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HIGHLIGHTS

Water quality monitoring

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Water is a primary resource for the presence of life on earth, and access to clean water is critical for humans and the ecosystem. Only 1% of the world's water supply is used to meet all of humanity's needs, i.e., agricultural, domestic, industrial, municipal, and residential. During the last decades, water quality has been negatively influenced by a continuously increasing population, rapid industrialization, increasing urbanization, and careless utilization of natural resources [1]. Heavy metals, organic matter, pharmaceutical and personal care products, pesticides, radionuclides, plastics, nanoparticles and pathogens are among the pollutants of major concern [2].

Nearly 2.2 billion people globally lack reliable access to safely managed drinking water [3]. Approximately 40% of the lakes and rivers of the planet have been polluted by heavy metals [4]. For example, around 140 million people in 50 countries regularly drink water that contains arsenic with concentrations higher than the World Health Organization (WHO) reference value of 10 µg/L [5]. Sustainable Development Goals (SDGs), which were set up in 2015 by the United Nations General Assembly, ensure availability and sustainable management of water and sanitation for all as Goal 6.

The sources of these pollutants can be natural and anthropogenic. Heavy metals, such as Pb, Cr, Cd, Hg, and As, tend to bio-accumulate, which is their overtime increase of concentration in living organisms. Even at very low concentrations they can induce multiple organ damage affecting lungs, kidneys, liver, prostate, esophagus, stomach and skin, and can also cause neurodegenerative disorders and diseases.

Natural sources include the interactions with metal containing rocks, normally present in the environment, and volcanic eruptions [6]. The contribution of volcanoes can occur due to large but sporadic emissions, explosive volcanic activity, or continuous low emissions, including geothermal activity and degassing [7]. Anthropogenic sources include those associated with industrial, agricultural and domestic activities [8]. Mining also produces large amounts of heavy metals that are released by mineral extraction and transported through rivers and streams [9]. More than 80 percent of wastewater resulting from human activities is discharged into rivers or sea without any pollution removal. For developing countries, one of the main limitations is a low economic capacity to develop and apply remediation technologies [10].

Anthropogenic activities, urbanization, and industrialization represent key factors in increasing the concentration of these pollutants, particularly in recent decades. It should be taken into account that micro-pollutants are not found in water resources individually. Therefore, this mixture can cause synergistic effects, making it more difficult their detection, quantification, and removal [11].

The need to analyze and manage water quality and supply to sustain human activities and ecosystems is widespread. Monitoring the aquatic environment and applying efficient methods for its protection is impossible without employing adequate chemical analytical methods. The technique to be selected for this purpose should be cost-effective, environmentally friendly, selective, and sensitive enough to detect traces with good precision [12].

The portable X-ray fluorescence (PXRF) equipment has relatively high detection limits [13], although it has a great advantage, which is the non-destructive analysis of liquid and solid samples [14]. Electrochemical techniques, such as the potentiometric, amperometric, voltammetric, coulometric, impedance, and electro-chemiluminescence methods, have their advantages because of their simplicity, low cost and speed. In addition, their derivations of these techniques have produced linear sweep anode (LSASV), square wave anode sweep (SWASV), differential pulse anode sweep (DPASV), cyclic cathodic sweep (CSV), cyclic (CV) voltammetry, and chrono-potentiometry (CP)

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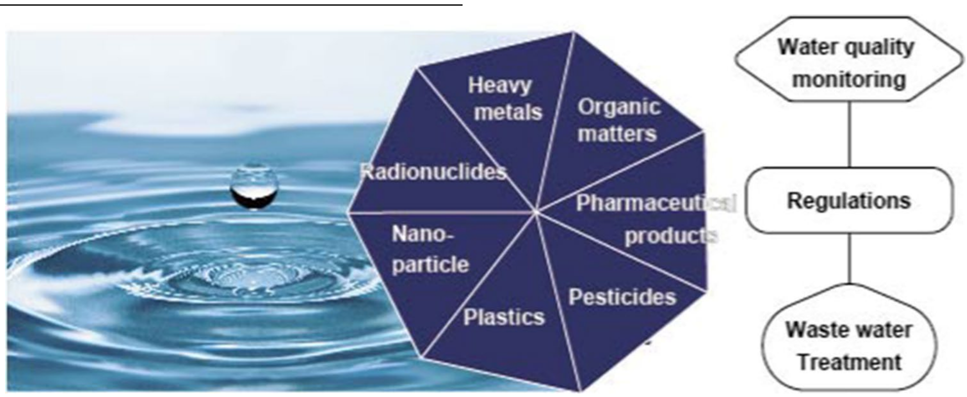
[15, 16]. Various electrochemical sensors have been developed for detecting pollutants in environmental waters [17].

Spectroscopic analytical techniques are simple, sensitive and precise analytical approaches, such as flame (FAAS) or electrothermal atomization atomic absorption (ETAAS), X-ray fluorescence (XRF), inductively coupled plasma optical emission (ICP-OES) spectroscopies, neutron activation analysis [12], ion chromatography ultraviolet–visible (IC-UV–Vis), total reflection X-ray fluorescence (TXRF), laser-induced breakdown (LIBS) and atomic fluorescence (AFS) spectroscopies, capillary electrophoresis (CE), and microprobes (MP) [15, 18]. These techniques have very low limits of detection (LOD), and allow the simultaneous determination of the concentration of a wide range of heavy metals, which is a great advantage.

Inductively coupled plasma mass spectrometry (ICP-MS) is the most widely used method for the analysis of heavy metals in water samples, although the high cost of implementation and the need for skill in the analysis remain challenging. The advantages of ICP-MS include the ability to analyze multiple elements simultaneously, in addition to having an extremely low LOD sufficient to assess health effects on human body. The effectiveness of direct measurement has been validated in seawater, where matrix effects are significant [19]. It is also a promising analytical system that has been proposed to be coupled with ICP-MS as an automated and flow-injection system [20].

to the investigation of chelating reagents and mobile phases according to the analytes to be analyzed, research and development continues on the development of stationary phases to achieve higher performances for selectivity, chemical recovery, and lower blanks [25]. Coupling of efficient separation techniques, such as HPLC, CE and gas chromatography (GC), with ICP-MS has opened up possibilities for elemental speciation with high sensitivity and selectivity. The bioavailability and toxicity of heavy metals in physiological systems depend on their different chemical species. The qualitative and quantitative analyses of elemental species especially the low abundant species are of great significance in the study of the biochemical behavior of the elements [26].

Heavy metal ions readily complex with organic substances, such as citric acid, ethylene-diamine-tetra-acetic acid (EDTA), nitrilo-tri-acetic acid (NTA), cyanide, antibiotics, and humic acid (HA) substances, to form stable metal complexes with various structures and toxicity [27–29]. The formation of these organic chelates not only affects their behavior in environmental water, but also has significant consequences, such as interference with measurements. Anthropogenic pollutants may consist of multiple components, which, in addition to making analysis difficult, can have compounding effects on biota in environment. To solve these problems, it will be necessary to take action, such as installing wastewater treatment facilities, based on the results of monitoring that selects the appropriate analytical techniques to assess their impact.



Isolating the analyte(s) from the sample matrix or the inclusion of a pre-concentration step results in an enhancement of the selectivity of determination and an improvement in the LOD. Among the pre-concentration procedures, liquid−liquid extraction (LLE) is one of the most efficient, simple, and affordable methods. LLE pre-concentration of heavy metals with complexing reagents is a well-developed field [21]. Chelating resin solid-phase extraction with high selectivity is used for chemical separation prior to measurement [22–24]. This method eliminates major components, such as seawater salt, and concentrates the analytes to enable highly sensitive and accurate analysis. In addition

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