUTAM *et al.*, 2014). However, according to Speight (2017), the classification of a metal as heavy should be analyzed carefully, since metals tend to be less dense when bound in other compounds and more reactive than in their elemental state. In addition, it is important to highlight that many metals play a fundamental role as micronutrients and, therefore, are essential in trace amounts, as for nervous system and in cellular growth (ALLOWAY, 2013).

According to Gheorghe *et al.* (2012), the occurrence of heavy metals in the environment due to human action comes from industrial effluents, domestic sewage, agrochemicals, mining, incorrect disposal of electronic waste and accidents involving handling, transport and/or storage of these substances. In recent years, increasing levels of toxic metals in the environment have caused concern in the scientific field and in management of water resources, mainly due to their ability to be transported by sediments and not be biodegradable, making them persistent in the environment and in the food chain, by the process of bioaccumulation (GAUTAM *et al.*, 2014; MEHMOOD *et al.*, 2019). However, the toxicity of a metal does not depend only on its exposure, but also on its chemical and/or physical speciation.

The term speciation refers to the occurrence of an element in different forms in a system, whose purposes of speciation analysis is to provide information on the bioavailability of the elements and, thus, determine the potential for toxicity and mobility in the environment (FORSBERG *et al.*, 2006; FYTIANOS, 2001; OSPINA-ALVAREZ *et al.*, 2014; TEMPLETON *et al.*, 2000). Therefore, natural or anthropogenic changes in the environment can considerably influence the metals type occurrence in the water. According to Magalhães *et al.* (2015), metals are also part of the chemical balance between water and sediments, and can be released into water or absorbed by the sediments due disturbances in the aquatic system, such as ionic strength of the medium, hardness, presence of organic matter, pH, redox potential and valence state.

Once in the biological system, the toxic metals can damage organs and intracellular components, such as the plasma membrane, enzymes, and DNA, inducing a toxic and carcinogenic effect (TCHOUNWOU *et al.*, 2012; WANG; SHI, 2001). Arantes *et al.* (2016), for example, shown that the poisoning by toxic metals can cause a decrease in reproductive and immunological capacity and even death in fish population. In humans, toxic metals can cause adverse effect on the nervous, cardiovascular, respiratory, immune, hepatic and renal systems, as well as induce neurological disorders and cancer development (IZAH; CHAKRABARTY; SRIVASTAV, 2016). In order to detail the importance, behavior and risks of the metals that will be addressed in this study, some of the main characteristics of Copper and Iron will be exposed.

The occurrence of Copper in the environment can come from natural and anthropogenic sources, such as the production of non-ferrous metals, wood, iron and steel, incineration of waste, burning of fossil fuels, mining and soil fertilization (GEORGOPOULOS *et al.*, 2001). There are four different forms of copper, Cu(O), Cu(I), Cu(II) and Cu(III), with Cu(II) being the oxidation state that usually occurs in water and can be found in free or bound in sediment or dissolved compounds in water (KARIM, 2018; REHMAN *et al.*, 2019). In plants and animals, copper is involved in diverse functions of enzymes and other proteins and its deficiency can lead to anemia and bone abnormalities, including osteoporosis and fractures (OLIVARES; UAUY, 1996). Copper intoxication can cause problems in the central nervous, gastrointestinal and renal systems and, in the cell, induce changes in DNA, membrane integrity, respiration and enzyme activity (CHAFFAI *et al.*, 2007; KARIM, 2018).

Iron is the second metal and the fourth most abundant element on earth (FREY; REED, 2012). Its presence in water bodies occurs through the weathering of rocks and soil, due to natural causes, and the release of sewage and river water discharges, due to anthropogenic influence (XING; LIU, 2011). In water, iron occurs in soluble form as ferrous iron Fe(II), complexed with ferric iron Fe(III) or associated with iron bacteria (CHATURVEDI; DAVE, 2012). Iron is an essential element in the human diet and is a vital component in the composition of proteins, such as hemoglobin (JAISHANKAR *et al.*, 2014; WHO, 2011). However, although harmless, iron is one of the main causes of clogged pipes and, in high concentrations, it can have a toxic effect in children, leading to gastrointestinal bleeding, vomiting and diarrhea (COLTER; MAHLER, 2006). In addition, the high concentration of iron is capable of producing free radicals that can directly attack DNA and cause several related diseases (GRAZULEVICIENE *et al.*, 2009).

According to Behmel *et al.* (2016), the monitoring of water quality is able to identify the presence of unwanted and harmful substances to humans and the environment, such as the metals, and thus enable the use of this information in support of water management and making decision. This pollution control strategy has led several countries to reformulate water governance towards sustainable development through an integrated approach, as recommended by Agenda 30 in 2018 (UN, 2018).

One of the ways of determining heavy metals in water is by the technique of colorimetry, field of spectrophotometry, which consists of measuring the absorbance of light that passes through a sample (at a certain wavelength) with the presence of a specific colorimetric chemical reagent (MARCZENKO; BALCERZAK, 2000). This method is based on the phenomenon of energy absorption at different electromagnetic wavelengths by specific atoms or molecules (AMORIM *et al.*, 2008). However, because of the high cost of this technique, skilled labor and use of complex equipment (GONZÁLEZ-MORALES *et al.*, 2020), many studies are looking for affordable, portable and low-cost alternatives that allow the measurement of substances in water by the spectrometry and electrochemical technique (ALAM *et al.*, 2020; DE OLIVEIRA *et al.*, 2017; KONG *et al.*, 2020).

Thus, this research aims to discuss the possibilities of using accessible equipment and technologies that allow obtaining water quality parameters and to investigate the feasibility of a portable solution to measure the concentration of Copper and Iron in water, using an adaptable spectrometer for smartphones and the colorimetry technique.

1.1 Research hypothesis

Knowledge of water quality helps decision makers in strategic planning for the maintenance of water resources and the prevention of unwanted substances that may have harmful effects on human health or even on the environment. In this way, smartphones and other technologies can be a tool applied to water resources to obtain *in situ* water quality parameters, quickly and safely, such as the spectrophotometry technique.

1.2 Purposes

1.2.1 General purpose

The debate on the use technological devices that allow their application to the monitoring of water resources and development of a portable, simple and effective system, that can be able to measure the concentration of Copper and Iron in water from a smartphone device and a portable spectrometer, by the spectrophotometry technique.

1.2.2 Specific purpose

1. To carry out a theoretical review regarding the use of portable, low-cost technologies, with *in situ* application, applied to the water quality monitoring;
2. To analyze the behavior of the intensity and absorbance curves of the visible light spectrum, obtained by the proposed spectrophotometry system;
3. To estimate the concentration of copper and iron in water, in prepared samples and samples with unknown concentrations;
4. Evaluate the performance of the proposed spectrophotometry system against conventional equipment.

1.3 Text organization

This master's dissertation is divided into five chapters, containing a chapter for the description of the general methodology of the work; a review chapter; a chapter on results and discussions of laboratory experiments; ending with general conclusions and recommendations for future work.

Chapter 2 is a description of the general methodology, which consists of an explanation of the research development, such as data acquisition, equipment used and theories about the spectrophotometry technique.

Chapter 3 is a literature review about scientific studies that present water quality monitoring technologies with *in situ* application. Thus, an analysis was carried out on the evolution of the number of annual publications about the theme and a description of new alternative technologies applied to the monitoring of the main physical, chemical and biological parameters of water.

Chapter 4 shown the Smartphone Handheld System of Spectrophotometry (SHSS), a device developed to monitor water quality using the spectrophotometry technique. This equipment uses a commercial sensor adaptable to smartphones to read the spectra and estimate the concentration of the analyte from the absorption spectrum analysis. In this research, Copper and Iron were analyzed as metals to evaluate the performance of the system, comparing it with a bench spectrophotometer.

Finally, Chapter 5 presents the general conclusions of this research and recommendations for future works related to the topic.

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2 GENARAL METODOLOGY

Two major segments were chosen for the development of this research: a review that presents different scientific studies related to technologies to monitor the quality of water *in situ*; and the development of an equipment that measure the concentration of Copper and Iron in water samples, using a smartphone device and a portable spectrometer.

As shown by the flowchart (Figure 2.1), the scientific review article (Chapter 3) described different technologies developed and presented by scientific studies for the monitoring of water quality, considering the main physical, chemical and biological parameters used in the monitoring of surface water and drinking water (ALLEY, 2007; BOYD, 2020; COTRUVO, 2018; OMER, 2019; SPELLMAN, 2017; WHO, 2011). Thus, the following parameters were considered, being the physical parameters: color, temperature and turbidity; the chemical parameters: chlorine, fluorine, phosphorus, metals, nitrogen, dissolved oxygen, pH, and oxidation–reduction potential; and the biological parameters: algae, cyanobacteria *Escherichia coli* and total coliforms. Finally, a discussion was carried out in the scientific works considering the terms *in situ*, low-cost, real-time and portable, as well as an analysis of the evolution of the number of annual publications on the subject.

Chapter 4 presents the development of a compact and portable equipment for smartphone devices, called Smarphone Handheld System of Spectrophotometry (SHSS), capable of measuring the concentration of metals in water samples using the colorimetry/spectrophotometry technique and the Beer-Lambert Law. Thus, a portable spectrometer (*GoSpectro*) was adapted to 3D box printed to obtain data from the light spectra of water samples. A white light emitting diode (LED), in the visible region, was used as a light source, whose spectra were read through a smartphone camera by the *SpectroLab App*. The experiments were carried out for the analysis of Copper and Iron, elaborating the standard curves, from samples prepared in the laboratory, and calculating the detection and quantification limits for each metal. As a way of evaluating the equipment's performance, the system was compared with a commercial spectrophotometer (*Hach DR3900*) and tested with samples with unknown concentrations of domestic sewage treated effluent, chemical laboratory wastewater and electroplating wastewater.

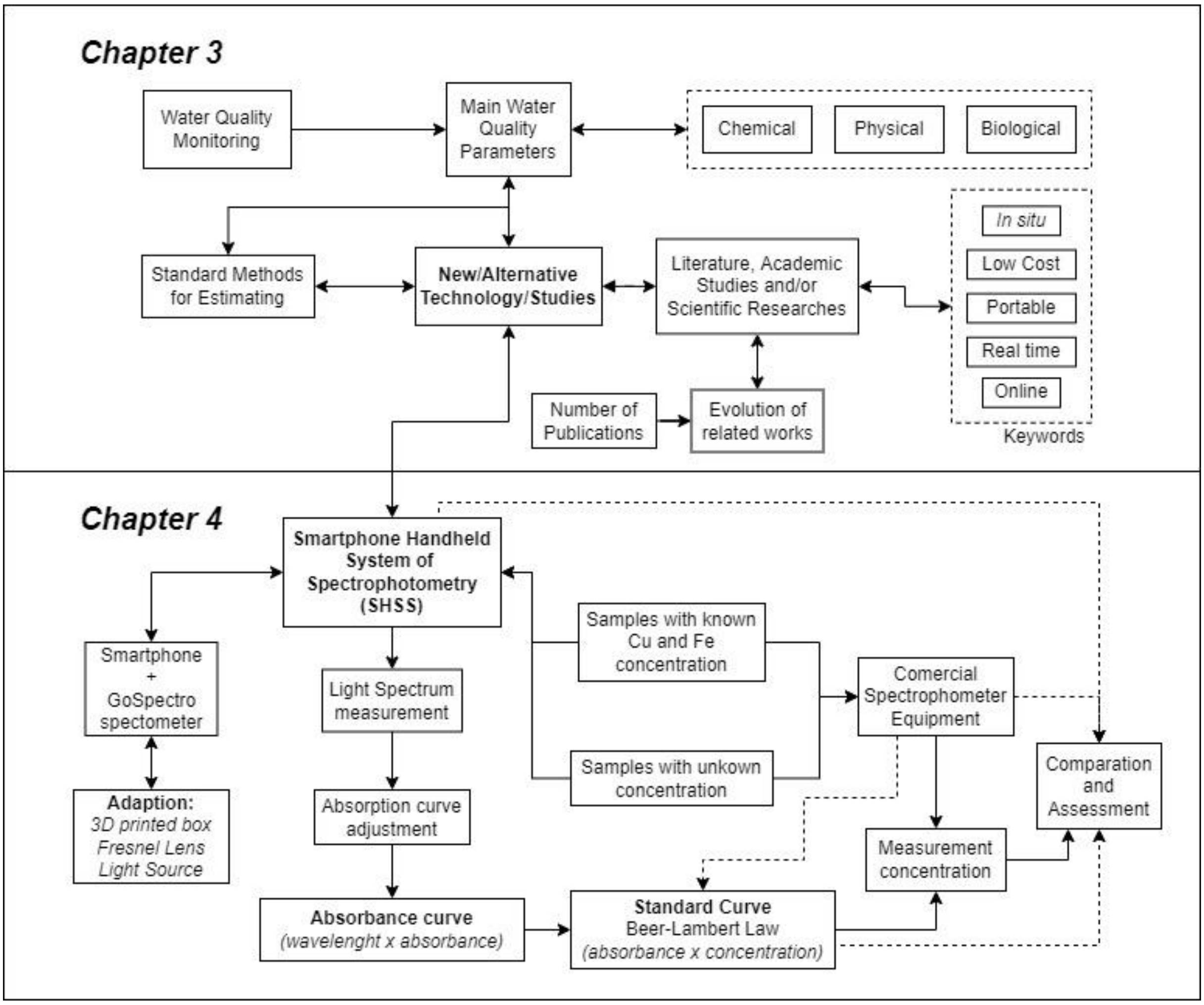

Figure 2.1 - Flowchart of the general methodology.

2.1 Spectrophotometry

According to Kafle (2019), spectroscopy can be defined as the science that studies the relationships between light, matter and energy. The spectroscopy is a great technique with application in constant growth to analyze and extract information about gases, liquids and solids, such as in the astronomy, chemistry, toxicology, terrestrial geography and food (COATES, 2006; OP-TEC, 2008). The classification of spectrometry technique is according to the type of radiation used, spectrophotometry being an area of spectroscopy that studies the spectra of ultraviolet (UV), visible (VIS) and infrared (IF) radiation (GERMER; ZWINKELS; TSAI, 2014).

Spectrophotometric techniques are one of the oldest techniques used by analytical chemistry. The method consists of analyzing the spectrum of light absorption by a chemical substance in order to determine its composition and concentration in an unknown sample (MARCZENKO; BALCERZAK, 2000). The same "colorimetry" is a spectrophotometric technique and, according to Marczenko and Balcerzak (2000), it consists of determining the analytical concentration of an unknown substance in a sample, from appropriate standard samples with known concentrations, analyzing the variation in light intensity due to the presence of a colorimetric chemical reagent.

The main equipment that allows the study of spectrometry is called spectrophotometer (Figure 2.2). It consists of a light source, a sample and a detector. The light source equipment usually emits a wide range of electromagnetic radiation spectrum, which is thereafter filtered by a monochromator. The monochromator separates the different wavelengths of light (λ), allowing measure the sample's intensity light by a photocurrent generated in the detector. In this case, the detector must be sensitive to the wavelengths emitted by the source and its response (photocurrent) must be calibrated before measuring the sample. It is also possible to integrate multiple detectors so that they cover a greater variety of specific wavelengths when reading electromagnetic radiation (GERMER; ZWINKELS; TSAI, 2014).

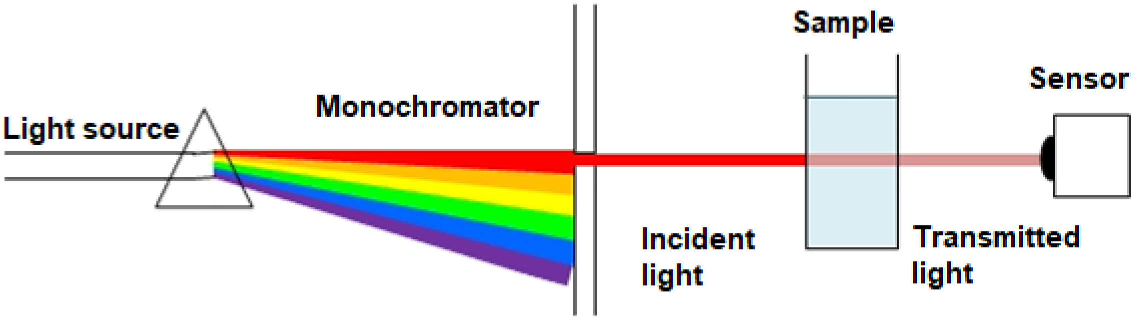

Figure 2.2 - Schematic of the spectrophotometry method. Source: Adapted from Diamantina Institute, 2017.

The analysis of a substance by the spectrophotometry technique can be qualitative and quantitative. According to Kafle (2019), qualitative analysis is performed by observing the absorption of light at a specific length of the analyzed spectrum, since the analyte is able to absorb light at a specific wavelength in contact with a reagent. For the other hand, the quantitative analysis is performed measuring the decrease in the intensity of samples light transmitted. The performance of a spectrophotometer, for a good measurement of substances, depends on the spectral resolution, calibration and reproducibility of the equipment. In addition, according to Burgess (2007), good laboratory practices also contribute to improving the performance of the spectrophotometer and the quality of measurements, such as periodic maintenance of equipment and cleaning of cuvettes.

2.1.1 Beer-Lambert Law

For a quantitative analysis in spectrophotometry, the estimation of the concentration of an analyte (substance or chemical component, in a sample, which is the target of analysis in an assay) is possible from the Beer-Lambert Law (1852). According to Lambert's law, the fraction of light absorbed by a transparent medium is independent of the incident light intensity and each successive layer of the medium absorbs an equal fraction of the light that passes through it, which can be expressed mathematically by Equation 1 (POOLE; KALNENIEKS, 2000).

$$\mathrm{Log}_{10}(\mathrm{I}_0/\mathrm{I}) = kl \tag{1}$$

where I_0 is the intensity of incident light (light from the source), I is the intensity of transmitted light, l is the path length of the light in the cuvette, and k is the absorption constant of the medium. According to Beer's Law, the amount of light absorbed in the sample is proportional to the number of molecules of a chromophore (set of atoms of a molecule responsible for its color), in which case the constant k is proportional to the concentration (C) of a chromophore. Therefore, this relationship can be expressed as k=εC , where ε is the molar absorption ($\mathrm{mol.L^{-1}}$) of a solution in 1 cm of width of the cuvette (POOLE; KALNENIEKS, 2000). Thus, from Equation 1, the Beer-Lambert Law can be express as

$$\mathrm{Log}_{10}(\mathrm{I}_0/\mathrm{I}) = \Delta A_\lambda = \Delta \varepsilon \mathrm{C} l \tag{2}$$

where (I_0/I) is called absorbance and is related to the wavelength λ (A_λ). According to Workman and Springsteen (1998), the absorptivity coefficient ε is different for each type of material, but this value is a constant for a given compound at a selected wavelength.

According to Perkampus (1992), the passage of light through a cuvette can also be represented by the transmittance (T), in percentage terms, given by the relation (I_0/I). However, Poole and Kalnenieks (2000) headline that absorbance (A_λ) is more commonly used by the unique linear relation with the chromophore concentration. Therefore, the relationship between absorbance and transmittance can be expressed as:

$$A_\lambda = \mathrm{Log}_{10}(1/T) \tag{3}$$

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3 ADVANCES IN TECHNOLOGICAL RESEARCH FOR ONLINE AND *IN SITU* WATER QUALITY MONITORING – A REVIEW

A modified version of this chapter has been submitted as: Gabriel Marinho e SILVA, Daiane Ferreira CAMPOS, José Artur Teixeira BRASIL, Marcel TREMBLAY, Eduardo Mario MENDIONDO, Filippo GHIGLIENO. **Advances in technological research for online and in-situ water quality monitoring – a review**. Sustainability.

Abstract

Monitoring water quality is an essential tool for the control of pollutants and pathogens that can cause damage to the environment and human health. However, water quality analysis is usually performed in laboratory environments, often with the use of high-cost equipment and qualified professionals. With the progress of nanotechnology and the advance in engineering materials, several studies have shown, in recent years, the development of technologies aimed at monitoring water quality, with the ability to reduce the costs of analysis and accelerate the achievement of results for management and decision-making. In this work, a review was carried out on several low-cost developed technologies and applied *in situ* for water quality monitoring. Thus, new alternative technologies for the main physical (color, temperature, and turbidity), chemical (chlorine, fluorine, phosphorus, metals, nitrogen, dissolved oxygen, pH, and oxidation–reduction potential), and biological (total coliforms, *Escherichia coli*, algae, and cyanobacteria) water quality parameters were described. It was observed that there has been an increase in the number of publications related to the topic in recent years, mainly since 2012, with 641 studies being published in 2021. The main new technologies developed are based on optical or electrochemical sensors, however, due to the recent development of these technologies, more robust analyses and evaluations in real conditions are essential to guarantee the precision and repeatability of the methods, especially when it is desirable to compare the values with government regulatory standards.

Keywords: water quality; *in situ*; sensors; green technology; water monitoring.

3.1 Introduction

Water is an important natural resource for life on earth and for human activities and, therefore, it is necessary to have abundant clean water to quench thirst, irrigate fields, and sustain all forms of life in the environment (VIGIL, 2003). Several sources contribute negatively to changing water quality, mainly caused by human action, such as population growth, industrialization, urbanization, agriculture, domestic sewage, and poor management (OWA, 2013; SPEIGHT, 2020). To improve water quality, the 2030 Agenda for Sustainable Development established, as a goal for 2030, the availability and sustainable management of water and basic sanitation for all human beings, with the improvement of water quality, the reduction in pollution, and the elimination of dangerous pollutants (UN, 2018).

Water quality monitoring allows the identification and quantification of polluting substances that can be compared to acceptable standards for each location, being a strategic management tool for decision-making and the improvement of water quality (BEHMEL *et al.*, 2016; GALLAHER; HEIKKILA, 2014). Tamm, Nõges, and Jävet (2008), for example, monitored the load supply of dissolved organic carbon (DOC) to Lake Võrtsjärv (Estonia) between 1990 and 2002 by ground and surface flow—parameters affected by hydrological factors—highlighting the importance of assessing the parameter both currently and under changing climatic conditions. Unfortunately, there is still a large gap in water quality data, especially in remote locations and in developing countries (EISENBERG; BARTRAM; WADE, 2016), raising concerns about the sustainability of water resources and risks to human health. Furthermore, the main conventional techniques for monitoring water are often expensive, requiring qualified professionals and complex equipment, and which, in many circumstances, do not allow direct analysis in the field with immediate results.

However, several studies have tried to fill the gap and overcome the lack of data provision, such as the incorporation of citizen science (HEGARTY *et al.*, 2021; CAPDEVILA *et al.*, 2020), for example, or the development of low-cost and *in situ* technologies, as will be described throughout this work. The development of low-cost, accessible, and easy-to-handle devices and sensors for water quality analysis can be a viable alternative for obtaining data, improving water quality, and, consequently, the security of the water (JUSTINO; DUARTE; ROCHA-SANTOS, 2017; Sarni *et al.*, 2019). Furthermore, *in situ* measurement contributes to cost minimization, as it eliminates the need for sampling, sample preservation, transport, and laboratory water analysis (CROCKER; BARTRAM, 2014).

The combination of technologies and water quality sensors with components of microsystems, associated with a software architecture and cloud computing (online), allows the development of a system in the conception of Smart Water Quality Monitoring Systems (SWQMS), from the point of view of the Internet of Things (IoT) (BORGIA, 2014; DONG *et al.*, 2015; GEETHA; GOUTHAMI, 2016). In addition, integration with the Big Data system can improve the modeling of the water system, reducing model uncertainties and ensuring more information in the management of risk analysis (CURL *et al.*, 2019; SHAFIEE; BARKER; RASEKH, 2018). Pehme *et al.* (2019), for example, highlighted the necessity of an advanced understanding of landfill hydrological regime, by modeling tools and evaluating the risks to environmental and human health related to landfill geomorphology and hydrological balance.

According to Sarni *et al.* (2019) and Hoolohan *et al.* (2021), digital technologies are seen as resilient, innovative, and efficient devices that can enhance the relationship between water and society, being a progression toward solving challenges in water systems and helping to mitigate social and environmental problems. An approach to water quality improvement, for example, is also the association of Real-Time Control systems (RTC) and Nature-Based Solutions (NBS) in urban drainage infrastructures, as described by Brasil *et al.* (2021).

Thus, this work aims at a literary review that brings together technologies and portable sensors aimed at monitoring the quality of water *in situ* (regarding physical, chemical, and biological water quality parameters), at low cost, which allows a prescreening of the condition of the water as a monitoring tool for decision-making and good water management.

3.2 Water Monitoring Parameters

Although there are several parameters for monitoring water quality, only a few are used as key parameters in the monitoring, which can vary according to the location or the purpose of water use (BOYD, 2020). Regarding water use, according to Boyd (2020) and Alley (2007), when intended for human consumption, such as drinking, for example, the water must not have high concentrations of minerals, taste, or odor, and must be free of toxins or pathogenic organisms; for recreation, despite being unsuitable for consumption, the water must not present risks of contagion or diseases through direct contact; for the environment, the water must not contain pollutants that cause adverse effects on flora and fauna. Alam *et al.* (2007), Rahman and Bakri (2006), Mohamed *et al.* (2015), and Rahmanian *et al.* (2015), for example, present water quality monitoring studies whose monitoring parameters were established according to the needs of each location.

For monitoring water quality, Boyd (2020), Alley (2007), the World Health Organization (2011), Spellman (2017), Cotruvo (2018), and Omer (2019) present a variety of physical, chemical, and biological parameters for drinking water, superficial water (fresh and saltwater) and groundwater, the sources of pollutants, types of speciation, and the main analysis techniques. In this work, the following were considered as physical parameters: (i) color, (ii) temperature, and (iii) turbidity; and as chemicals: (iv) chlorine, (v) fluorine, (vi) phosphorus, (vii) metals, (viii) nitrogen, (ix) dissolved oxygen, (x) pH, and (xi) redox potential or ORP (Oxidation–Reduction Potential).

In biological monitoring, although it is possible to identify numerous pathogenic species in water, the methods of isolation and the enumeration of such microorganisms make this a complex and time-consuming task, making it impractical to monitor all microorganisms that may be present in water (FAO, 2014). To solve this problem, the monitoring of biological contamination is conventionally carried out by the analysis of key microorganisms present in human and warm-blooded animal feces, (xii) total coliforms and *Escherichia coli* being the most-used parameters to assess the microbiological safety of drinking and surface water supplies (MEDEMA *et al.*, 2003; ZULKIFLI; RAHIM; LAU, 2018).

The monitoring of (xiii) algae and cyanobacteria is also important, since in many aquatic ecosystems, including drinking water supplies, there is a proliferation of these microorganisms called Harmful Algal Blooms (HAB) (BERKMAN; CANOVA, 2007). As emerging contaminants, the occurrence of HAB depends on several environmental conditions, such as the presence of nutrients and water temperature, and it is responsible for producing a variety of toxins released into water, which are dangerous for public health (PAL *et al.*, 2014; SCHAAP; ROHRLACK; BELLOUARD, 2012; WANG; WU, 2009).

Many of the parameters mentioned above make up the Water Quality Index (WQI), such as dissolved oxygen, total coliforms, pH, temperature, nitrogen, phosphorus, and turbidity (UDDIN; NASH; OLBERT, 2021). The WQI appeared in 1960 (Horton Index), being a simple and concise tool that allows the expression of the quality of water bodies and their derivations, such as for recreation, irrigation, and public supply, for example (KACHROUD *et al.*, 2019; LUMB; SHARMA; BIBEAULT, 2011). Nowadays, there are different numbers of models developed by different international organizations and used for WQI calculation, such as the

National Sanitation Foundation Water Quality Index (NSFWQI) and the Weighted Arithmetic Water Quality Index (WAWQI), for example (TYAGI *et al.*, 2020).

3.3 Development of Technologies for Water Quality Monitoring

The main technologies under development are based on colorimetric techniques or electrochemical sensors to analyze drinking water, rivers, lakes, and salt water (ALBERTI *et al.*, 2020; GEETHA; GOUTHAMI, 2016; RAINBOW *et al.*, 2020). However, as will be presented later, there are also technologies and methodologies capable of simplifying and improving existing water monitoring techniques, reducing costs, integrating them with the IoT, and accelerating data acquisition, such as the use of automatic samplers and autonomous analyzers.

According to Alberti *et al.* (2020), with the progress of nanotechnology and materials science, various sensors and biosensors based on nanomaterials, such as nanoparticles (NPs), quantum dots (QDs), carbon nanotubes and nanofibers (CNTs/CNFs), nanowires, and graphene, for example, were developed for monitoring the environment. Figure 3.1 shows the evolution of the number of publications per year in research related to the topic, considering the terms water quality, low-cost, *in situ*, real-time, online, and portable. It is possible to identify a significant growth in this topic since 2012, with about 641 works published in 2021.

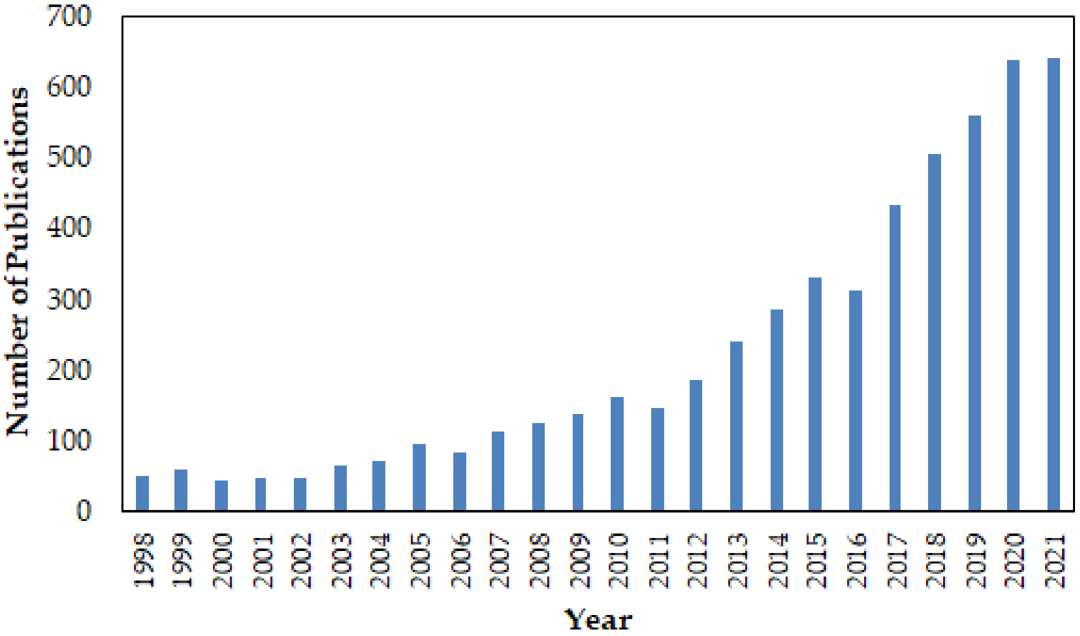

Figure 3.1 - Evolution of the number of studies published per year related to the topic.

3.3.1 Technologies for physical monitoring of water quality

3.3.1.1 Color

The color of water refers to the reflection of light in tiny particles of organic or mineral origin, being an old indicator of water quality, even before technological development and the emergence of environmental sensors. However, when technology became part of our society's configuration, there was research directed toward water color measurements, such as Edwards (1998), for example, who developed a sensor to measure the color and turbidity of natural waters using a four-beam intensity compensation technique for robust measurement. This prototype was operated in a water treatment plant, and at the time, it was considered very visionary research. The development of new technologies for color measurement will be described below, as well as presented in Table 3.1.

With the evolution of optical physics, studies such as Murphy *et al.* (2015) reported a low-cost optical sensor for water monitoring, in which the sensor is based on a multi-wavelength light source with two photodiode detectors capable of measuring the transmission and lateral scattering of light at the detector head, estimating the parameters of color and turbidity. The tests were carried out in the laboratory, but the researchers' intention is to test the sensor in the future as a real-time water pollution monitoring system.

Given the importance of understanding the variation of color with other water quality parameters, Yang (2014) developed a multisensory system for measuring water quality parameters (temperature, dissolved oxygen content, pH value, ammonia nitrogen, and color) for fish farming through algorithmically optimized sensors, in which the measurement of color parameters in the water is sent in real-time via the ZigBee communication standard (HAQUE *et al.*, 2021). Further, Saravanan *et al.* (2018) also described a real-time IoT-based water quality monitoring system, which includes color as one of the parameters to be monitored in situ. In India, the real-time monitoring of water quality was integrated through an innovative alternative, as reported by George *et al.* (2021), who described the initiative as a network of citizen scientists to monitor the color of water through Mini Secchi Disks, with Forel–Ule color scale stickers. This technique utilized a mobile app called "TurbAqua" to facilitate near real-time data transmission.

Table 3.1 - Summary of studies that present new alternative technologies to monitoring the Color parameter in water.

Author(s)	Type	Description	Research Findings
Murphy *et al.* (2015)	Optical	Developed a low-cost Optical Colorimetric Sensor (OCS), equipped with telecommunication to assess the transmission of light in water.	The results show strong linear correlations between the signal response and the studied parameters.
Yang (2014)		Introduced a multi-sensory system to monitor water quality parameters in fish ponds, with Zigbee wireless interface communication.	The system was able to collect water quality parameters and transmit them to the central station host computer, being a tool for fishing pond production management.
Saravanan *et al.* (2018)		Proposed a low-cost system, called Supervisory Control and Data Acquisition (SCADA), to monitor various water quality parameters with remote communication (using a GSM module).	The device was able to measure the selected parameters in drinking water (including color) in real-time and with good accuracy.
George *et al.* (2021)		Developed Mini Secchi Disks, with Forel–Ule color scale stickers used to measure water color and clarity, and a mobile app, called TurbAqua, was developed to facilitate near real-time data transmission.	The study presents a low-cost method for monitoring water quality on a voluntary basis, where the data can be used to validate satellite water quality products and be a tool for decision-makers to improve water issues.

3.3.1.2 Temperature

As with pH sensors, temperature sensors are present in most multi-parametric sensors. This is due, on the one hand, to the importance of temperature in relation to water quality; since several processes of other parameters occur as a function of temperature (e.g., biological activity, pH, dissolved oxygen, and conductivity), and, on the other hand, its easy monitoring, since there is a close linear relationship between temperature and resistivity, or electromotive force (MARTÍNEZ-MÁÑEZ *et al.*, 2005; QIN *et al.*, 2015; ZHOU, Bo *et al.*, 2017).

The measurement of water temperature can be performed by different methods, such as the thermal expansion of a material, thermoelectric processes, electrical resistance, semiconductors, optical fiber, and capacitance (CHILDS; GREENWOOD; LONG, 2000). However, the most common low-cost temperature measurement process is the use of thermoelectric devices and/or resistive sensors. These techniques are mainly used for their accuracy, low cost for the operating temperature range required for water monitoring, robustness, and simplicity (WU *et al.*, 2020). As most sensors and technologies presented in this review show the temperature measurement combined with some technique, only a few articles reported in the literature will be described in order to present the different techniques applied in the delimitation of this article (real-time, *in situ,* and low cost), as described in Table 3.2 also.

The most-used method for measuring temperature is the resistive method. This is not only due to the ease of development of the sensors but also because thermoelectric sensors (specifically, thermocouples) often use resistive sensors to determine the standard temperature required for this technique (CHILDS; GREENWOOD; LONG, 2000). Alam, Clyne, and Deen (2021) used sensors based on the Wheatstone bridge configuration to obtain a high sensitivity temperature measurement with low variability between 0 and 50 °C. Two of the four bridge terminals were produced with P-type Silicon Wafers, with a high Temperature Coefficient Resistance (TCR)—the calculation of a relative change of resistance per degree of temperature change—and the other two were produced with polystyrene sulfonate (PEDOT:PSS), with negative TCR values. Alam *et al.* (2020) developed a sensor using the same principles (Wheatstone bridges); however, it used two separate layers of a glass substrate using a bulk silicon wafer, poly(3,4-ethylenedioxythiophene), and PEDOT:PSS. The authors also integrated the sensor into an Arduino platform with an Android systems interface application.

Still related to resistive sensors, Wu *et al.* (2020) developed a sensor for temperature measurement using a platinum (Pt) layer, since this material is a good conductor and has good characteristics for temperature measurement. Finally, another option for resistive temperature sensor measurement was presented by Simic *et al.* (2017), using a low-cost and commercially available sensor (LM35). They performed a calibration of the device in the laboratory and obtained an accuracy of ±0.25 °C. Srivastava, Vaddadi, and Sadistap (2018), aiming at a quick response of the temperature sensor and a low cost, used a K-type thermocouple. A K-type thermocouple is a thermocouple (a device that converts thermal energy into electrical energy) that uses a non-magnetic positive terminal (usually Chromel) and a magnetic negative terminal (usually Alumel) and performs the measurement based on the output voltage.

Finally, Huang (2014) and Huang *et al.* (2013) used optical fiber to measure the temperature. Despite being a method with a high cost, this technique is usually applied to temperature when the optical fiber is also used to measure other parameters. As the parameters monitored by the authors have high temperature sensitivity, two insulated fiber optic terminals were used. Thus, through the variation of the different central wavelengths, it was possible to find a linear relationship with the temperature, therefore calibrating the device.

Table 3.2 - Summary of studies that present new alternative technologies to monitoring the Temperature parameter in water.

Author(s)	**Type**	**Description**	**Research Findings**
Alam, Clyne and Deen (2021)	Electrical	Developed a temperature sensor fabricated with p-type Si and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) film in a Wheatstone bridge configuration.	The results show that the sensor was able to measure temperature between 0 and 50 °C with high sensitivity and low variability.
Alam *et al.* (2020)		Presented a sensor-based using poly(3,4-ethylenedioxythiophene) and PEDOT:PSS to measure temperature in water.	The experiments present an accuracy above 85% for temperature sensor measurement.
Wu *et al.* (2020)		Developed a platinum (Pt)-based sensor for temperature measurement integrated into a micro-electro-mechanical system (MEMS).	The Pt thermistor with a three-wire orthogonal structure has a temperature response of 5.95 Ω/°C.
Simic *et al.* (2017)		Used a commercial sensor (LM35) to measure temperature in water.	The results show an accuracy of ±0.25 °C.
Srivastava, Vaddadi and Sadistap (2018)		Presented a K-type thermocouple sensor as a low-cost way to measure temperature integrated with a smartphone.	The system presents itself as a low-cost tool for monitoring water quality parameters in several urban locations.
Huang (2014) Huang *et al.* (2013)	Optical	A temperature sensor was developed using long-period fiber grating (LPFG).	The sensor can effectively monitor the temperature with a maximum difference of ±1 mm for water level, ±0.005 for refractive index, and 1 °C for temperature.

3.3.1.3 Turbidity

The turbidity of water is a parameter that indicates the degree of interference that a light beam encounters when crossing it, mainly because of the presence of suspended solids such as inorganic particles and organic debris, which can give a murky appearance to that water (VON SPERLING, 2014). Because of this, turbidity is a fundamental parameter to assess water quality, being able to identify whether the water is fit for consumption and, consequently, prevent waterborne diseases (AZMAN *et al.*, 2017).

Given the importance of turbidity, there are several turbidity sensors, commercially available, that can be integrated into water quality monitoring systems, as used and described in much research, to develop IoT-based online monitoring combined with other water quality parameters. Some examples of these studies are presented by Geetha and Gouthami (2016), Lambrou *et al.* (2014), Samijayani *et al.* (2018), and Chowdury *et al.* (2019). In addition, the following works present the development of new technologies applied to the monitoring of water turbidity, as shown in Table 3.3 also.

With the intention of optimizing, and reducing the costs associated with detecting turbidity, some recent research, such as Azman *et al.* (2017), has developed low-cost technology based on a nephelometric turbidity sensor for the continuous monitoring of water quality. According to the authors, the electronic sensor's operation is based on the intensity of scattered light in relation to light scattering in solids and liquids, using LED (Light Emitting Diode) as a transmitter, LDR (Light Dependent Resistor) as a receiver, and an RS232 module for communication between sensor and computer. Arifin *et al.* (2017) researched the development of a sensor for water turbidity measurement using an infrared LED, a polymer optical fiber, and a photodetector as main materials, in which the experiments showed promising sensitivity results with 0.046 μW/NTU and 0.022 NTU resolution.

Wang *et al.* (2018) also worked on a low-cost turbidity sensor and online water quality monitoring project, using an 850 nm infrared LED, dual orthogonal photodetectors, and, for communication, a custom IoT platform. The research showed that the device was able to measure the turbidity parameter with accuracy and robustness comparable to commercial sensors. Rahman *et al.* (2019) also evaluated the performance of an LED-based sensor for water turbidity measurement, observing the response to different colors of light sources used for water turbidity measurement and determining the best photodetector according to the voltage variation during the ON/OFF condition. The authors showed that the white LED gives the best performance with less than 10% systematic error in most measurements and followed by the UV LED, but both lights were suitable for water turbidity measurements ranging from 0 to 1000 NTU. Finally, Schima *et al.* (2019) developed an open-source optical sensor system for real-time and *in situ* turbidity monitoring, using detectors in the infrared range of the electromagnetic spectrum, which presented high accuracy when compared to standards methods in the laboratory. In addition, a Python script used on the Raspberry Pi was responsible for communication with the sensor, with which it was possible to show, even in the laboratory phase, that open-source technology can be a key to resilient and promising systems.

Table 3.3 - Summary of studies that present new alternative technologies to monitoring the Turbidity parameter in water.

Author(s)	**Type**	**Description**	**Research Findings**
Azman *et al.* (2017)	Optical	Presented a low-cost nephelometric turbidity sensor for the continuous monitoring of water quality and communication using the RS232 module.	The results show that the developed low-cost sensor presented results as a commercial turbidity sensor.
Arifin *et al.* (2017)		Developed a polymer optical fiber sensor for measuring turbidity in water.	The experiments provided promising results, with 0.046 µW/NTU and 0.022 NTU resolution for the sensor.
Wang *et al.* (2018)		Presented a low-cost and online monitoring sensor for turbidity using an infrared LED and photodetectors.	The device was able to measure turbidity with high accuracy as a commercial device.
Rahman *et al.* (2019)		Evaluated the performance of an LED-based sensor for measuring turbidity in water.	The use of visible and UV LED was able to measure turbidity between 0 and 1000 NTU.
Schima *et al.* (2019)		Developed an open-source optical system for real-time and turbidity monitoring using detectors in the infrared range of the electromagnetic spectrum.	The developed *in situ* sensor system showed a very high agreement with the results obtained using a laboratory photometer but with less methodological effort.

3.3.2 Technologies for chemical monitoring of water quality

3.3.2.1 Chlorine

Chlorine is one of the main disinfectants in public water supplies since its oxidizing characteristic can eliminate pathogenic microorganisms present in the water (DI BERNARDO; DANTAS, 2006). Therefore, detecting the concentration of free chlorine in the water is essential for monitoring and detecting the presence of contaminants. The consolidation of free chlorine sensors in water has taken place gradually, so that, even after many years have passed since the first attempts, many sensors are still under development and improvement. The development of new technologies for chlorine measurement will be described below, as well as presented in Table 3.4.

Cassidy *et al.* (2002), for example, studied a low-cost spectrophotometric sensor for chlorine detection with real-time data collection capability, aimed at increasing the acquisition time and improving the mechanical stability of chlorine sensors. The main components of this optical system were a xenon light source and a flow sample chamber. For communication, a DSP (Digital Signal Processor, EVM56303, produced by Motorola, Austin, TX, United States) board was used, which provides control signals and interacts with external devices. Overall, the device performed positively in the laboratory, but improvements are still pending for field applications and real-world scenarios.

Hall *et al.* (2007) focused on the detection of parameters online to indicate contamination in the distribution system, using commercial sensors, including free chlorine sensors. Altogether, three sensors with different chlorine detection principles (colorimetric, polarographic, and voltammetric) were tested with costs ranging from US$3,000 to US$10,000. The free chlorine was the best parameter, among the analyzed parameters, which responded to the presence of contaminants, but the authors point out that the technologies used were still in the consolidation phase and needed future improvements.

The quest to improve and reduce the costs of chlorine measurement was also presented by Gimenez-Gomez *et al.* (2015), who proposed a compact portable device to simultaneously measure five water quality parameters, including amperometric parameters, using microelectronic technology with low power consumption. The electronic system was tested, and the analytical signals were compared with commercial equipment. In addition, the authors claim that the communication between the computer and the portable device can be carried out using a wireless protocol, such as a Wi-Fi or a low-power ZigBee interface.

To facilitate and modernize the detection of contaminants, Cui *et al.* (2018) designed a Water Quality Monitoring System based on the STM32F103 microcontroller integrated system and the nRF24L01 wireless communication module. Various types of sensors were used to detect harmful components in the water, including the commercial residual chlorine sensor CLE3-DMT to detect free chlorine and monochloramine. The system’s proposal was to allow users to use their smartphones to carry out the real-time and online monitoring of various parameters in water quality. As the system has been successful in experiments, the authors believe that the device can be widely used with further research.

With the objective of facilitating portability, Yen *et al.* (2020) also broke new ground in chlorine monitoring and presented a chemo-resistive sensor based on a nanohybrid paper that can be used with smartphones to detect free chlorine ions. The sensor was manufactured using a simple, standardized coating process on graphene paper and PEDOT:PSS, whose results presented a linear range of 0.1–500 ppm for free chlorine measurement, with a detection limit of 0.18 ppm. The sensor was integrated into an electrical reading system, using Arduino Uno Rev3 SM, designed for miniaturization and wireless transmission to a smartphone by a Bluetooth module. The authors emphasize that the system is advantageous for its portability, low cost, and allowing real-time readings on a smartphone.

Furthermore, the innovation of chlorine sensors is ongoing, as shown by Alam *et al.* (2021), who developed a reusable, reagent-free sensor based on a thin gold film. The sensor presented high sensitivity, which is often a challenge for other commercial sensors, and due to simple fabrication and good detection performance, the proposed device enables mass production and future application in distant regions with low investment.

Table 3.4 - Summary of studies that present new alternative technologies to monitoring the Chlorine parameter in water.

Author(s)	**Type**	**Description**	**Research Findings**
Cassidy *et al.* (2002)	Optical	Developed a spectrophotometric device for chlorine detection in real-time using a xenon light source and a flow sample chamber.	Device performed well, but improvements are needed for field application.
Hall *et al.* (2007)	Optical and Electrical	Assessed electrical and optical sensors for chlorine detection in water.	The sensors were able to determine chlorine with good accuracy, but more analysis is needed to improve the devices.
Gimenez-Gomez *et al.* (2015)	Electrical	Presented a low-cost, compact portable multisensory electronic system to measure parameters of water quality.	The device presented good performance compared to commercial equipment, including free chlorine analysis.
Cui *et al.* (2018)		Described the development of a microcontroller system, with wireless communication, to measure water quality parameters.	The device allowed online communication and the commercial residual chlorine sensor used (free chlorine and monochloramine) showed good results.
Yen *et al.* (2020)		Developed a low-cost chemo-resistive sensor based on nanohybrid paper to measure free chlorine ions.	The developed sensor showed a linear range of 0.1−500 ppm, and the limit of detection was 0.18 ppm.
Alam *et al.* (2021)		Proposed a reusable, reagent-free sensor based on a thin gold film for chlorine measurement.	The sensor showed high-sensitivity accuracy, like commercial sensors.

3.3.2.2 Dissolved Oxygen (OD)

Dissolved oxygen (DO) is an important parameter in water quality and essential for aquatic life. According to Hou *et al.* (2020), when the DO concentration is less than 3 mg/L, there is an impact on the health of the fish, which can even lead to death by asphyxia. Furthermore, according to Hsu *et al.* (2014), a low concentration of DO can negatively affect a water system by facilitating the excessive growth of anaerobic bacteria. The DO concentration can also indicate various contaminants in water bodies, making DO one of the most important parameters for monitoring.

There are two types of DO sensors: electrochemical and optical. Electrochemical DO sensors are based on the electrical current produced to measure the concentration of dissolved oxygen in water and can be polarographic or galvanic (WEI *et al.*, 2019). Optical DO sensors, also called luminescent DO sensors (LDO), measure the concentration of dissolved oxygen in water according to the extinction of luminescence in the presence of oxygen, being able to measure the intensity or lifetime of luminescence, since oxygen affects both (WANG; ZHANG; LI, 2019).

Research to optimize DO measurement technologies is directed towards both electrochemical and optical sensors, however, DO electrochemical sensors are currently seen as more promising and are more widely used, mainly because they perform online *in situ* measurements (WEI *et al.*, 2019). The following works present the advances in technologies for DO measurement in water, as summarized in Table 3.5 also. Thus, *in situ* and online monitoring systems for aquaculture and other water uses have been using commercial dissolved oxygen sensors with electrochemical detection, as described by Liu (2016), Luo *et al.* (2015), Vijayakumar and Ramya (2015), and He (2021). Liu (2016) and He (2021) were able to monitor OD and other water quality parameters (turbidity, pH, temperature, and electrical conductivity) for fishery management based on the IoT concept. From the same approach, Vijayakumar and Ramya (2015) also were able to measure DO in water for aquaculture management using a Raspberry PI B+ core controller and an IoT module (USR WIFI 232). Finally, Luo *et al.* (2015) used a commercial YCS-2000 dissolved oxygen sensor and Zigbee and GPRS modules to monitor water quality parameters in real-time at a low cost, including DO.

The development of new technologies for DO sensors is ongoing, as presented, for example, by Lee *et al.* (2007), who studied a new DO sensor for *in situ* water analysis with a needle-like microelectrode arrangement, obtained by microfabrication technologies, which aims to integrate sensors with IC (Integrated Circuit) chips for online data acquisition. Thus, the authors obtain a rapid 15 s linear response in the 0–9 mg/L (0–21% O2) range. Penso *et al.* (2021) described the development, fabrication, and characterization of a low-cost, high-sensitivity optical sensor for DO detection with the potential for *in situ* measurement in a marine environment (between 0 and 5.5 mg/L) based on a PDMS membrane coated with a platinum octaethylporphyrin (PtOEP) film. Mahoney *et al.* (2019) also innovated the optimization of a multilayer optical-fluidic sensor device based on the measurement of fluorescence suppression in a ruthenium-based oxygen-sensitive dye to obtain increased sensitivity in the *in situ* detection of DO in water between 0 and 20 ppm.

Table 3.5 - Summary of studies that present new alternative technologies to monitoring the Dissolved Oxygen parameter in water.

Author(s)	**Type**	**Description**	**Research Findings**
Liu (2016)	Electrical	Designed an IoT system for monitoring the water quality environment for fishing in real-time.	The system was able to acquire DO, turbidity, pH, temperature, and electrical conductivity parameters in real-time, storing them in a database.
Luo *et al.* (2015)		Developed a real-time monitoring system to measure DO in water using a YCS-2000 sensor.	The system could fulfill the real-time remote monitoring of aquaculture water quality and had great practical significance in the reduction in labor intensity.
Vijayakumar and Ramya (2015)		Present a low-cost system for real-time water quality monitoring (including DO) using a Raspberry PI B+ model.	The device was presented as a low-cost and real-time monitoring system, being capable of processing, analyzing, sending, and viewing the data in the cloud.
He (2021)		Designed and developed an embedded aquaculture intelligent water quality monitoring system based on STM32F103VET6.	The system could provide technical support for the design and development of an aquaculture monitoring system.
Lee *et al.* (2007)		Designed a DO sensor for *in situ* water quality analysis using a needle-like microelectrode arrangement (MEA).	The DO MEA exhibited a rapid 15 s linear response in the 0–9 mg/L (0–21% O_2) range.
Penso *et al.* (2021)	Optical	Used a PDMS membrane coated with a platinum octaethylporphyrin (PtOEP) film to measure DO in water.	In a liquid medium, the sensor was able to measure DO in a range of 0–5.5 mg/L.

Mahoney *et al.* (2019)	Optimized a multilayer optical-fluidic sensor for DO *in situ* measurement.	The results showed a comparable sensitivity and sensing range (0–20 ppm) compared to previously developed miniaturized DO sensors.

3.3.2.3 Fluorine

Fluoride analysis is essential for human health, especially concerning dental health (FU *et al.*, 2014; MORADI *et al.*, 2020). For this reason, there are several techniques for the analysis of fluorine in water, such as the potentiometric and colorimetric methods, with the zirconium dye complex (SPADNS) method being the most used (APHA, 2005). According to WHO (2011), fluoride is usually determined by means of an ion-selective electrode, which makes it possible to measure the total amount of free and complex-bound fluoride dissolved in water. The description of new technologies for measuring fluoride in water will be described below, as well as presented in Table 3.6.

In the field of *in situ* and low-cost technologies development, Jadhav *et al.* (2017), using a fiber optic sensor based on Fiber Bragg Grating (FBG), were able to detect low concentrations of fluoride in water by observing the linear relationship between light transmitted by the fiber and the increase in fluoride concentration. In addition, the research observed a resolution of 0.03 nm for the spectrum light, which allows an accuracy of ±20 ppm for fluoride analysis in the range of 0.05–8 ppm. Additionally, Moradi *et al.* (2020) presented a technique that consists of coating a fiber optic terminal with aluminum by Direct Current Sputtering to reduce the sensor costs, making it possible to evaluate samples down to 5 ppm. As described by the authors, when the sensor is in contact with the fluorine in solution, a reaction occurs between the fluorine and the aluminum, removing the aluminum coating and causing a change in the light intensity proportional to the fluoride concentration.

Using other techniques to detect fluoride, Levin *et al.* (2016) and Mukherjee *et al.* (2020) also tested the development of a smartphone camera technique to measure fluoride in real-time, *in situ*, and at low cost. In the study by Levin *et al.* (2016), an optical device was connected to the smartphone camera by a suitable case to measure the fluoride concentration in water samples. In this way, using the smartphone camera, it was possible to assess the relationship between the red, green, and blue (RGB) colors of the water samples to estimate the fluoride concentration. The authors obtained consistent results in the laboratory, although it is important to highlight that the turbidity and chlorine may interfere with the results of the analysis. Mukherjee *et al.* (2020) used an external bicomponent sensing material, powered and operated by a smartphone, for fluorine analysis. The sensor used a mixture of near-cubic ceria−zirconia NC and XO dye that rapidly changes color from yellow to red based on interaction with fluorine. The authors also evaluated the device's accuracy against other laboratory equipment such as XPS and NMR spectroscopy, as well as testing the system for high concentrations of other anions also present in water. Thus, the results were similar to the laboratory methods and showed that the device has a good selectivity for fluorine, showing no influence of other anions in the analysis.

Table 3.6 - Summary of studies that present new alternative technologies to monitoring the Fluorine parameter in water.

Author(s)	Type	Description	Research Findings
Jadhav *et al.* (2017)	Optical	Used a fiber optic sensor based on Fiber Bragg Grating (FBG) to detect fluorine in water.	The sensor allowed fluorine detection with a good accuracy between 0.05 and 8 ppm.
Moradi *et al.* (2020)		A simple method for fluoride detection is presented. The sensor comprises a 35 nm aluminum coating on the distal end of a length of single-mode optical fiber.	The fabricated sensor measures fluoride concentration within the range of 0–5 mg/L.
Levin *et al.* (2016)		Determined fluorine in water using an optical device connected to a smartphone camera.	It was possible to measure fluorine in water by assessing RGB color, although the presence of other substances may interfere with the results.
Mukherjee *et al.* (2020)		Used external bicomponent sensing material, powered and operated by a smartphone, for fluorine analysis.	The results were similar to the laboratory methods and showed good selectivity for fluorine.

3.3.2.4 Metals

The pollution of the aquatic environment by heavy metals is a growing problem worldwide. There are several sources of heavy metals, many of them originating from human action, mostly domestic sewage, hospital waste, and industrial and mining activities, among others (MWITA, 2011; SIBAL; ESPINO, 2018). Since heavy metals cannot be biodegraded, they are continuously deposited, accumulated, and incorporated into water, sediment, and aquatic organisms (LINNIK; ZUBENKO, 2000). Within organisms, some heavy metals can exert a toxic and harmful effect and alter the functioning of the kidneys, liver, and nervous system, for example (HAMILTON *et al.*, 1998; PARTANEN *et al.*, 1991). However, it should be noted that many metals, such as iron, copper, zinc, and magnesium, are essential for living beings in low concentrations, but exert a toxic effect in high concentrations (VALKO; MORRIS; CRONIN, 2005).

According to Sibal and Espino (2018), the mainly lab-based techniques to measure metal in water are atomic absorption spectrometry (AAS), mass spectrometry (MS), inductively coupled plasma MS (ICP-MS), atomic emission spectrometry (AES), X-ray fluorescence (XRF), and optical techniques. For Ferrari *et al.* (2020), such techniques are characterized as being sophisticated and expensive and may require the use of pre-concentration and separation techniques for high-analysis performance. On the other hand, when it comes to *in situ* analysis, methods with electrochemical sensors can be considered more appropriate, mainly due to the small size of the equipment, easy installation, low cost, and simple handling (FERRARI *et al.*, 2020). Gumpu *et al.* (2015), for example, present techniques for measuring metallic ions, based on electrochemical biosensors for measuring arsenic (As), cadmium (Cd), mercury (Hg), lead (Ld), chromium (Cr), silver (Ag), zinc (Zn), and copper (Cu). The development of new technologies for measuring metals in water are presented below, as well as shown in Table 3.7.

In the development of portable optical systems for the determination of metals in water, Oliveira *et al.* (2017), Zhou *et al.* (2018), and Srivastava and Sharma (2021) presented simple, low-cost solutions for measuring lead, copper, hexavalent chromium, and iron. The portable spectrophotometry system developed by Oliveira *et al.* (2017), in Medium Density Fiberboard (MDF) material, using a DVD as a diffraction medium, and a smartphone device camera, was able to measure Fe^{2+} in a range of 0.5–15 mg/L, with a LOD of 0.02 and LOQ of 0.07 mg/L. Srivastava and Sharma (2021) also developed an ultra-compact and portable spectrophotometry system, which integrates with a smartphone device and a cloud database (IoT), for measuring iron and copper in drinking water. Zhou *et al.* (2018), using portable X-ray fluorescence (pXRF) equipment, were able to estimate the concentration of Pb and Cu directly in a lake, yielding results of 28 and 21 mg/L for Pb and Cu, respectively.

In the development of electrochemical sensors for metal determination, Wu *et al.* (2020), Alam *et al.* (2020), Wang *et al.* (2021), Yen and Lai (2020), and Li *et al.* (2021) were able to measure copper, lead, mercury, and zinc in an aqueous medium, with portable, low-cost electrochemical sensors that could be integrated with other electronic devices for *in situ* and real-time responses. Alam *et al.* (2020), from sensors made of multi-walled carbon nanotubes and β-cyclodextrin (MWCNT-βCD), were able to determine a concentration of Pb^{+2} in water between 5 and 100 mg/L, even in the presence of other metals, such as Cd^{2+}, Zn^{2+}, Cu^{2+}, Hg^{2+}, and Ni^{2+}. Wu *et al.* (2020) and Wang *et al.* (2021) used a sensor manufactured by MEMS (Micro-Electro-Mechanical System) technique to measure Cu^{+2} between 0.0 and 0.6 mg/L and 0.0–400 mg/L, respectively. Wu *et al.* (2020) observed an accuracy of 0.04 mg/L for the equipment, while Wang *et al.* (2021) observed that the sensor suffered no interference by the presence of other metals (such as Pb^{2+}, Zn^{2+}, and Mg^{2+} ions). Yen and Lai (2020), by the technology based on a metal-oxide-semiconductor microelectromechanical system (CMOS-MEMS), which can be operated in real-time and *in situ*, were able to detect Pb^{2+} between 0.01 and 100 mg/L with a detection limit of 0.005 mg/L. Finally, Li *et al.* (2021) developed a portable device, costing less than U$160.00, based on plastic pipetting equipment using a Disposable Electrode-Printed (DEP) chip, for the determination of Pb, Hg, Cu, and Zn at different concentrations. Furthermore, the experimental results demonstrated that the limits of detection for Pb, Hg, Cu, and Zn were 2.2 ng/mL, 2.5 ng/mL, 15.5 ng/mL, and 10 ng/mL, respectively, and the limits of quantification for them were 10 ng/mL, 25 ng/mL, 25 ng/mL, and 14 ng/mL, respectively.

Table 3.7 - Summary of studies that present new alternative technologies to monitoring the Metals parameter in water.

Author(s)	Type	Description	Research Findings
Oliveira *et al.* (2017)	Optical	Developed spectrophotometry using a DVD as a diffraction medium to measure iron in water.	The system was able to measure iron between 0.5 and 15.0 mg/L.
Zhou *et al.* (2018)		Used portable X-ray fluorescence (pXRF) equipment to estimate lead and copper in a lake.	The equipment was capable of determining the concentrations of heavy metals in polluted water, especially for heavily polluted water with relatively high concentrations.
Srivastava and Sharma (2021)		Developed ultra-compact portable spectrophotometry, integrated with a cloud database, to measure iron and copper in drinking water.	The spectrophotometer system provides an innovative chemo-electronic cost-effective system to measure heavy metal contamination present in water samples in real-time.
Wu *et al.* (2020)	Electrical	Used a sensor manufactured by MEMS (Micro-Electro-Mechanical System) technology to measure copper in water.	The sensor was able to detect copper between 0.0 and 0.6 mg/L, with an accuracy of 0.04 mg/L.

Wang *et al.* (2021)		The sensor suffers no interference from other metals and was able to measure copper between 0.0 and 400 mg/L.
Alam *et al.* (2020)	Developed a multi-walled carbon nanotubes and β-cyclodextrin (MWCNT-βCD) sensor to measure lead in water.	The sensor was able to detect lead in water between 5 and 100 mg/L.
Yen and Lai (2020)	Designed a metal-oxide-semiconductor microelectromechanical system (CMOS-MEMS) sensor to detect lead in water.	The sensor was able to detect lead in water between 0.01 and 100 mg/L.
Li *et al.* (LI *et al.*, 2021)	Used a Disposable Electrode-Printed (DEP) chip, integrated with a plastic pipette, to measure Pb, Hg, Cu, and Zn.	The device was able to measure the metals at different concentrations, which demonstrated that there existed a linear relationship between the peak current and the concentration.

3.3.2.5 Nitrogen

Nitrogen can be found in different sources, such as decomposed plants, human waste, animals, and chemical fertilizers (LAMBROU *et al.*, 2014). For nitrogen monitoring, several techniques can be applied, such as chromatography, electrochemistry, and spectroscopy methods (SOHAIL; ADELOJU, 2016). Chromatography is the most suitable method when there is organic matter in the samples, since this method does not suffer interference from other compounds; however, it is the most complex and expensive method of application, as it uses different techniques and specialized materials in the process (YI *et al.*, 2017). Spectroscopy can also suffer interference, but it is easier to apply than the other two methods, in addition to the advantage of obtaining results faster (OBROVSKI *et al.*, 2016). Monitoring through electrochemistry has great potential for low-cost applications, but it can be influenced by ions and organic matter present in the samples (OUNI; RAMAZANI; FARDOOD, 2019). The development of new technologies for nitrogen measurement will be described below, as well as presented in Table 3.8 also.

As it is an important parameter from a monitoring point of view, the development of low-cost sensors for the real-time and *in situ* detection of nitrogen has gained attention in the literature. Akhter *et al.* (2021a), for example, developed an electrochemical sensor using

Polydimethylsiloxane as a flexible substrate with multi-walled carbon nanotubes as a conductive material. Although graphene has better electrical properties, the mass production of this material is complex, which can change the repeatability of the developed sensor. In addition, the authors developed an IoT platform based on LoRa (Long Range) (WU; KHAN, 2019) to send the collected data in real-time, finding a relationship between temperature and resistivity for different concentrations of nitrate. When evaluating repeatability, the authors observed that the Relative Standard Deviation (RSD) was below 2% when comparing three different readings from the same sensor, and an RSD below 5% when compared to the other five sensors of the same manufacture. Finally, the values obtained by the developed sensor were compared with those obtained by the UV-vis spectrometry method to validate the results, obtaining a higher maximum concentration with a difference of 4.91% in relation to the standard method.

Obrovski *et al.* (2016) used a chemical fiber optic probe based on the HSV (Hue, Saturation, and Value) color model. The sensor is based on the principle that when water is exposed to light, certain wavelengths are transmitted while others are absorbed depending on the color of the evaluated sample. Then, the device uses three RGB LEDs and a TLS250 photodetector to detect the transmitted light. The device was compared to the UV-vis spectrometer, and it was found that nitrate was the only parameter with which it was possible to obtain a correlation with the concentration variation, the detection limit of this sensor being between 0 and 0.7 mg/L. In addition, the authors performed only laboratory evaluation; therefore, it is not possible to verify the performance of the device in real applications, nor evaluate the repeatability and durability of this sensor in field conditions.

Finally, Ingles, Louw, and Booysen (2021) developed a sensor that can be used with smartphones based on a laboratory photometer spectrum, however, with fewer components, more portability, and less expense. The device has four parts: the light source, the wavelength filter, a cuvette, and a scintillator. For the light source, the only one commercially available and capable of emitting light at the indicated wavelength was the CompactFiberlight D2. The wavelength filter was developed with quartz, which is a material that has a negligible absorbance at a wavelength of 205 nm: the ideal wavelength for nitrogen evaluation (DROLC; VRTOVŠEK, 2010; KARLSSON; KARLBERG; OLSSON, 1995). The cuvette was 3D printed in plastic with a 1 cm opening to isolate external light while allowing instrument light to pass through. With this device, the authors obtained a maximum deviation of 27% compared to the analysis performed by the photometer spectrum, with the sensor operating range between 1 and 10 mg/L for nitrate.

Table 3.8 - Summary of studies that present new alternative technologies to monitoring the Nitrogen parameter in water.

Author(s)	Type	Description	Research Findings
Akhter *et al.* (2021a)	Electrical	Developed an electrochemical sensor using Polydimethylsiloxane as a flexible substrate with multi-walled carbon nanotubes nitrate in water.	The sensor had a difference of 4.91% in relation to the standard method for measuring nitrate.
Obrovski *et al.* (2016)	Optical	Used a chemical fiber optic probe based on the HSV model to detect nitrate in water.	The detection limit of this sensor was between 0 and 0.7 mg/L.
Ingles, Louw and Booysen (2021)		Presented a low-cost, portable sensor that can be used with a smartphone to measure nitrate in water.	The sensor operating range was between 1 and 10 mg/L for nitrate, with a 27% deviation compared to commercial equipment.

3.3.2.6 pH

As pH is an essential parameter to ensure good water quality, this parameter is widely monitored and found in practically all multiparameter equipment. Different techniques can be applied to measure the pH in a water sample, namely visual analysis, photometric and potentiometric methods (SILVA *et al.*, 2020; DUTTA; SARMA; NATH, 2015). While the visual method uses color change as a pH indicator using specific materials (litmus paper), this method does not have good accuracy and only provides approximate pH values. The potentiometric method is based on the Nernst equation, which measures the change in hydrogen ion concentration due to chemical reactions. The photometric method is based on spectrophotometry, which provides information about the change in wavelength absorption based on the pH change of the samples. The following research presents the development of alternative technologies for measuring pH in water, as described in Table 3.9 also.

Alam, Clyne, and Deen (2021), Wu *et al.* (2020), and Simic *et al.* (2017) developed pH sensors using the potentiometric method in different ways. Alam, Clyne, and Deen (2021) used a special ink made of palladium (Pd) with the silver/silver-chloride electrode (Ag/AgCl) as a reference in a polyimide substrate. Wu *et al.* (2020) used the ruthenium (Ru) redox to measure pH; compared to Pd, Ru has low contamination potential, easy preparation, and good chemical resistance. The authors were able to measure pH between 4.01 and 10.87 with an accuracy of

1.02%. Finally, Simic *et al.* (2017) used titanium dioxide (TiO_2) as the main film in the pH sensor, which was connected to an integrated circuit (using an AD5933 module) for online communication.

In the study by Hossain *et al.* (2015), the authors used a multi-parametric sensor to assess water quality. For pH, a Photo-Induced Electron Transfer (PET) method was used with 4-aminonapthlimide as a dye for analysis. Regarding further photometric methods, Dutta, Sarma, and Nath (2015) sought to perform analyses in colorless liquids, that is, without the use of dyes for analysis. The sensor uses the capture of the image spectrum and, through an optical preparation and consequent conversion into intensity and wavelength distribution, performs the pH measurement. Finally, Silva *et al.* (2020) used a device based on the measurement of colorimetry using a smartphone camera and a microfluidic paper-based device (IPAD) to measure the pH of the samples. For the method, 3D printer supports were developed to ensure the stability of the device, in which the device was able to determine pH in the 4.7–12 range.

Table 3.9 - Summary of studies that present new alternative technologies to monitoring the pH parameter in water.

Author(s)	**Type**	**Description**	**Research Findings**
Alam, Clyne and Deen (2021)	Electrical	Used a special ink made of palladium (Pd) with a silver/silver-chloride electrode (Ag/AgCl) to measure pH in water.	The sensor was able to measure pH in real-time with high accuracy.
Wu *et al.* (2020)		Used the Ruthenium (Ru) redox to measure pH in water.	The sensor has a sensitivity of −57.34 mV/pH in pH detection and was able to measure pH in a 4.01–10.87 range.
Simic *et al.* (2017)		Used Titanium Dioxide (TiO_2) as the main film in the pH sensor.	The design ensured reliable *in situ* measurement.
Hossain *et al.* (2015)	Optical	A Photo-Induced Electron Transfer (PET) method was used with 4-aminonapthlimide (integrated into a smartphone) to measure the pH parameter in water.	The application of a novel smartphone-based pH meter showed a rapid assessment and mapping of the quality of drinking water.
Dutta, Sarma amd Nath (2015)		Used a simple laboratory optical components and the camera of a smartphone as a low-cost, portable device to measure pH in water.	The sensor presented reliable data for pH measurement.
Silva *et al.* (2020)		Developed a smartphone camera and a microfluidic paper-based device (IPAD) to measure pH.	The device was able to measure pH between 4.7 and 12.

3.3.2.7 Phosphorus

Phosphorus is an essential nutrient used by plants and microorganisms, mainly for growth and energy transport, and it is a limiting element for primary production in terrestrial and aquatic ecosystems (ELSER, 2012; XIE *et al.*, 2013). In the aquatic environment, phosphorus usually occurs in dissolved forms, such as orthophosphates, and organic phosphorus (KOROSTYNSKA; MASON; AL-SHAMMA'A, 2012). However, high concentrations of phosphorus in rivers and lakes can favor the proliferation of plankton and algae, accelerating eutrophication (MAINSTONE; PARR, 2002).

The determination of phosphorus in water depends on the type to be analyzed, such as dissolved, precipitated, associated, organic, or inorganic (JARVIE; WITHERS; NEAL, 2002), with the main methodologies used being based on electrochemical sensors, such as potentiometry, voltammetry, and amperometry techniques (BERCHMANS; ISSA; SINGH, 2012), and in optical sensors (KALKHAJEH *et al.*, 2019). Although the spectrophotometry technique is one of the most widely used for the detection of phosphorus (WORSFOLD; MCKELVIE; MONBET, 2016), according to Berchmans, Issa, and Singh (2012), the use of potentiometric systems offers a simple and low-cost instrumentation for monitoring phosphorus in the environment, clinical analysis, and remote sensing. However, electrochemical sensors can be influenced by several factors, such as temperature fluctuation and the presence of other substances (such as metals), hindering the results (CHEN *et al.*, 2019). The following research presents the development of new technologies for measuring phosphorus in water, as summarized in Table 3.10.

Based on the colorimetry technique, Lin *et al.* (2018) developed a sensor for the automatic monitoring of phosphate *in situ*, and at a low cost (US$200), through the use of an automatic collector of water samples, called "Fish-Bite", which contains multiple capsules of reagents for analysis. The equipment was developed to be used to monitor water intended for agriculture and is capable of measuring phosphate concentrations up to 1.00 mg/L, with a lower detection limit of 0.01 mg/L. Akhter *et al.* (2021b) were also able to determine phosphate in water for agricultural use, with concentrations between 0.01 and 40 mg/L and with 95% accuracy. The measurement technique is based on an electrochemical sensor, produced from multi-walled carbon nanotubes (MWCNTs) and Polydimethylsiloxane (PDMS), with the possibility of integration with smart devices (Internet of Things) for continuous monitoring.

Table 3.10 - Summary of studies that present new alternative technologies to monitoring the Phosphorus parameter in water.

Author(s)	Type	Description	Research Findings
Lin *et al.* (2018)	Optical	Developed an automatic collector of water samples, called “Fish-Bite” to measure phosphorus in water.	The device was able to detect phosphorus up to 1.00 mg/L, with a lower detection limit of 0.01 mg/L.
Akhter *et al.* (2021b)	Electrical	Used multi-walled carbon nanotubes (MWCNTs) and Polydimethylsiloxane (PDMS) to detect phosphorus in water for agricultural use.	The sensor was able to measure phosphorus between 0.01 and 40 mg/L, with 95% accuracy.

3.3.2.8 Oxidation Reduction Potential (ORP)

The Oxidation Reduction Potential (ORP) is a measure of the molecular charge corresponding to the oxidation or reduction capacity of a substance and is an important indicator of water quality, capable of contributing to the understanding of variations in other parameters. For this reason, the ORP sensors are commonly coupled in multiparameter systems (COPELAND; LYTLE, 2014; SUSLOW, 2004). The development of new technologies to measure ORP in water are presented below, as well as in Table 3.11.

In developing new techniques for monitoring ORP, Qasem *et al.* (2019) built a remotely operated underwater vehicle containing ORP sensors, and sensors for three more parameters (electrical conductivity, dissolved oxygen, and temperature), to identify oil spills in ocean waters using Raspberry Pi 3 connected to the internet via Wi-Fi. Dejus *et al.* (2018) also used a system containing online ORP sensors and five more parameters to detect drinking water contamination events. For water quality control, Helmi, Hafiz, and Rizam (2014) developed a surface water quality monitoring buoy with ORP, pH, and temperature sensors, also remotely controlled by an internet-connected computer that sends instructions to the Intel Atom N2600 board, which, in addition to the quality data, sends the physical location coordinates. Subsequently, Siyang and Kerdcharoen (2016) innovated with a small, unmanned vehicle coupling an Arduino Uno with standard Wi-Fi, where ORP, Electrical Conductivity, Dissolved Oxygen, pH, and Temperature sensors were connected, whereupon the acquisition and transmission of data took place by XBee wireless communication directed to the control station and then to the database server on the internet. Similar system designs were studied by Khatri *et al.* (2021) and Ilie *et al.* (2017), who developed a low-cost drinking water quality monitoring station, with ORP as a parameter, for online and real-time monitoring using commercial sensors.

The systems described above refer to projects in the laboratory phase, not consolidated in the market, although the ORP sensors used are commercial probes for embedded systems. In contrast, due to the lack of low-cost, *in situ* devices for ORP measurement, Lee *et al.* (2006) studied the fabrication of microelectrode sensor arrays (MEAs) for *in situ* ORP measurements using a chemical etching technique, where MEAs exhibited a substantially faster response time in the order of seconds rather than minutes, as compared to the commercial milli-electrodes. Jang *et al.* (2005) also developed arrays of microelectrode sensors for ORP measurements, in an easier and more robust method, which presented readings equal to or more accurate than conventional ones. Finally, Lin *et al.* (2017) were able to measure ORP, as well as pH, chloride, and conductivity, using microfabricated platinum electrodes deposited on a glass substrate as a sensor. The authors described that the sensor was able to measure ORP from 150 to 800 mV and, due to its simple fabrication, the sensor costs about US$0.10.

Table 3.11 - Summary of studies that present new alternative technologies to monitoring the Oxidation Reduction Potential (ORP) parameter in water.

Author(s)	**Type**	**Description**	**Research Findings**
Qasem *et al.* (2019)	Electrical	Built a remotely operated underwater vehicle with an ORP sensor.	The proposed hardware and software designs can monitor ORP in water.
Dejus *et al.* (2018)		Used a commercial ORP sensor to monitor water quality.	Mahalanobis distance method with DW quality sensors has a good potential to be applied in warning systems (EWS).
Helmi, Hafiz and Rizam (2014)		Developed a mobile buoy for water quality assessment, with the ORP parameter, operated remotely.	The device was able to measure the ORP parameter and transmit the water quality reading data in real-time.
Siyang and Kerdcharoen (2016)		Described the development of a low-cost unmanned surface vehicle to monitor water quality.	The system has the capability to perform water quality assessment (including the ORP parameter) missions on inland water resources.
Khatri *et al.* (2021)		Presented the development of a sustainable water quality monitoring system, with ORP as a parameter.	The developed system can be a suitable replacement for traditional water quality monitoring techniques, with which the ORP measure uncertainty was equal to 0.029.

Ilie *et al.* (2017)		Developed a Smart Water kit connected to the internet for real-time water quality monitoring.	The developed system can be used in many environmental conditions, to give an idea about the state of the water in real-time.
Lee *et al.* (2006)		Developed a microelectrode array for the *in situ* sensing of ORP.	The sensor developed exhibited a very fast response time and proved to be extraordinarily stable.
Jang *et al.* (2005)			The sensor performance was equal to or more accurate than the commercial sensors.
Lin *et al.* (2017)		Used micro-fabricated platinum electrodes to measure ORP in water.	The sensor was able to measure ORP from 150 to 800 mV.

3.3.3 Technologies for biological monitoring of water quality

3.3.3.1 Algae and cyanobacteria

The determination of algae and cyanobacteria in water can be conducted through numerous techniques, such as cell counting with the aid of an optical microscope or the analysis of indicator substances, such as chlorophylls (BOWE, 2002). Chlorophyll analysis is widespread because it is an active optical pigment capable of being determined by spectrophotometry, fluorimetry, and High-Performance Liquid Chromatography (HPLC) (BERKMAN; CANOVA, 2007; ZHANG; ZHANG, 2014). In addition, the analysis of such organisms can also be done remotely by observing different bands of satellite images (ZHANG; ZHANG, 2014) and by means of cytometry (LINKLATER; ÖRMECI, 2013), which allows counting the number of cells. The following works present the development of new technologies for Algae and Cyanobacteria in water quality monitoring, as also summarized in Table 3.12.

In algae analysis, several studies have sought to use new sensors and low-cost techniques to obtain *in situ* data with good accuracy. Lee *et al.* (2019) developed a portable, 3D-printed device that uses a smartphone and utilizes opto-electrowetting (in the acronym OEW, being a method of manipulating liquid droplets used in microfluidic applications) for the determination of algae in freshwater (*C. reinhardtii* and *M. aeruginosa*) and seawater (*Amphiprora sp.* and *C. closterium*). Saboe *et al.* (2021) studied the determination of algae using a microbiological potentiometric sensor, through the analysis of electrical signal patterns, as a means of diagnosing changes in water quality and the presence of algae in the aquatic environment. For this, the authors made use of machine learning to differentiate the sensor response under different conditions and in the presence of other contaminants, resulting in a linear relationship between the microbiological concentration of algae and the potentiometric signal of the sensor.

Using optical sensors, Lee *et al.* (2017) developed a device connected to a biological optical sensor and an ARM Cortex-M3 processor, with a wireless connection, for the diagnosis of algae growth in a water treatment plant, whose control and monitoring could be performed remotely. Izydorczyk *et al.* (2009), in turn, were able to monitor cyanobacteria in a water supply reservoir, through chlorophyll analysis using a system called Algae Online Analyzer (AOA). The AOA device is composed of five light-emitting diodes (450, 525, 570, 590, and 610 nm), which, through the fluorescence technique, allow the determination and differentiation of algae from the *Chlorophyceae*, *Bacillariophyceae*, *Cyanophyceae*, and *Cryptophyceae* classes.

In the use of multiparametric probes, Zamydi *et al.* (2012) detected cyanobacteria (*Phycocyanin* and *Chlorophylla*) in the Yamaska River Reservoir and Lake Champlain Bay, Canada, using the fluorescence technique and the YSI 6600 V2–4 probe. Beckler *et al.* (2019) were also able to monitor and map the algae bloom on the coast in an automated way using a fluorometer sensor (Cyclops Integrator/C3) coupled to a remotely operated boat (Navocean Nav2 ASV). Naughton *et al.* (2020) monitored microalgae on an aquaculture farm for 10 months using the AlgaeTorch® probe, in the Republic of Ireland, as a tool for monitoring seasonal changes in cultivation and for decision-making by producers.

Finally, Yamahara *et al.* (2015) presented the integration of an automatic sampler that, through molecular analytical techniques, allows the *in situ* detection of fecal indicators (fecal coliforms) and harmful algae in surface waters. The equipment, called an Environmental Sampling Processor (ESP), is capable of measuring and issuing reports with a certain frequency and uses the qPCR (real-time Polymerase Chain Reaction) technique in chemical-biological analysis.

Table 3.12 - Summary of studies that present new alternative technologies to monitoring the Algae and Cyanobacteria parameter in water.

Author(s)	**Type**	**Description**	**Research Findings**
Lee *et al.* (2019)	Electrical	Developed a portable, 3D-printed device with a smartphone and opto-electrowetting to measure algae in water.	The device offers a highly portable, user-friendly, low-cost tool that enables simple on-chip sample preparation and the detection of viable algae.

Saboe *et al.* (2021)	Optical	Used a microbiological potentiometric sensor to measure algae in water by electrical signal patterns.	The very low NRMSE <3% for algal and chlorophyll concentrations demonstrated that these and similar biological parameters could be monitored in natural waters with extremely high precision.
Lee *et al.* (2017)		Developed a device connected to a biological optical sensor for the diagnosis of algae growth in a water treatment plant.	The proposed system emulated a real-time water treatment plant for algae monitoring.
Izydorczyk *et al.* (2009)		Presented an Algae Online Analyzer (AOA) system to monitor algae in water.	A positive correlation between cyanobacteria, as determined by conventional methods, was found ($p < 0.05$).
Zamydi *et al.* (2012)		Used multi-parametric commercial probes to detect cyanobacteria using the fluorescence technique.	The analysis revealed significant correlations between the extracted Chl-a, extracted PC, and cyanobacterial biovolume and in vivo fluorescence parameters measured.
Beckler *et al.* (2019)			The results demonstrated the potential for mapping unispecies of harmful algae using a Navocean autonomous sail vehicle (Nav2).
Naughton *et al.* (2020)			The sensor allowed algae monitoring over 10 months, data from which can be used as a way to improve reservoir management.
Yamahara *et al.* (2015)	Polymerase Chain Reaction	Designed an automatic sampler to detect harmful algae and fecal indicators in water using the qPCR technique.	The device showed good performance, with qPCR efficiencies ranging from 86% to 105%.

3.3.3.2 Total coliforms and *Escherichia coli*

According to the APHA (2005), the main methods for rapid coliform detection in water are based on radiometric, glutamate decarboxylase, electrochemical, gas chromatographic, colorimetric, and potentiometric techniques. The Membrane Filter Coliform Test, for example, is a method for coliform analysis that can detect 50–200 CFU in water samples in 24 h with the aid of a microscope (ALLEY, 2007). The analysis of total coliforms and *E. coli* can also be done by the commercial tests Colitag^{TM} and Colilert$^{®}$ (SZCZERBIŃSKA; GAŁCZYŃSKA, 2015) and by the Multiple Fermentation Technique (USEPA, 2002) with high performance and results between 24 and 48 h. The following research presents the development of alternative technologies for monitoring total coliforms and *E. coli* in water quality, as also shown in Table 3.13.

In the development of new methodologies for the detection of pathogens in water, Simões and Dong (2018) were able to perform the continuous and real-time monitoring of *E. coli* and *Legionella* in drinking water distribution networks using a fluorescent optical sensor fluid (Hamamatsu H17023), at a low cost, and whose equipment had a detection limit equal to 1.4 × 103 CFU/mL. Bedell *et al.* (2020), in turn, used the Tryptophan-Like Fluorescent (TLF) technique, with deep-ultraviolet light-emitting diodes (UV-LEDs), sensitive semiconductor photodiodes, and photomultipliers to detect the presence of *E. coli* with a sensitivity of 4 CFU/mL.

Based on the use of smartphones, Gunda *et al.* (2014) and Patil *et al.* (2019) were able to detect the presence of total coliforms and *E. coli* in water. The device developed by Gunda *et al.* (2014), called the Mobile Water Kit (MWK), was able to detect such microorganisms in 30 min, using chemical reagents such as colorimetric/fluorescent sensors and a smartphone, which captures and analyzes the images obtained. The system developed by Patil *et al.* (2019) is operated by a smartphone that captures images of a water sample contained in a chamber and, through an algorithm, analyzes the images to identify the growth of bacteria through the increase in turbidity and/or changes in the color. The system can issue an alert when contamination is detected.

Tok *et al.* (2019) and Huynh, Hausot, and Angelescu (2016) discussed *in situ* devices for sampling and the automatic testing of total coliforms and *E. coli*, with a low cost and high efficiency. The device developed by Tok *et al.* (2019) is operated by a Raspberry Pi microcontroller and a camera that measures water absorption and fluorescence, through a blue LED and UV light, in 100 mL samples each 24 h. Huynh, Hausot, and Angelescu (2016) presented the Autonomous Microbiological Alert Sensor (AMAS), whose bacterial presence is monitored using multispectral measurements (colorimetry and fluorimetry), and the data are transmitted wirelessly to a remote server.

Finally, Grossi *et al.* (2013) and Zhang *et al.* (2018) were able to detect bacterial growth (which may indicate the presence of *E. coli* and total coliforms) using electrical sensors. The system developed by Grossi *et al.* (2013) is composed of two electronic boards—one to measure the electrical parameters and the other to control the temperature of the sample. It can be used for *in situ* analysis on different types of samples, with results between 3 and 12 h. On the other hand, Zhang *et al.* (2018) used a capacitively coupled multichannel contactless conductivity detector (C4D) to detect bacterial growth in an apparent normalized relationship between conductivity and incubation time.

Table 3.13 - Summary of studies that present new alternative technologies to monitoring the Total coliforms and *Escherichia coli* parameter in water.

Author(s)	**Type**	**Description**	**Research Findings**
Simões and Dong (2018)	Optical	Used a fluorescent optical sensor to monitor *E. coli* and *Legionella* in drinking water.	The equipment had a good performance, with a detection limit equal to 1.4 × 103 CFU/mL.
Bedell *et al.* (2020)		Used a Tryptophan-Like Fluorescent (TLF) technique to monitor *E. coli* in drinking water.	The results showed a close correlation between TLF and *E. coli* in model waters and proof of principle with a sensitivity of 4 CFU/mL for *E. coli*.
Gunda *et al.* (2014)		Developed the Mobile Water Kit (MWK) to detect microorganisms in water based on the colorimetric method.	The device was able to detect the total coliform and *E. coli* bacteria in water samples within 30 min or less.
Patil *et al.* (2019)		Presented a quick screening and alerting of coliform and *E. coli* contamination in water samples using a device attached to a smartphone.	The system was able to measure coliforms and *E. coli* contamination and issued an alert when contamination was detected.
Tok *et al.* (2019)		Presented a cost-effective and automated device to monitor coliforms and *E. coli* in water based on fluorescent techniques.	The system can automatically detect the presence of both *E. coli* and total coliforms in drinking water within ∼16 h, down to a level of one colony-forming unit (CFU) per 100 mL.
Hausot and Angelescu (2016)		Described the development of an Autonomous Microbiological Alert Sensor (AMAS) for bacterial monitoring in water based on colorimetric and fluorimetric techniques.	The sensor is able to quantify initial concentrations of pathogens present in each sample and alert operators in the case of high bacterial contamination.
Grossi *et al.* (2013)	Electrical	Presented a portable sensor implemented as an electronic embedded system for microbial concentration assessment.	The system provides a much faster response than standard techniques and can be used for *in situ* microbial tests rather than taking samples to a laboratory for analysis.
Zhang *et al.* (2018)		Developed an automatic electrical bacterial growth sensor (EBGS) based on a multichannel, capacitively coupled, contactless conductivity detector (C4D).	The sensor was able to detect the bacteria as much as the conventional online monitoring methods.

3.4 Conclusions

Monitoring water quality is an important water management tool, acting to control pollution and minimize impacts on the environment and human health. However, due to the high cost of monitoring, through the sampling process, sample preservation, transport, qualified professionals, and the use of expensive laboratory equipment, unfortunately, there is a lack of water quality data for the correct management of this resource. With the development of new technologies and the progress of nanotechnology and material sciences, integrated with the Internet of Things, it is possible to accelerate and minimize the costs of obtaining water quality data. In this review, several studies were described that presented the development of low-cost technologies, with *in situ* applications, that can accelerate the collection of data for the monitoring of physical, chemical, and biological parameters of the waters. It was also possible to observe that there was an increase in the number of publications related to the topic, mainly from 2012, with a total of 641 studies being published in 2021 alone. However, although many technologies presented have the potential for monitoring water quality, it is important to highlight that more robust analyses are necessary to guarantee its efficiency, such as equipment useful for life and interference from the environment, being indispensable with the help of standard methodologies at first. Moreover, it should be noted that reporting values for governmental regulatory purposes require that methods undergo exhaustive scrutiny with regard to accuracy and repeatability before being authorized for use.

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4 SMARTPHONE-BASED SPECTROMETRY SYSTEM AS A PRESCREENING ASSESSMENT OF COPPER AND IRON FOR REAL TIME CONTROL OF WATER POLLUTION

A modified version of this chapter has been submitted as: Gabriel Marinho e SILVA, José Augusto GARCIA, Julia de Alencar GARITTA, Davi Gasparini Fernandes CUNHA, Nícolas Reinaldo FINKLER, Eduardo Mario MENDIONDO, Filippo GHIGLIENO. **Smartphone-based Spectrometry System as a Prescreening Assessment of Copper and Iron for Real Time Control of Water Pollution.** Journal of Environmental Management.

Abstract

Due to anthropic action, the presence of pollutants in water bodies, such as toxic metals, are increasingly negatively affecting overall water quality and biodiversity and sustainable goals worldwide. Therefore, decentralization of water pollution monitoring with low-cost devices, using smartphones, suggests an innovative green technology for real-time control. In this study, a portable smartphone-based spectrometry system (SHSS) for estimating copper and iron concentration in surface water samples was developed. The system mainly comprises a portable commercial spectrometer capable of measuring the spectrum of light in the visible region. The results showed that SHSS performed well when compared to a conventional benchtop spectrophotometer (B.S.), with the LOD and LOQ of the SHSS for Copper analysis equal to 0.589 and 1.784 mg.L^{-1}, respectively; and the LOD and LOQ of the SHSS for Iron analysis equal to 0.479 and 1.450 mg.L^{-1}, respectively. In addition, the estimated values of copper and iron concentrations in samples with unknown concentration by the SHSS equipment were equivalent to the B.S. The device developed proved to be a tool with a potential application for monitoring water resources and provides further possibilities with other pollutants as a new green technology for water quality management.

Keywords: smartphone, spectrophotometer, water quality monitoring, green technology.

4.1 Introduction

Monitoring water quality is an important constituent of the programs towards water resources management, allowing decision-making to improve the quality of water sources and minimize the environmental impacts caused by human action (DZURIK; KULKARNI; BOLAND, 2018). Thus, monitoring the quality of water resources currently goes far beyond the characterization of the water itself, but rather the study of the effects of pollutants, together with seasonality, on the structure and functioning of water bodies (ADEJUMOKE *et al.*, 2018; BEHMEL *et al.*, 2016). In addition, considering overpopulation, human activities and industrialization, the presence of toxic substances on water bodies, such as heavy metals, is commonly more significant each day (VARDHAN; KUMAR; PANDA, 2019).

According to Gheorghe *et al.* (2012), toxic metals in the environment have grown considerably in recent years, mainly due to anthropogenic action, such as the use of agrochemicals and mining. Additionally, due to their non-biodegradable characteristic, these substances end up becoming persistent in the environment and in living beings through the process of bioaccumulation and biomagnification (GAUTAM *et al.*, 2014; MEHMOOD *et al.*, 2019). Once in the biological system, the toxic metals can damage organs and intracellular components, such as the plasma membrane, enzymes, and DNA, inducing a toxic and carcinogenic effect (TCHOUNWOU *et al.*, 2012; WANG; SHI, 2001).

Toxic metals can be measured mainly through spectrophotometry, which consists of analyzing the absorption of light by the change in the intensity of a light beam that passes through a sample (MARCZENKO; BALCERZAK, 2000). With the advent of new technologies, several studies have addressed the determination of different substances using smartphones and applying the concepts of spectrophotometry and colorimetry methods (BISWAS *et al.*, 2021; HATIBORUAH *et al.*, 2021; HUSSAIN; AHAMAD; NATH, 2017; SARGAZI; KAYKHAII, 2020). According to Zhang, Song and Yuan, (2018), the colorimetric analysis is the technique normally used to determine the concentration of analyte through comparing the color changes of the solution with the aid of a color reagent.

One of the main characteristics linked to the analysis of water quality using smartphones is the cost reduction and the relative simplicity of the equipment's operation. Hussain, Ahamad and Nath (2017), for example, developing a smartphone spectrophotometer for detecting fluoride in drinking water incurring a total cost of $206.23. On the other hand, the accessibility of this type of analysis can contribute to citizen science, allowing the population to monitor water quality on a voluntary or educational basis (GRASSE; TORCASIO; SMITH, 2016; HO;

XU; LEE, 2020). Also, the presence of a variety of sensors, coupled with the possibility of integration with the Internet of Things (IoT), allows smartphones to be a promising tool for analyzing water quality and communication (MCGONIGLE *et al.*, 2018; ŠIROKA *et al.*, 2021).

The use of this type of technology, aimed at monitoring water quality, can play a fundamental role in analyzing water in remote locations with difficult access or in situations that require continuous monitoring (SRIVASTAVA; VADDADI; SADISTAP, 2018). Thus, these technologies, which have portable characteristics, can be favorable to the user, allowing an *in situ* analysis, with real-time prescription and dispensing with the need for water sampling for laboratory analysis. Furthermore, the additional data can play an important role, for example, on water quality improvement by the Real-time control system (RTC) for urban drainage and sewage system (BRASIL *et al.*, 2021).

Thus, this research aimed at developing a spectrophotometer, using a smartphone, called Smartphone Handheld System of Spectrophotometry (SHSS) for detecting metals in water based on the spectrophotometry technique. In this system, integration with a commercial portable spectrophotometer, available for smartphones, was carried out. The evaluation of the equipment's performance was compared with a bench-top spectrophotometer in the analysis of copper and iron in water samples.

4.2 Material and Methods

4.2.1 System of spectrophotometer with a smartphone

The SHSS (Figure 4.1.a) consists of a portable device that connects to smartphone cameras and can estimate the concentration of an analyte in water samples through spectrum analysis from light. This equipment consists of a module (Figure 4.1.g), made from 3D printing, associated with a commercial portable spectrometer, called GoSpectro (Figure 4.1.f), which allows the analysis of the light spectrum in the region of the visible. In addition, the SHSS comprises a cold white LED light source (Figure 4.1.c), with temperature of 6000-6500K, light intensity of 18000-20000 mcd, power of 60 mW and a viewing angle of 20-30°; a 3.7v battery; a potentiometer of 10 kΩ (WH148-1); a Fresnel lens (Figure 4.1.d), made of a transparent polymer, with 17mm focal length; and a 10 mm quartz cuvette (Figure 4.1.e), where the samples are placed.

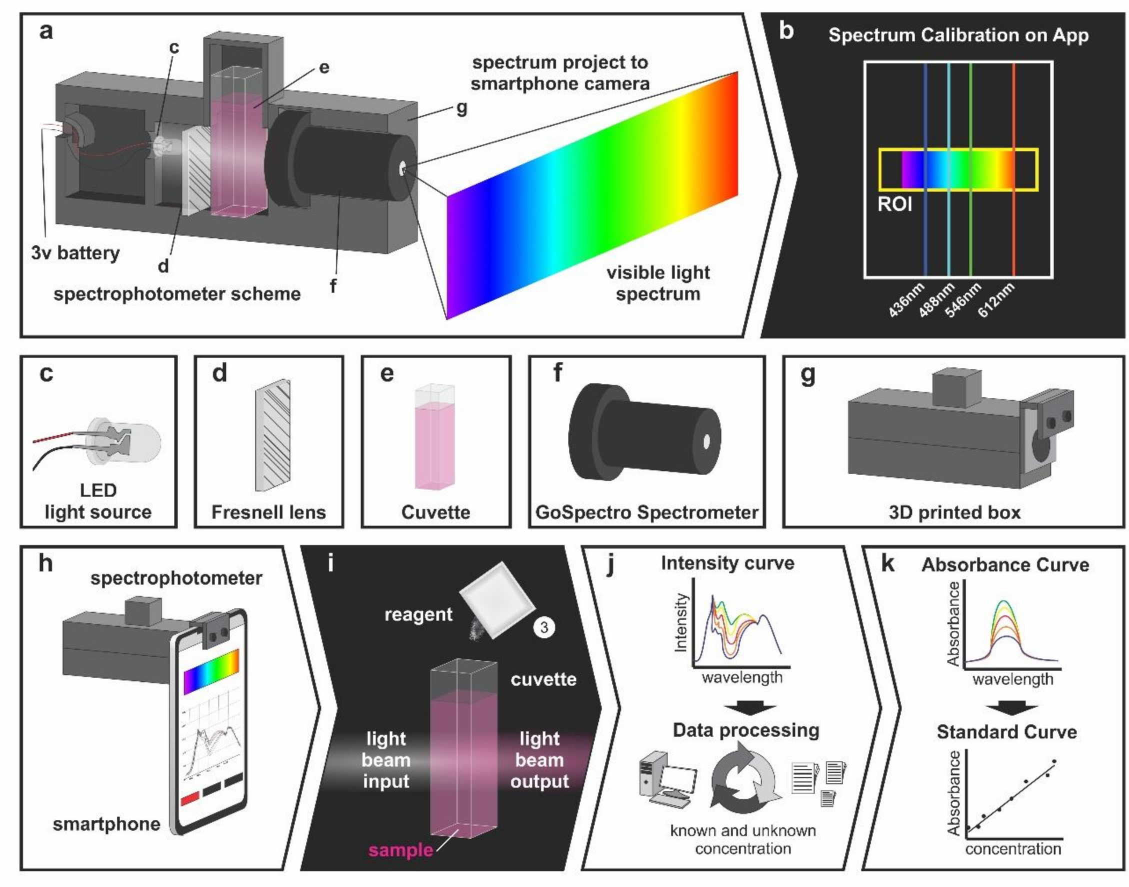

Figure 4.1 - Layout of the Portable Spectrophotometry System for Smartphones (SHSS) for measuring metals in water samples. In item (a), the configuration of the equipment and its main components can be observed, detailed in (c), (d), (e), (f) and (g). Item (b) presents the GoSpectro spectrometer calibration scheme, through the SpectroLab application, and the wavelengths used for calibration. Finally, item (h) presents the SHSS associated with a smartphone device, detailing in (i), (j) and (k) the procedures adopted for sample preparation (by adding reagents), analysis of spectra, data processing and generation of absorption and calibration curves.

A potentiometer and a Fresnel lens were incorporated in the system to attenuate the light intensity, and thus avoid saturation in the smartphone camera. In this study, the Asus® Zenfone 3 smartphone (ASUS_X00DDA, Android 8.1.0 system, Quad-core 1.4 GHz processor and 16-megapixel camera (with f/2.0 aperture lens, 1/3" and Phase Detection AutoFocus - PDAF) was used, whose spectra were read using the SpectroLab application (available for android system on Google Play Store). Figure 4.2 presents the SHSS device operating by the smartphone in the laboratory, as well as its main elements, as mentioned above.

Consequently, the SHSS device is capable of measuring the intensity of light in the visible range, which later allows the generation of light absorbance in a sample based on the concepts of the Beer-Lambert Law, comparing the changes in light intensity by the addition of a colorimetric chemical reagent, as shown in Figure 4.1.i (POOLE; KALNENIEKS, 2000). In addition, the analysis of a variety of samples prepared with known concentrations allows the generation of calibration curves by the peaks of the absorbance curves, which in turn allow estimating the concentration of an analyte in samples with unknown concentrations.

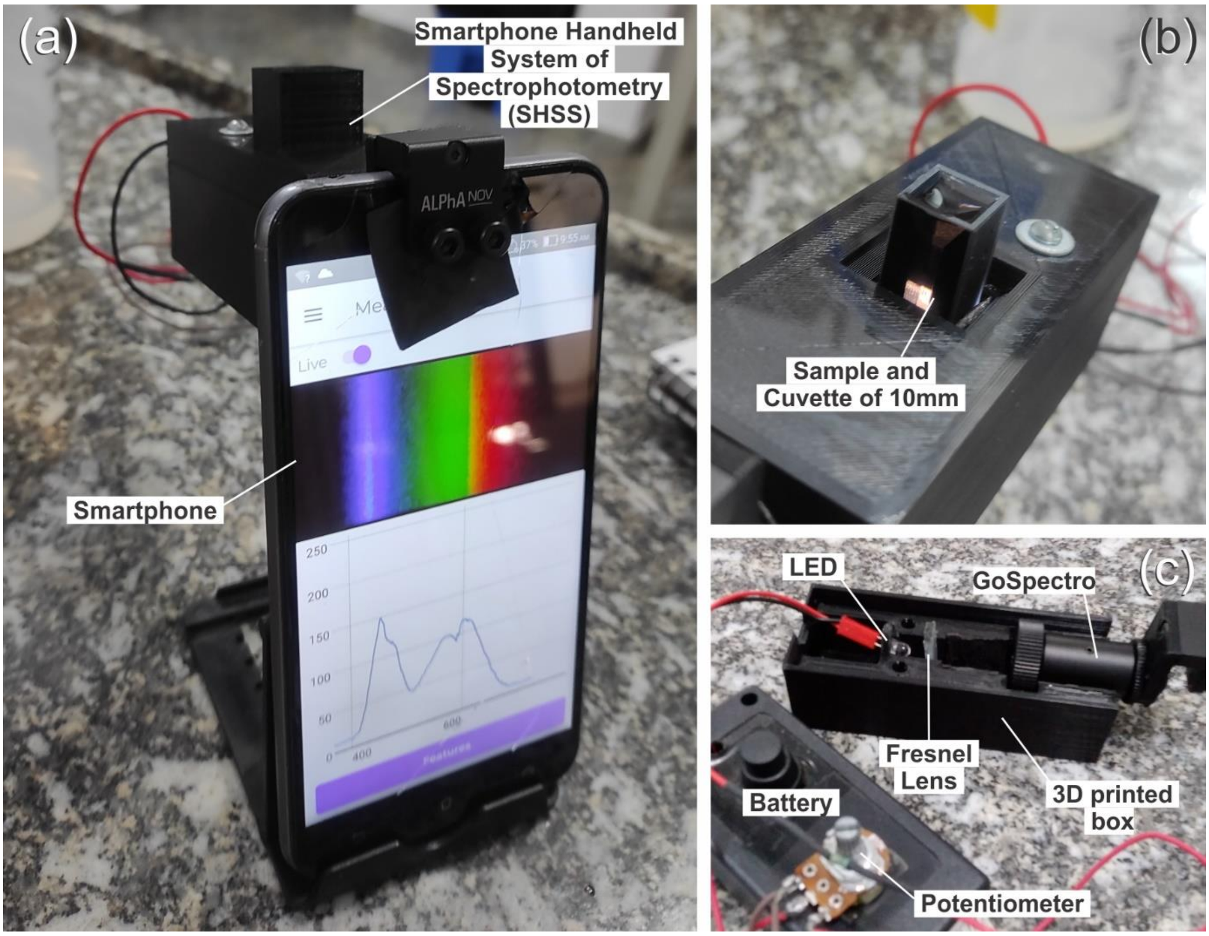

Figure 4.2 – Smartphone Handheld System of Spectrophotometry in the laboratory. In (a) it is possible to observe the device attached to the smartphone. In (b) the cuvette in the SHSS device is shown. Finally, in (c) the SHSS device is presented with its main elements.

4.2.2 Calibration and operation

The calibration of SHSS was made by the SpectroLab application itself by analyzing the colors generated by the spectrum. To do this, using the equipment installed on the smartphone, a region of interest (ROI) of the spectrum produced by the LED light source (Figure 4.1.b) is selected, following the GoSpectro manual guidelines. Afterward, an application algorithm automatically identifies the positions of wavelengths equal to 436, 488, 546 and 612 nm in the ROI and then generates, through linear interpolation, the other wavelength values for the rest of the spectrum. After calibration, the equipment was ready to read the spectra in water samples.

The SHSS operates similar to a bench spectrometer (B.S.), that is, by analyzing absorbance between a blank solution and a target sample, comparing the absorbance values with a calibration curve. The spectra readings taken by SHSS, through the SpectroLab application, were saved in a text file (.txt) and later analyzed by the Matlab© (MathWorks Inc) and Excel© (Microsoft) software to generate the absorbance and calibration curves, as well as for linear regression analysis (DARLINGTON; HAYES, 2017) and estimation of unknown concentrations in samples. In order to reduce interference, the average of three spectra readings by the SHSS device for the same sample was analyzed.

4.2.3 GoSpectro Handheld Spectrometer

The GoSpectro Handheld Spectrometer sensor is Goyalab® compact equipment that uses a smartphone camera to generate the intensity spectrum light curve and allows the spectral characterization of light sources, as well as measured spectra in emission, transmission or reflection. According to the manufacturer, the GoSpectro sensor is sensitive over the entire visible range (400 nm – 750 nm) with a spectral resolution of less than 10 nm and a reproducibility of 1 nm. Comparing the GoSpectro light range with the other developed devices by related works, Hussain, Ahamad and Nath (2017) was able to measure the absorbance of light between 400-700 nm, as well as Das *et al.* (2022) between 440-924 nm and Kong *et al.* (2020) between 430-680 nm.

4.2.4 Reagents and solution

In this research, copper and iron were used as analysis parameters by the USEPA CuVer® and USEPA FerroVer® methods, respectively, as will be described later. The experiments were simultaneously carried out by a Bench Spectrophotometer (B.S.), model *HACH DR3900*, and by SHSS. The B.S. equipment was used due to the similarity of the methodology for determination and measurement of substances in water through the colorimetric/spectrophotometric technique. In addition, for B.S., the samples were analyzed in glass cuvettes, with an internal length of 25 mm, while for SHSS, samples were analyzed in quartz cuvettes, with an internal length of 10 mm. The analyses were carried out in two stages, the first for creating calibration curves from standard solutions, and the second for measuring the respective metals in unknown samples. All measures were made in light visible, the best range for measure the absorbance peak for the chemical reagents used.

To make the calibration curves for copper, the known samples were made with standard copper solution with concentrations equal to: 0.04, 0.10, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 3.00, 4.00 and 5.00 mg.L^{-1}. For the calibration curves of iron, the known samples were made with standard iron solution with concentrations equal to: 0.02, 0.04, 0.10, 0.30, 0.50, 1.00, 1.50, 2.50, 2.80 and 3.00 mg.L^{-1}. In evaluating the measuring capacity of the equipment, samples of chemical laboratory wastewater, electroplating wastewater and domestic sewage treated effluent were used as unknown concentration samples. For the chemical laboratory wastewater sample analysis, a dilution in ultrapure water at a proportion of 1/100 was performed as the sample had a high copper and iron concentration that exceeded the operating range of the used reagents.

4.2.4.1 Copper analysis: CuVer® method

The CuVer® method (or Bicinchoninate method) is a Method 8506 USEPA approved for reporting water, wastewater and seawater analysis with total dissolved copper concentrations (free and complexed) in the range of 0.04 to 5.00 mg.L^{-1}. The reagent used comprises 2,2-Bicinconinate Dipotassium, Sodium Phosphate Dibasic and Potassium Phosphate monobasic, whose absorbance peak is situated at 560 nm.

4.2.4.2 Iron analysis: FerroVer® method

The FerroVer® method (Method 8008 USEPA) is indicated for the determination in water, wastewater and seawater of total iron between 0.02 and 3.00 mg.L^{-1}, including the forms (Fe^{+3}) and (Fe^{+2}), complexed iron compounds (Fe-EDTA) and iron in the presence of copper. The reagent used consists of Sodium metabisulfite, Sodium dithionite, 1,10-phenanthroline, mono(4-methylbenzenesulfonate), whose absorbance peak is situated at 510 nm.

4.2.5 Calibration curve

The calibration curves were important for estimating the concentrations of metals in samples with unknown concentrations, and were generated using the Excel© linear regression tool. To generate the curves, the data generated by the readings of the SHSS and B.S. equipment were analyzed for standard samples, whose peak absorbance values for the SHSS were adjusted for the best performance of the equipment.

Peak absorbance adjustments were made so that the extracted absorbance values coincided with the wavelength whose absorption peak was the maximum. This adjustment is due to the portable spectrometer (GoSpectro) presenting a spectral resolution equal to or less than 10 nm (Section 2.1.) and due to the possibility of errors occurring during the calibration by the application (SpectroLab). Therefore, to analyze standard solutions and unknown samples, the wavelengths with maximum absorption were adjusted from 560 nm to 570 nm, for copper analysis, and from 510 nm to 513 nm, for iron analysis.

4.2.6 Beer-Lambert Law

The analytic measurement on an aqueous sample using light is made possible by the Beer-Lambert law (CLARK, 2019). This law is a combination of the Beer Lambert law, in which, according to the Lambert law, the fraction of light absorbed by a transparent medium is independent of the light intensity, and each successive layer of the medium absorbs an amount of light equal to what passes through it (Eq. 4); and, according to the Beer law, the quantity of light absorbed by the sample is proportional to the number of molecules of the chromophore, where the *k* constant is proportional to the chromophore concentration (Eq. 5) (POOLE; KALNENIEKS, 2000). Thus, the Beer-Lambert law can be expressed by Eq. 6, in which the ratio between the incident light (I_0) and transmitted light (I) is equal to absorbance (A).

$$\mathrm{Log}_{10}(\mathrm{I}_0/\mathrm{I}) = kl \tag{4}$$

$$\mathrm{k} = \varepsilon \mathrm{C} \tag{5}$$

$$\mathrm{Log}_{10}(\mathrm{I}_0/\mathrm{I}) = \Delta A_{\lambda} = \Delta\varepsilon \mathrm{C} l \tag{6}$$

where A_λ is the absorbance; ε is the molar attenuation coefficient or absorptivity of the attenuation species; *l* is the optical path length of the sample, in cm; *C* is the concentration of the attenuating species; I_0 is the incident light on the sample; and I is the transmitted light by the sample.

4.2.7 Limit of Detection (LOD) and Limit of Quantification (LOQ)

According to Currie (1999), the detection and quantification capacity of the equipment represents a fundamental characteristic in the performance of the chemical measurement process. Thus, the Limit of Detection (LOD) and the Limit of Quantification (LOQ) were calculated for the portable spectrophotometry system and for the *Hach DR3900* equipment. LOD is understood as the lowest concentration of the analyte that can be detected by the equipment, while the LOQ is the lowest concentration level of the analyte that can be determined by the equipment with an acceptable performance (SHRIVASTAVA; GUPTA, 2011). The LOD and LOQ can be represented by Eq. 7 and 8, respectively.

$$\mathrm{LOD} = 3 \times s_0/b \tag{7}$$

$$\mathrm{LOQ} = k_Q \times s_0/b \tag{8}$$

where s_0 is the standard deviation obtained by linear regression of the calibration curve, b is the slope of the calibration curve and and k_Q is the LD multiplication factor, whose adopted multiplier value was 10, according to the criteria of (MAGNUSSON; ÖRNEMARK, 2014).

4.3 Results

4.3.1 Standard curve analysis

The experiments carried out using the SHSS enabled the generation of spectral curves, in which, later, from the absorbance analysis, gave rise to the calibration curves and estimate metals in unknown concentration samples. Figure 4.3 shows the graphs of the intensity and absorbance curves generated by the SHSS for total dissolved copper and total dissolved iron. A variation of intensity and absorbance curves can be observed as a result of the increase in concentration. This occurs due to the addition of the colorimetric reagent, specific for each metal, which causes a decrease in light transmittance, and consequently an increase in absorbance. Furthermore, the analysis of absorption curves made it possible to identify and adjust the wavelengths with the highest absorption peaks.

The calibration curves generated from the absorbance curves (Figure 4.3) are shown in Figure 4.4. Through linear regression analysis, for both devices, a good fit of the calibration curves was observed, whose R^2 values were above 0.99, with the lowest value obtained equal to 0.994 for the total iron analysis by SHSS (Figure 4.4.c.). The difference between the absorbance values observed in the results is due to the difference in the optical path existing between the two evaluated methods (25 mm for the B.S. and 10 mm for the SHSS).

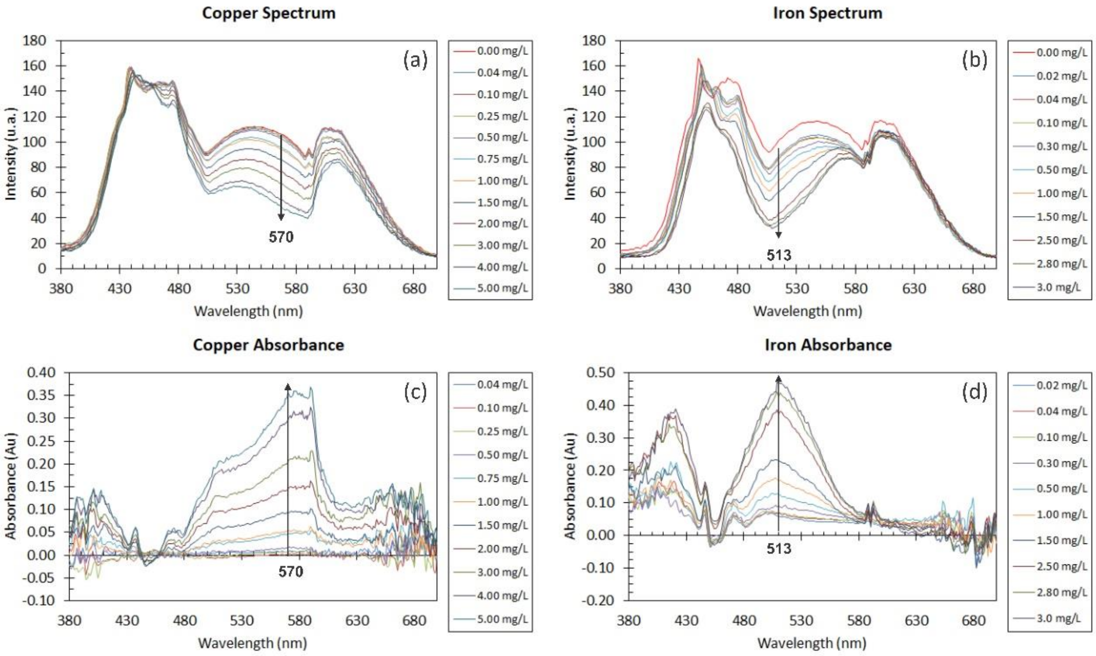

Figure 4.3 - Intensity and absorbance curves generated by SHSS for the analyzed metals, which are (a) intensity curves for the analysis of copper; (b) intensity curves for iron; (c) absorbance curves for copper; and (d) absorbance curves for iron. The graphs show that there was a variation in the shape of the curves (indicated by the arrows) due to the increase in the concentrations of metals in contact with the respective reagents.

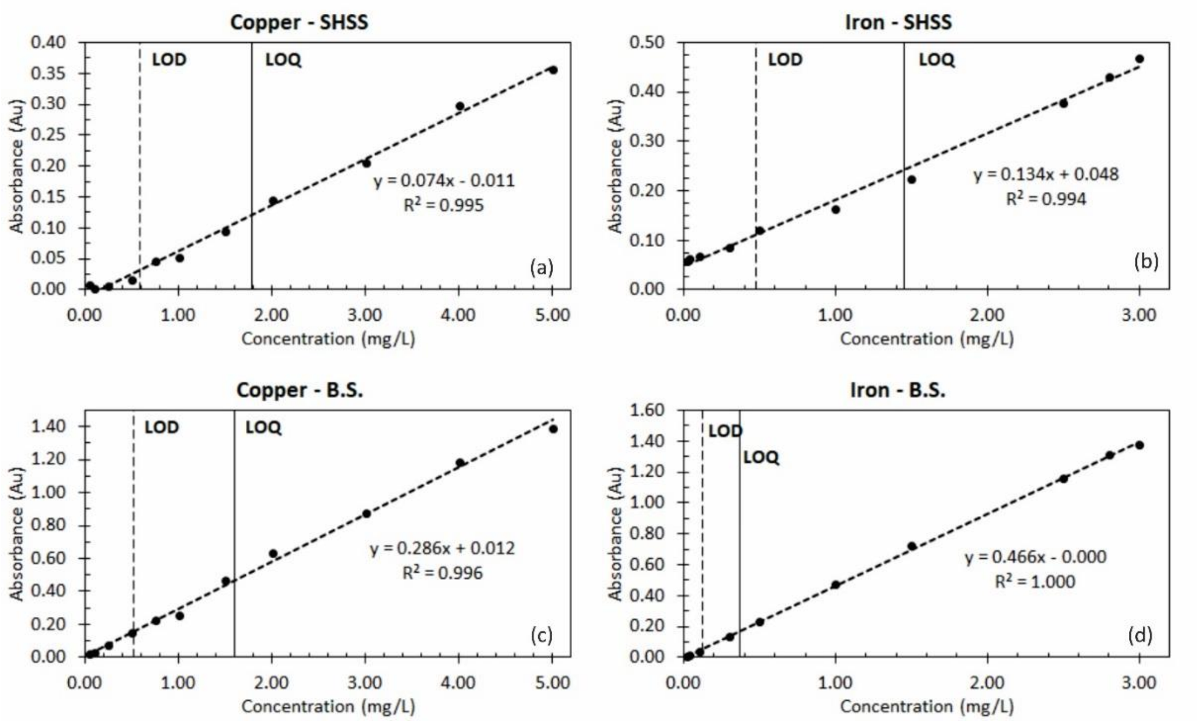

Figure 4.4 - Calibration curves, and their respective detection and quantification limits, for the analysis of copper (a, c) and iron (b, d). Graphs (a)-(b) and (c)-(d) refer, respectively, to the calibration curves generated by SHSS and B.S.

Figure 4.4 also shows the detection (LOD) and quantification (LOQ) capacities computed for the calibration curves. The LOD and LOQ results show that the SHSS has an equivalent quantification and determination capability for copper analysis and a smaller extent of concentration determination and quantification capability for iron analysis when compared with B.S. equipment.

4.3.2 Analysis of Real samples

Estimates of the concentrations of copper and total dissolved iron in unknown samples were made by analyzing the spectra and light absorbance by SHSS (Figure 4.5).

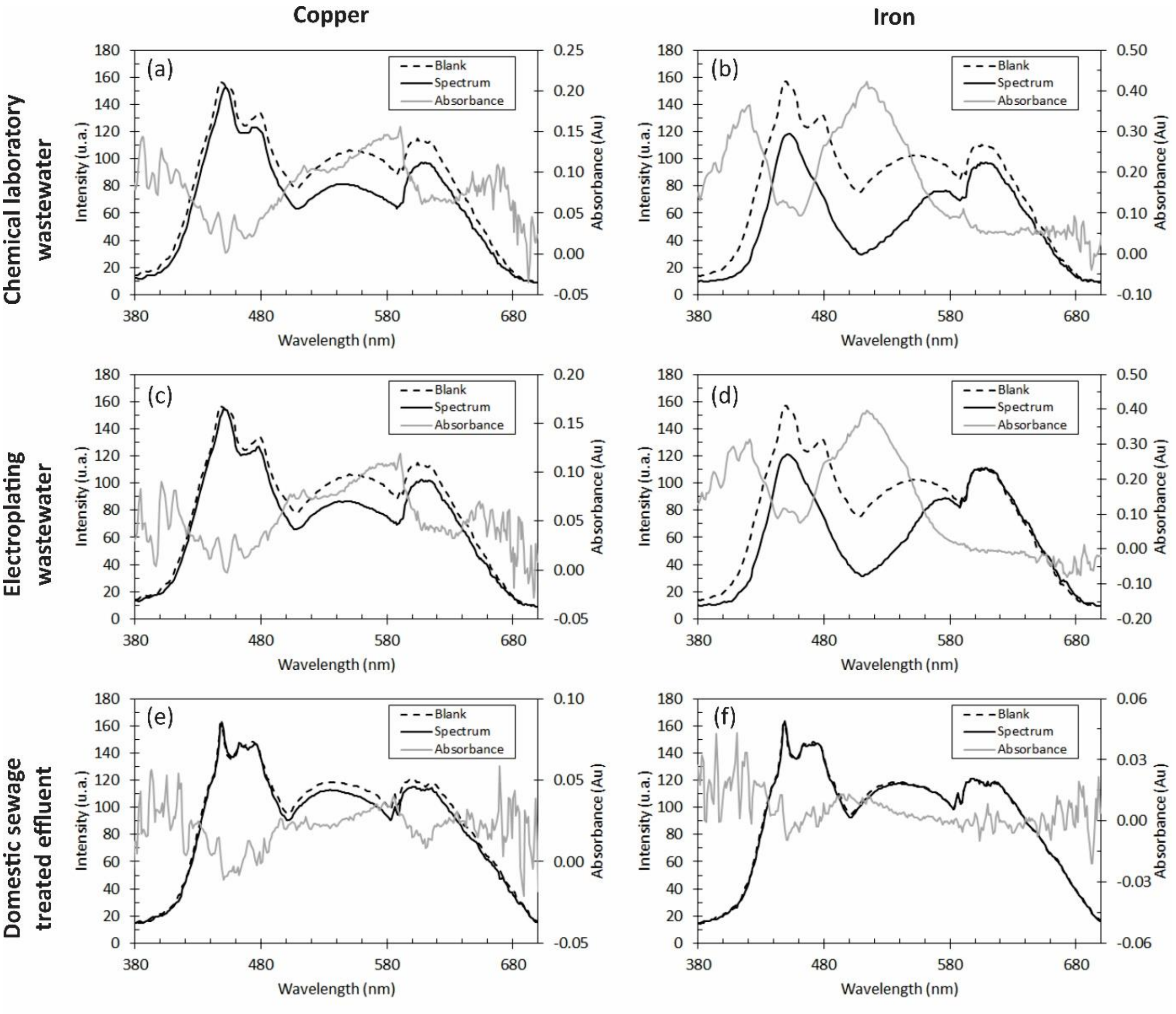

Figure 4.5 - Light and absorption spectrum of real samples with unknown concentrations for copper - in (a), (c) and (e) -, and iron - in (b), (d) and (f). Samples of chemical laboratory wastewater, (a) and (b), electroplating wastewater, (c) and (d) and domestic sewage treated effluent, (e) and (f), were analyzed.

Figure 4.6 shows the results of the estimated concentrations for the real samples, obtained from the linear regression equation (Figure 4.4) and the absorbance values (Figure 4.5). When analyzing the analytical capacity, the SHSS equipment was able to measure concentrations of metals above the LOQ, as in the samples from the chemical laboratory wastewater and electroplating wastewater in the iron analysis and chemical laboratory wastewater in the copper analysis; and in the range between LOD and LOQ, as in the sample for domestic sewage treated effluent in copper analysis. However, the SHSS equipment could not detect iron concentrations above the LOD for the domestic sewage treated effluent sample and showed a concentration of total dissolved copper between the LOD and LOQ for the electroplating wastewater sample.

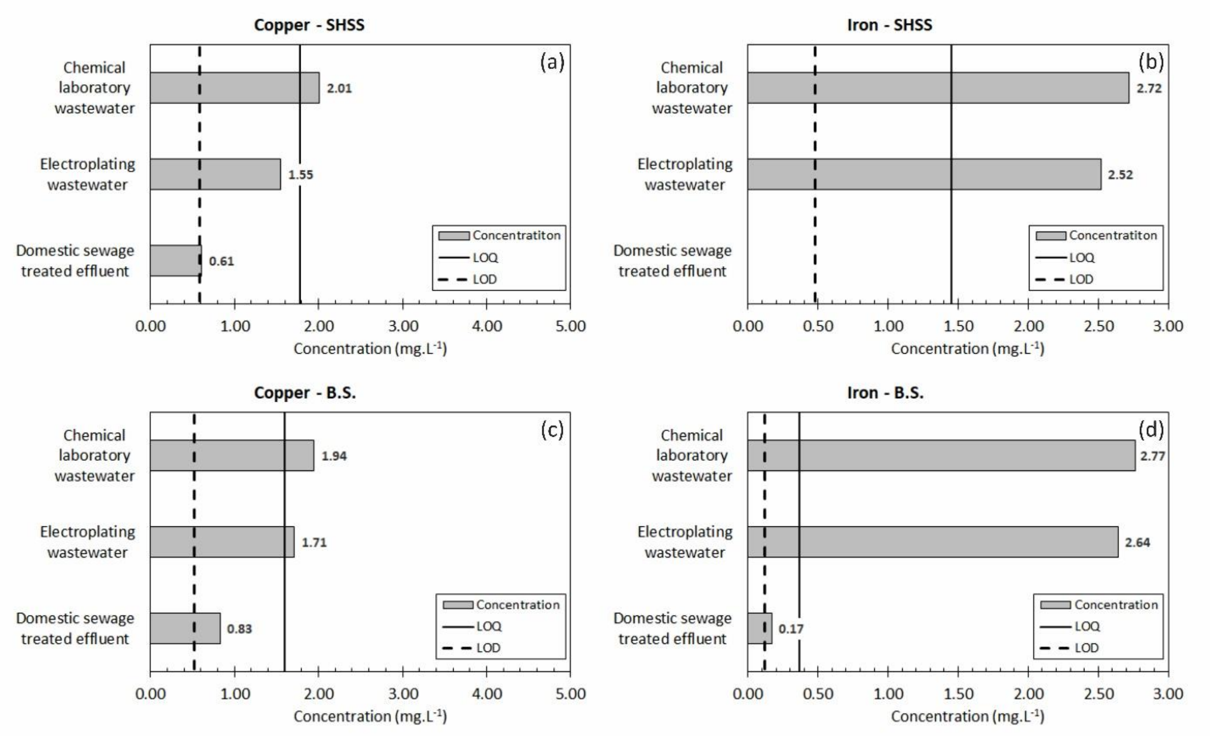

Figure 4.6 - Estimation of the concentration of copper, (a) and (c) and iron, (b) and (d), by SHSS, (a) and (b), and BS, (c) and (d), in samples of chemical laboratory wastewater, electroplating wastewater and domestic sewage treated effluent.

4.4 Discussion

The results obtained showed that the SHSS presented a performance similar to the bench spectrometer for measuring the concentration of metals. Several studies have also demonstrated the possibility of using smartphones to analyze water quality through the spectrophotometry technique, as in: sodium and iron (OLIVEIRA *et al.*, 2017), chlorine and nitrite

(HATIBORUAH *et al.*, 2021; SARGAZI; KAYKHAII, 2020), ammonia (AMIRJANI; FATMEHSARI, 2018), phosphate (DAS *et al.*, 2022; LAGANOVSKA *et al.*, 2020), pH (DUTTA; SARMA; NATH, 2015), organic dyes (KOOHKAN *et al.*, 2020) and fluoride (HUSSAIN; AHAMAD; NATH, 2017).

The use of smartphones in these studies proved to be a viable alternative, which were accurate and had a low cost associated with the equipment. OLIVEIRA *et al.* (2017), for example, could measure sodium (Na^+) in natural water samples using a Digital Versatile Disc (DVD) as a light diffracting medium. In turn, Sargazi and Kaykhaii (2020), who also used a DVD, were able to determine the concentration of chlorine (Cl) and nitrite (NO_2) in different samples. The operating range was between 1.00 to 4.00 mg.L^{-1} for chlorine and 0.05 to 1.20 for nitrite.

Several factors can interfere in the results of water analyses using smartphone spectrophotometry. Regarding the samples, the spectral interference caused may occur due to the emission or absorption of electromagnetic radiation, at the same wavelength in which the species of interest is determined, by other species and substances present in the medium (KAFLE, 2019). On the other hand, non-spectral interferences, associated with the physical effects of the sample matrix - such as density, viscosity, turbidity and surface tension - can trigger differences in the calibration relationships, making it difficult to quantify the elements (DAMS; GOOSSENS; MOENS, 1995).

According to Matinrad *et al.* (2020), the error structures in a smartphone spectrometer highly depend on the optical elements, camera quality, type of spectrophotometer design, for example. Regarding the spectral analysis, one way to improve technology, for example, is by using artificial intelligence in spectral analysis, both for calibration and for absorbance analysis (ABASI *et al.*, 2021; CHATZIDAKIS; BOTTON, 2019; SALEHIAN; SOHRABI; DAVALLO, 2021).

4.5 Conclusion

In this work, a portable device was developed based on the spectrophotometry technique using smartphones to determine the total dissolved copper and total dissolved iron in water samples. The experiments provided the creation of calibration curves for each analyzed metal and, later, the determination of concentrations of the respective metals in unknown samples that were accurate, when compared with a bench spectrophotometer. It was also observed that the detection and quantification limits of SHSS were above the B.S., which means that the SHSS is less accurate for determining analyte concentrations in lower concentrations. For future work, it is intended to integrate the device with an online platform (big data), through remote communication, to obtain the results immediately, in addition to carrying out post-processing for calibration and wavelength improvements. Therefore, this device proved to be a tool with a potential application for monitoring water resources and that can be applied to determine different parameters of water quality.

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5 GENERAL CONCLUSIONS

Overall, conducting this work made it possible to observe the existence of a growing interest in research for develop sensors and technologies to monitoring water quality, in order to minimize costs and speed up the achievement of results of the main quality parameters of surface water and drinking water. In 2021, 641 published studies related to the topic were observed, considering the terms *water quality, low-cost, in-situ*, *real-time, online* and *portable*. Many of the technologies observed were aimed at an integration between optical and electrochemical sensors with microsystems for *in situ* application and online monitoring (IoT). However, it is important to highlight that, due to the recent development of these technologies, their application still requires further studies on adverse conditions, equipment life and interference by other substances. Thus, the review presented in Chapter 3 made it possible to achieve the specific objective: "*To carry out a theoretical review regarding the use of portable, low-cost technologies, with in situ application, applied to the water quality monitoring*".

The *Smartphone Handheld System of Spectrophotometry* (SHSS) proved to be a portable, ultra-compact and easy-to-operate device to water monitoring, as presented in Chapter 4. The creation of calibration curves for copper and iron analysis was possible thanks to the analysis of the absorbance curves, whose R^2 values were above 0.99, achieving a specific objective "*To analyze the behavior of the intensity and absorbance curves of the visible light spectrum, obtained by the proposed spectrophotometry system*". When comparing the SHSS with a benchtop spectrophotometer (B.S.), in compliance with the specific objective "*Evaluate the performance of the proposed spectrophotometry system against conventional equipment*", it was observed that the limits of detection (LOD) and quantification (LOQ) were similar to copper, but different for iron. However, as proposed by the specific objective "*To estimate the concentration of copper and iron in water, in prepared samples and samples with unknown concentrations*", the SHSS equipment was able to determine the concentration of copper and iron in samples with unknown concentrations of chemical laboratory wastewater, electroplating wastewater and domestic sewage treated wastewater, whose results were similar to the bench spectrophotometer.

Therefore, it can be concluded, in general, that the results presented in this work make it possible to extend knowledge about the development of technologies for water quality monitoring, as presented in the general objective: " *The debate on the use technological devices that allow their application to the monitoring of water resources and development of a portable,* *simple and effective system, that can be able to measure the concentration of copper and iron in water from a smartphone device and a portable spectrometer, by the spectrophotometry technique* ”.

5.1 Recommendation for future studies

- Although the SHSS equipment can connect to smartphones through the camera, it should be noted that its compatibility with smartphones depends on the positioning of the camera and the smartphone model used. Thus, one way to make SHSS compatible with as many smartphones as possible would be through the development of an independent system, connecting with smartphones via Bluetooth technology.
- The copper and iron results obtained were successful for samples with high concentrations (as shown in Chapter 4 by the chemical laboratory wastewater and electroplating wastewater samples). However, to estimate the concentration in surface waters (such as rivers) or domestic sewage treated effluent, it is recommended to use reagents that act in a smaller concentration range.
- It is possible to develop an application and create a database that allows the smartphone to communicate with a cloud server to obtain the results in real time. In addition, the analysis of absorbance curves and the generation of calibration curves can be improve using models or/and artificial intelligence.
- It is possible to investigate interferences in the light spectrum readings due to the presence of other substances in the water sample.
- The equipment can be tested also with other light sources for the detection of compounds by fluorescence or for biological monitoring.