Colorimetric Sensor for Heavy Metal Ions Detection: A Short Review

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Colorimetric Sensor for Heavy Metal Ions Detection: A Short Review

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Abstract. Colorimetric is a fascinating technique for the detection of heavy metal ions working based on their color formation. This review critically analyzes the latest advancements in colorimetric sensors for detecting heavy metal ions in water. It highlights the advantages of colorimetric sensors, such as their high sensitivity, selectivity, portability, and capability for on-site detection. Further, the review focuses on various materials used as matrices in the sensors. Different material-based colorimetric sensors, including agarose, paper-based, sol-gel, and polymer materials, are explored, and their unique attributes and effectiveness in sensing different heavy metals are discussed. For instance, agarose is noted for its non-toxic nature and long sensor lifetime. In contrast, paper-based sensors are commended for their ease of use and effectiveness in detecting chromium (VI) ions. The sol-gel method is recognized for its application in detecting Ni^{2+} ions. Meanwhile, PVC membranes are appreciated for their stability and mechanical strength. Overall, the state-of-the-art of colorimetric sensor technology is overviewed. Besides, this review underscores the importance of the colorimetric sensor in monitoring environmental pollution and protecting human health from the detrimental effects of heavy metal contamination.

Keywords: optical chemical sensor; colorimetric; heavy metals; sensor

1. Introduction

Water is a vital resource for all living things and plays a crucial role in all aspects of life. Water serves as the foundation for ecosystems. It provides habitats for countless species and supports the growth and development of aquatic plants and animals[1,2]. Most importantly, it is an essential component for human survival, as it is needed for drinking, cooking, hygiene, and agriculture.

Unfortunately, water can be contaminated with various pollutants, such as heavy metals. Heavy metals are naturally occurring elements that can enter water bodies through both natural and anthropogenic processes. Once present in water, they can persist for long periods and accumulate in the food chain, leading to biomagnification[3]. Biomagnification refers to the process where concentrations of pollutants increase as they move up the food chain. It results in higher levels of contamination in organisms at higher trophic levels. The presence of heavy metals in water can lead to a range of negative impacts. These impacts include detrimental effects on aquatic ecosystems, such as reduced biodiversity, disrupted food chains, and impaired reproduction and growth of aquatic organisms. The worst is that heavy metals will cause fatal effects on human health if consumed. The presence of heavy metals in water requires detection to overcome and mitigate its severe impacts, one of which is using the colorimetry strategy.

Colorimetry is the scientific method of measuring color where subjective color perceptions are converted into an objective numerical system. It is crucial in all aspects related to creating, reproducing, and perceiving colors. The color of an object is influenced by three main factors: the lighting conditions, the optical characteristics of the object, and the response of the human eye. Colorimetry quantifies these aspects and introduces the concepts of standard lighting and observers, resulting in color representations such as RGB[4]. The RGB value can be converted to intensity and ED value by using software like Image J or other color software analysis[5].

Based on the publication, since 2001 (Fig. 1), the colorimetric method has been widely employed in the detection of heavy metal ions. Paper-based and sol-gel materials were primarily used in this field, followed by agarose and polymer materials. Due to the high toxicity of

heavy metals and for continuous monitoring, colorimetry is an alternative technique for future chemical analysis. The method has several advantages over others, such as low cost and ease of use and preparation. Further, most importantly, it can be used for in situ analysis and environmental monitoring.

The main aim of this review paper is to overview the recent advancements in colorimetric sensors for the detection of heavy metal ions. Prior to this, this review discusses several primary heavy metal pollutants, their properties, and their impacts on the environment and human health. Additionally, this review discusses several potential materials used as matrices in the fabrication of these sensors, including their advantages and disadvantages, as well as the synthesis and fabrication processes.

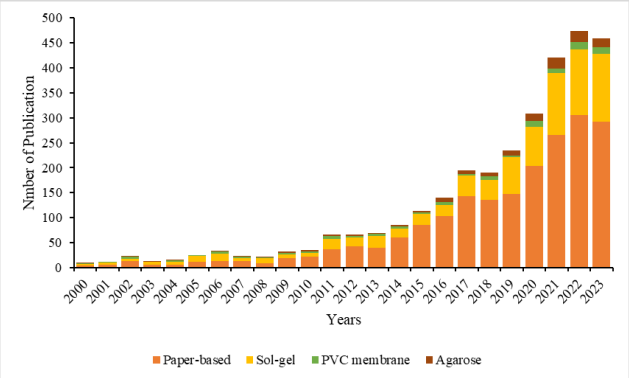

Fig. 1: Number of Scopus-indexed articles discussing colorimetric sensors for heavy metals detection

2. Pollution of Heavy Metals

Heavy metals are a group of non-biodegradable elements that possess high atomic weights and density. These elements have various industrial, agricultural, and pharmaceutical applications, making them widely present in the environment. Heavy metals play a crucial role in numerous industries, such as mining, manufacturing, and energy production. Nevertheless, they are characterized by their toxicity and long-lasting effects on human bodies and the environment. Heavy metals can be present in the form of contaminants in soil, water, and air due to activities such as industrial waste disposal and the use of certain pesticides and fertilizers[6]. Further, heavy metals are not degraded into harmless substances, causing them to persist in the environment for extended periods.

The increasing levels of heavy metals in the environment have raised concerns regarding their impacts on human health and the ecosystem. This phenomenon can be attributed to the rapid industrialization that has occurred in the last few decades since the 1970s[7]. Environmental exposure to heavy metals has become a growing apprehension due to their toxic nature and potential detrimental effects on human health.

Figure 2 and Table 1 summarize various ways metals enter the aquatic environment, classified as natural and human sources. Natural sources can be from geological processes, weathering and minerals, soil and sediment deposits, and volcanic activities. Meanwhile, human sources are primarily wastewaters from industrial activities[8–12], such as the electronics and metal finishing industries, as well as leachate from landfills, mining, urban sewage, and municipals[13,14]. Table 1 presents the primary heavy metals, their permissible levels in the environment, and their impacts on human health.

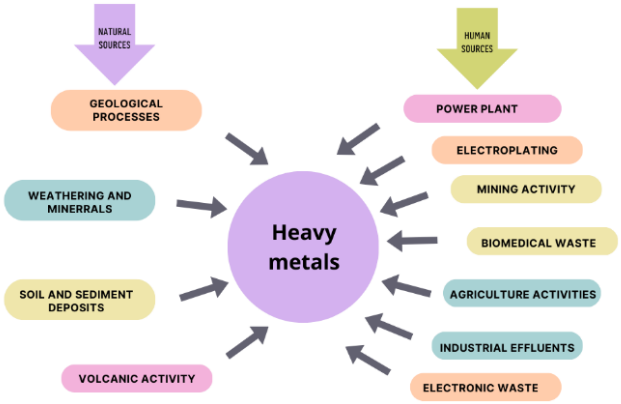

Fig. 2: Different sources of heavy metals

Table 1. Effects of heavy metals ion on human health[15]

No	Heavy metals ion	Adverse effects on human health	Permissible levels (mg/L)
1	Mercury (Hg)	Symptoms include tremors, gingivitis, protoplasm poisoning, nervous system damage, and spontaneous abortion	0.01
2	Nickel (Ni)	Allergic reactions (dermatitis), respiratory issues, and potential carcinogenic effects	0.07
3	Cadmium (Cd)	Renal dysfunction, lung disease, lung cancer, bone defects, kidney damage, bone marrow	0.06
4	Lead (Pb)	Children's mental retardation, developmental delays, neonatal encephalopathy, chronic nervous system damage, liver damage, and kidney damage	0.1
5	Chromium (Cr)	Damage to the nervous system, dermatitis	15
6	Copper (Cu)	Anemia, liver and kidney damage, stomach imitation	0.1

Table 2 summarizes the sources and the impacts of the primary heavy metals when present in the environment. Although they can naturally exist in nature and, in some

cases, are essential for various industrial applications or biological functions, these metals can cause significant problems when excessively present in the environment.

As we discuss each element in detail, it is essential to consider the dual nature of these metals and their absolute necessity in modern industry and technology against their potential toxicity. The discussion aims to analyze the intricate balance between beneficial uses and detrimental effects on human health and the ecosystem. By examining each metal individually, the specific contexts in which they become hazardous, how they affect biological systems, and the environmental dynamics contributing to their spread and concentration can be better understood. This approach not only deepens our comprehension of these elements but also underscores the importance of developing strategies to reduce their negative impacts while exploiting their beneficial properties.

Table 2. Sources, health effects, and environmental impacts of primary heavy metal elements[16,17)]

Ions metals	Description	Sources	Health Effects	Environmental Impact
Hg	Naturally occurring element; transforms into highly toxic methylmercury.	Volcanic activity, industrial processes, burning of fossil fuels, power plants, gold mining, etc.	Neurological disorders, cognitive impairment, developmental delays, cardiovascular damage.	Impairs wildlife reproduction disrupts aquatic ecosystems, and affects biodiversity.
Ni	A hard, ductile, silvery-white transition metal used in various industries	Mining, electroplating, battery production, etc	Nausea, vomiting, headache, dizziness, respiratory issues, increased risk of cancers, heart attack, asthma	Toxic to humans and the environment in high concentrations.
Cd	Common in industrial effluents; highly toxic heavy metal.	Pigments, batteries, electroplating, paint manufacturing, cigarette smoke, plastic products	Adverse effects on plant growth and human health	Significant risks to human health and ecosystems
Pb	Naturally occurring heavy metal; highly malleable and corrosion-resistant	Construction, plumbing, batteries, ammunition, paints, ceramics	Neurological and developmental disorders, kidney damage, reproductive issues, cardiovascular problems	Major environmental pollutant; harmful to humans and animals
Cr	Steely-grey, lustrous, hard, and brittle transition metal	Industrial pigments, tanned leather, rubber, ceramics, and chroming of metal components	Toxic in excess; necessary for glucose utilization in humans	Utilized in various industries; environmental concerns due to industrial use.
Cu	Essential trace element; crucial for heme synthesis	Excessive intake or poor excretion can lead to toxicity.	Liver and kidney damage, anemia, immunotoxicity, Wilson's disease	Can accumulate in the environment and food chain and pose health risks

2.1 Mercury

Mercury is a naturally occurring element found in volcanic activity, industrial processes, and the combustion of fossil fuels. The primary sources of atmospheric mercury are power plants that burn coal or oil, gold and metal mining, cement production, waste disposal, and the manufacturing of caustic soda. These activities release mercury into the water, air, and soil, which causes significant risks to human health and the ecosystem[18)].

When released into the environment, mercury transforms, ultimately, into methylmercury through a microbial action. Methylmercury is highly toxic and can accumulate in the bodies of organisms, including humans[19)]. Consequently, mercury exposure and the consumption of contaminated food can lead to numerous health effects in humans. These effects include neurological disorders, cognitive impairment, developmental delays in children, and damage to the cardiovascular system. Additionally, mercury pollution in the environment can impair the reproductive systems of wildlife, disrupt aquatic ecosystems, and negatively impact biodiversity[20)].

2.2 Nickel

Nickel is a hard, ductile, and silvery-white transition metal. It is widely used in various applications in manufacturing industries, including stainless steel, batteries, and electronics. Nickel is also present in inexpensive jewelry, keys, paper clips, and clothing fasteners. Despite its many usages, nickel can be toxic for humans and ecosystem[21)]. The decomposition of nickel is sourced from the mining industries, such as rocks and soil. The pollution of nickel ions is not only caused by natural processes but also by human and industrial activities such as electroplating, batteries, mobile phones, medical equipment, and household appliances[22)].

Nickel is an essential micronutrient for the human body and plays a vital role in maintaining overall health and

proper functioning. Nevertheless, its excessive intake can lead to poisoning and various health problems such as certain cancers, heart attack, stroke, asthma, chronic bronchitis, and respiratory failure. Excess nickel can accumulate in the liver, kidneys, bones, and aorta, causing symptoms such as nausea, vomiting, headache, dizziness, difficulty breathing, coughing, chest pain, and skin rash[23]. Therefore, it is vital to maintain a balanced and moderate nickel intake to avoid these health risks.

2.3 Cadmium

Cadmium is commonly found in numerous industrial effluents and products. It is released into the environment through industrial processes such as pigments, batteries, electroplating, and paint manufacturing. The presence of cadmium in the environment has become increasingly severe in recent decades, causing harmful risks to human health and the ecosystem[24]. Cadmium, in particular, is considered one of the most toxic heavy metals due to its prevalence in the environment and its harmful effects on both plant growth and human health. Various sources contribute to the release of cadmium into the environment. These sources include cadmium-based paints, cigarette smoke, plastic products, industrial discharges, and even natural occurrences in base metal ores and coal deposits[26].

In this context, identifying heavy metals in environmental samples has become one of the most critical subject areas in analytical chemistry[25]. Understanding the presence and concentration of heavy metals, such as cadmium, is crucial for assessing their potential risks to human health and the surrounding ecosystems.

2.4 Lead

Lead has been exploited for various purposes throughout history due to its unique properties. It is a highly malleable and corrosion-resistant metal, making it useful in applications such as construction, plumbing, and batteries. Additionally, lead is used in the manufacturing of ammunition, paints, and ceramics. However, lead is a well-known toxic heavy metal generally found in industrial areas and is known to have damaging effects on humans and animals[27,28].

Lead exposure can occur through inhalation, ingestion, or dermal contact. Once inside the body, lead can accumulate in organs and cause various adverse effects. These effects can include neurological and developmental disorders, kidney damage, reproductive issues, and cardiovascular problems[27]. It is particularly harmful to young children, as their developing bodies and brains are more susceptible to its toxic effects. Lead has been recognized as a significant pollution in the environment, and efforts have been made to reduce its use and mitigate its harmful effects. It is vital to implement proper waste management practices to prevent further contamination and minimize lead exposure.

2.5 Chromium

Chromium is a hard and brittle transition metal. Although it is comparatively abundant in the earth's crust, free chromium is never found in the natural world. The majority of ores are made of the mineral chromite, which is largely found in natural deposits and is frequently tainted with silica, magnesium, oxygen, and aluminum. Chromium is mainly used in ferrous alloys, where the pure metal is not needed. Additionally, chromium compounds are utilized in industry as pigments and catalysts[29]; for instance, chromium (IV) gives rubies a red hue. Although chromium is toxic in excess, it is a necessary trace element for humans as it helps utilize glucose. Anthropogenic sources of chromium include the chroming of metal components, industrial pigments, tanned leather, rubber, and raw materials used in ceramics[30].

2.6 Copper

Copper is an essential nutrient for the human body as it plays a crucial role in heme synthesis. However, excessive intake in the body or the inability to excrete excess copper can lead to toxicity and result in Wilson's disease[31]. Besides, high levels of copper exposure can cause harmful health effects[32], including liver and kidney damage, anemia, and a weakened immune system. Copper toxicity is a significant concern due to the potential risks it poses to human health and ecosystem. Therefore, it is essential to regulate and monitor copper levels to prevent toxicity and ensure the well-being of individuals and the environment.

3. Various Materials for Colorimetric Sensors

This section discusses and underlines various materials that can be used in the fabrication of colorimetric sensors. Each contributes differently to the sensor's sensitivity, selectivity, and overall effectiveness in the detection of heavy metal ions. These materials include agarose, paper-based, sol-gel, and polymer, as presented in Fig. 3. Each material offers unique properties and advantages for sensor development.

Agarose is highlighted for its non-toxic nature and ease of chemical immobilization with ionophores, resulting in sensors with long lifetimes and minimal hysteresis. Paper-based sensors are noted for their use in detecting chromium (VI) ions, utilizing gold nanoparticles for visible color changes. Sol-gel is mentioned for its application in detecting Ni^{2+} ions using 2,2-furildioxime in a transparent glass-like matrix[22]. Lastly, the section discusses the use of polyvinyl chloride (PVC) in sensor membranes, valued for its stability, mechanical strength, and compatibility with various ionophores and additives.

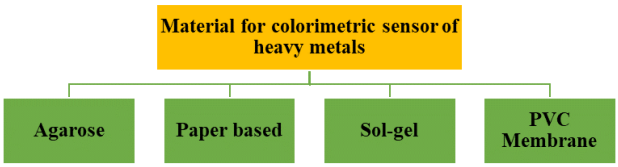

Fig. 3: Classification of materials-based colorimetric sensors for heavy metals detection

3.1 Agarose

Agarose is a non-toxic gel that can be easily activated and chemically immobilized with ionophores, allowing for the covalent immobilization of indicators. This immobilization method produces sensors with a long lifetime and minimal hysteresis or leaching of the immobilized dyes[33]. Agarose membranes also provide stable and transparent support for the immobilized ionophores, allowing for accurate and sensitive detection of trace metal ions. Table 3 compares various agarose sensors reported in the literature. Alizadeh et al. [34] studied the performance of sensors made of agarose membranes immobilized with specific ligands (1-p-tolyl-3-(3-(trifluoromethyl)phenyl) triaz-1-ene 1-oxide) for detecting trace nickel ions. They reported that the produced sensors had good selectivity, reproducibility, and fast regeneration. Besides, the sensors exhibited linear relationships between absorbance changes and ion concentrations at 6.28 x 10^{-5} to 2.80 x 10^{-10} mol L^{-1}, with a low detection limit at 1 x 10^{-10} mol L^{-1}. Zargoosh et al.[35] developed a colorimetric sensor from agarose membranes immobilized with dithizone through covalent bonding. This resulting sensor demonstrated enhanced selectivity and performance compared to other optical sensors for detecting Hg^{2+} and Pb^{2+} ions. Besides, Fries et al. [36] developed a sensor demonstrating high selectivity for specific ions compared to numerous alkali, alkaline earth, transition, and heavy metal ions. It could selectively determine the concentration of target ions in the presence of excess amounts of potential interferences such as CN^- and I^- [36]. The sensor also showed a satisfactory agreement with results obtained from ICP-MS measurements.

Alizah et al.[37] prepared an agarose membrane-based sensor for Hg(II) detection using ligan 2-[(2-sulfanylphenyl)ethanimidoyl]phenol (L) and ligand solution (1 × 10^{-2} mol L^{-1}) in alkaline condition. The resulting yellow color membranes were thoroughly washed with and then immersed in 50% methanol overnight. The proposed membrane sensor was cut into a size of 1 cm × 2 cm and mounted in a polyacrylamide holder to determine its absorbance. You et al.[38] converted water samples into semi-solid hydrogels using agarose and then dried them into agarose films to measure the signal intensities for heavy metal detection using laser-induced breakdown spectroscopy (LIBS). Pizzoferrato et al.[39] reported a selective optical sensor response to copper ions through naked-eye color using an agarose membrane. The sensor indicated the complex formation of cuprammonium through the coordination of copper ions with amino functional groups of NSCDs (nitrogen and sulfur co-doped carbon dots), resulting in a positively charged surface.

Table 3. Colorimetric sensors using agarose membrane.

Heavy metals	Color changes	Limit of Detection	Ref.
Hg^{2+}	N/A	2 x 10^{-6} mmol L^{-1}	35)
Hg^{2+}	Yellow to green-blue	1 x 10^{-6} mg L^{-1}	37)
Cu^{2+}	Light yellow to deep green	0.1 µmol L^{-1}	39)
Cr(I)	N/A	0.118 mg L^{-1}	38)
Cd(I)	N/A	0.011 mg L^{-1}	38)
Pb(I)	N/A	0.122 mg L^{-1}	38)
Hg^{2+}	N/A	2.0 x 10^{-9} mol L^{-1}	35)
Pb^{2+}	N/A	4.0 x 10^{-9} mol L^{-1}	35)
Hg^{2+}	Colorless to violet	0.2 µg L^{-1}	40)
Cu^{2+}	Light brown to dark brown	1 µM	41)
Ni^{2+}	N/A	9.30 x 10^{-11} M	42)
Ni^{2+}	N/A	1 x 10^{-10}	34)

In general, agarose membrane layers can be formed by heating agarose powder in a water solution for 15 minutes at 100 ^{0}C (Fig. 4). The solution needs to be cooled to room temperature to solidify into a hydrogel.

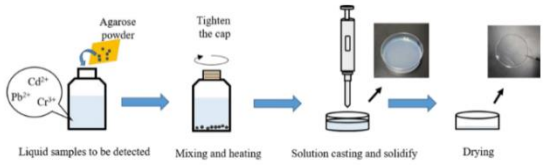

Fig. 4: Illustration of the preparation of agarose films[38]

Agar-agar is a natural polysaccharide derived from red algae that consists of D-galactose and 3,6-anhydro-L-galactopyranose. It is eco-friendly, compatible with living organisms, and cost-effective. Its strong gelling properties and lack of interaction with other molecules make it popular in pharmaceutical, food, and biotechnology sectors[43,44]. Additionally, agar-agar remains stable at high temperatures and low concentrations. Nshnsh et al.[40] reported an agarose membrane-based colorimetric sensor for detecting Hg^{2+}. The sensor had good durability for at least 12 weeks when stored at 25^{0}C in dark conditions and could be recycled by dropwise KI 10% (w/v) to the surface. The results also denoted that it is recommended to store the sensor in an ascorbic acid solution with a concentration of 0.1 mM[45].

3.2 Paper-based

Paper-based sensors are typically less expensive due to their inexpensive components, efficient manufacturing processes, disposable nature, and flexible integration and design. These characteristics make paper-based sensors a good option for many applications, particularly those that need scalable and affordable sensing solutions.

Guo et al. [46] exposed the development of a paper-based sensor for the colorimetric detection of Cr (VI) ions. The sensor utilized gold nanoparticles immobilized on cellulose paper through redox upon reaction with Cr (VI), resulting in naked-eye color changes (Fig. 5). The sensor demonstrated high selectivity, sensitivity, and resistance to interference ions. Besides, it had a low detection limit and was successfully applied to real environmental samples. The sensor utilized bovine serum albumin-capped gold nanoparticles (BSA-Au NPs) decorated on a silanization-titanium dioxide-modified filter paper (STCP). When Cr (VI) ions were present, they gradually etched the BSA-Au NPs, causing a visible color change. This color change was due to the damping of the surface plasmon resonance (SPR) of the gold nanoparticles. The etching process was facilitated by the presence of hydrobromic acid (HBr). The paper-based sensor demonstrated high selectivity for Cr (VI) ions and could detect concentrations ranging from 0.5 to 50.0 µmol L^{-1}. The limit of detection was 280 nmol L^{-1}.

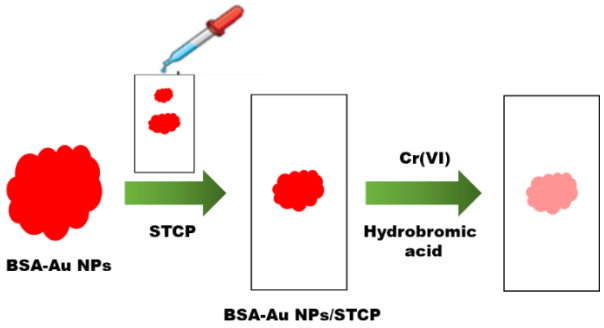

Fig. 5: Schematic illustration of colorimetric detection of Cr(VI) using paper-based sensor[46]

Pourreza et al.[47] fabricated a highly selective and portable paper-based sensor using curcumin nanoparticles (CURNPs) for Hg^{2+} detection. Due to the complexation between Hg(II) and CURNPs, a color change from yellow to light yellow occurred on a PAD (paper-based analytical device). Despite the relatively high LOD (0.17 ppm) observed, the PAD's sensitivity was increased by several additions, resulting in a detection limit of 0.003 ppm.

Cui et al.[48] exposed a paper-based sensor to detect Pb^{2+} in water using inkjet printing technology. The sensor was inexpensive, had a wide dynamic range, and was not affected by the presence of chloramine disinfectants. It also had a shorter response time compared to traditional sensors and could be used in pump-free microfluidic devices. The linearity was 10 to 10 M.

Idros and Chu[49] conveyed a low-cost, paper-based microfluidic analyzer (µPAD) designed for simple, portable, and disposable detection of Hg, Pb, Cr, Ni, Cu, and Fe ions. Triple indicators or ligands were embedded in the µPADs, producing visible color changes upon interaction with metal ions. These colorimetric changes could be visually observed and quantitatively analyzed using digital imaging and color calibration techniques in the red, green, and blue (RGB) color space. The sensor platform had high accuracy and could detect and distinguish different metal ions simultaneously, even in real water samples.

The performance, stability, and durability of the sensor are greatly influenced by the selection of paper materials that are compatible with the type of ligand. Materials commonly used in the fabrication of paper-based sensors are filter paper, Whatman filter paper, nylon paper[50], chromatography paper[51], cellulose paper, and nitrocellulose paper[52]. Table 4 summarizes various types of paper employed as sensor materials.

Table 4. Various paper-based materials for colorimetric sensors

Heavy metals	Material	Ligand	LOD	Ref.
Hg^{2+}	Filter paper	Rhodamine	27.2 ppb	53)
Hg^{2+}	Filter paper	Dithizone	930 ppb	54)
Hg^{2+}	Whatman filter No. 1	Dithizone	200 ppb	55)
Cu^{2+}	Whatman filter No. 2	Rhodamine B/Silica NPs	0.7 mg L^{-1}	56)
Cr^{6+}	Glass fiber filter paper	1,5-diphenylcarbazide	0.01 mg L^{-1}	57)
Pb^{2+}	Whatman filter No. 1	Dithizone	10 mg L^{-1}	58)
Ni^{2+}	Whatman filter No. 1	Dimethylglyoxime	0.92 mg L^{-1}	59)
Hg^{2+}	Filter paper	Chitosan-gold nanocomposite	5.0 x 10^{-5} mM	60)
Hg^{2+}	Cellulose-based paper	1,4-disubstituted azine	10 mg L^{-1}	61)

3.3 Sol-gel

Table 5 compares various sol-gel materials-based sensors employed for detecting heavy metals. Suherman et al. [22] developed an optical chemical sensor for the determination of Ni^{2+} ions in water using the sol-gel method. The method was done by incorporating 2,2-furildioxime as a sensitive reagent into the nanopore of a transparent glass-like material. The sensor was composed of tetraethoxysilane (TEOS), 2,2-furildioxime, methanol,

hydrochloric acid, and Triton X-100. When the sensor was exposed to a solution containing Ni^{2+} ions, the 2,2-furildioxime reacted with the Ni^{2+} ions to form a color complex (Fig. 6). This complex formation caused a change in the optical characteristics of the sensor, which could be measured and correlated to the concentration of Ni^{2+} ions in the solution.

Manivannan et al.[62] stated the development of a biosensor probe for the optical detection of mercury ions in water. The probe utilized a combination of silver nanoparticles and M13-bacteriophage to effectively concentrate and detect Hg(II) ions in the sol-gel matrix. The sensor exhibited high selectivity and a limit of detection of 10.8 nmol L^{-1}. The study highlighted the potential of using nanomaterials and bacteriophages for the development of effective metal ion sensors. Jayabal et al. [63] exhibited the use of gold nanorods embedded in a functionalized sol-gel matrix for the selective sensing of Hg^{2+} ions. The gold nanorods demonstrated a blue shift in the absorption spectra after the addition of Hg^{2+} ions, allowing for the colorimetric detection.

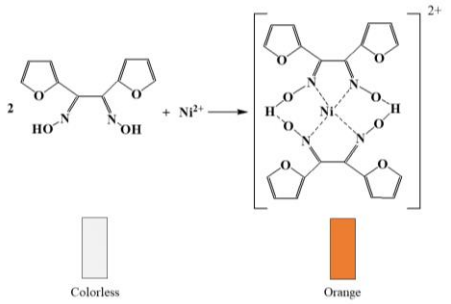

Fig. 6: Schematic of color formation of Ni^{2+}-FDO complex on sol-gel matrix [22]

Feng et al.[5] described a colorimetric method for trace copper(II) ions detection in aqueous solutions using a cellulose acetate/nitrate membrane coated with DPC immobilized sol-gel matrix. The technique involved the filtration process and a complex reaction between copper(II) ions and DPC, resulting in color changes that can be quantitatively determined. The method was selective for copper(II) ions, even in the presence of other metal ions, and was sensitive with a detection limit of 0.16 µmol L^{-1}. Several factors could affect the colorimetric response of the DPC immobilized sol-gel membrane and influence the detection of copper(II) ions, such as concentration of metal ions, pH, and interference from other metal ions.

Thohir et al.[64] reported that sol-gel formed in the filter paper matrix filled its pores without forming chemical bonds but physical interactions with the surface of the supporting media (Fig. 7). This physical interaction between the sol-gel matrix and the filter paper simplifies the preparation process and eliminates the need for complex chemical reactions or bonding agents. The sol-gel matrix with filter paper reached a good aging time of only two days, compared to sol-gel coated in glass media, which required up to 14 days of age[65].

Feky et al.[66] designed an optical thin film sensor to detect Mn(II) ions in aqueous solutions. The sensor incorporated synthesized 2-(2'-hydroxynaphthylazo)-benzothiazole (HNABT) as a selective ionophore into a nonporous glass-like material through the sol-gel method. The prepared sol was constructed onto a glass plate by spin-coating. The optimal sonication time for immobilizing HNABT into the silica matrix was found to be 25 minutes, resulting in stable thin films without sensitivity fluctuations.

Yari and Abdoli[67] developed a robust and highly selective optical sensor for detecting Hg^{2+} ions by embedding an indicator dye in a sol-gel matrix. This sensor demonstrated a significant absorbance shift in the presence of mercury(II) ions, with a wide detection range from 1.52×10^{-9} to 1.70×10^{-2} M and a detection limit of 1.11×10^{-9} M at pH 5. Besides, it exhibited excellent selectivity, high stability, and reproducibility. Further, the sensor's performance in real sample testing correlated properly with results from CV-AAS spectrometry, confirming its effectiveness for practical environmental monitoring.

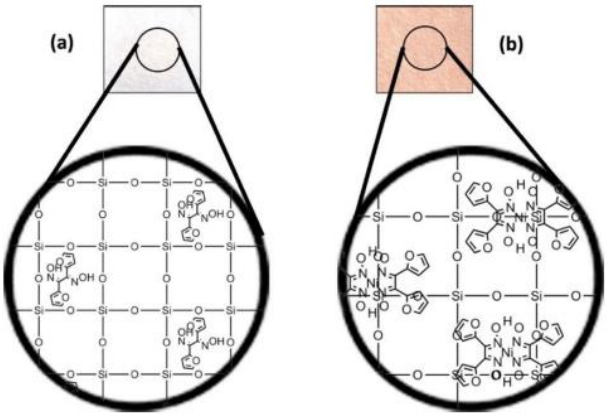

Fig. 7: Interaction between (a) xerogel and α-furil dioxime, and (b) xerogel and Ni- α-furil dioxime[64]

Table 5. Colorimetric sensors using sol-gel matrix

Heavy metals	Color changes	Limit Detection	Ref.
Zn^{2+}	Colorless to pink	0.016 µg mL^{-1}	65)
Ni^{2+}	Colorless to orange	0.11 mg L^{-1}	22)
Ni^{2+}	Colorless to orange	0.1 mg L^{-1}	64)
Fe^{2+}	Colorless to blue-violet	1.68 ng mL^{-1}	68)
Pb^{2+}	Orange to pink	0.11 mg L^{-1}	69)
Cu^{2+}	Colorless to purple	1.6 x 10^{-4} mM	5)
Hg^{2+}	Yellow to colorless	10.8 nM	62)

3.4 PVC membrane

Polyvinyl chloride (PVC) is widely utilized as a sensor membrane material due to its numerous advantageous

properties. It is highly stable and exhibits robust mechanical strength, which ensures its durability under various environmental conditions, making it well-suited for long-term applications. This inherent stability enables PVC membranes to maintain their structural integrity, a crucial factor in sensor reliability. Moreover, PVC is easily adjustable and can be functionalized to improve its selectivity and sensitivity towards specific analytes, allowing for the precise detection of target ions or molecules. Its versatility extends further with its compatibility with a broad range of ionophores and additives, which can be integrated into the membrane to optimize its performance. Additionally, PVC is relatively inexpensive and easy to manufacture, making it an economically viable option for large-scale production of sensors. This cost-effectiveness, coupled with its technical attributes, makes PVC-based sensors an appealing choice across diverse scientific and industrial applications.

Ghaedi et al.[70] presented the development of a PVC-based optical sensor for the detection of Cu^{2+} ions. The sensor utilized a plasticized PVC membrane and a synthesized ionophore to achieve high sensitivity and selectivity for Cu^{2+} ions detection. Moersilah et al.[71] described a portable sensing approach for tracing Cd^{2+} using 1-(2-pyridilazo)-2-naphtol (PAN) immobilized by PVC. The result revealed that the dark yellow color changed to dark red in the presence of Cd^{2+} as a result of the complexing process (Fig. 8). A limit of detection was obtained at 0.048 mg L^{-1}. The maximum wave number of Cd^{2+} was achieved at a wavelength of 558 nm.

Because PVC membranes are easy to prepare, low cost, and reliable, Firooz et al.[72] developed an optical chemical sensor from bis(thiophenal)-4,4'-methylenedianiline immobilized by PVC membrane for Hg detection. The results demonstrated high sensitivity and selectivity in the linear range of 2.51 x 10^{-13} to 1.02 x 10^{-5} mol L^{-1}. Table 6 compares various results of PVC membrane-colorimetric sensors.

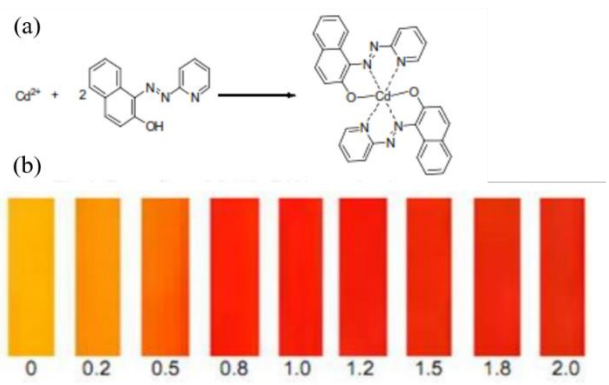

Fig. 8: (a) Complex reaction of Cd(II)-PAN, and (b) Color change of the sensor at various Cd(II) concentrations[71].

Table 6. Comparison of colorimetric sensor using PVC membrane

Heavy metals	Complexing reagent	Color changes	Limit Detection	Ref.
Cu^{2+}	(E)-N′-(pyridin-2-ylmethylene)isonicotin-ohydrazide	Colorless to yellow	1.9 x 10^{-7} mol L^{-1}	[70]
Cd^{2+}	1-(2-pyridilazo)-2-naphtol (PAN)	Dark yellow to dark red	0.048 mg L^{-1}	[71]
Hg^{2+}	bis(thiophenal)-4,4′-methylenedianiline	N/A	3.43 x 10^{-14} mol L^{-1}	[73]
Zn^{2+}	4-(2-arsonophenylazo) salicylic acid	Yellowish-orange to red	0.22 ng mL^{-1}	[74]
Zn^{2+}	5-(2′,4′-dimethylphenylazo)-6-hydroxy-pyrimidine-2,4-dione	N/A	1.6 x 10^{-9} mol L^{-1}	[75]
Cd^{2+}	2-amino-4-(3-chloro-phenylazo) pyridine-3-ol	Orange to violet	1.6 ng mL^{-1}	[76]
Zn^{2+}	2-acetylpyridine benzoylhydrazone (2-APBH)	N/A	0.03 mg L^{-1}	[77]
Zn^{2+}	dithizone	N/A	8.0 x 10^{-9} mol L^{-1}	[78]
Cu^{2+}	Calmagite	Colorless to violet	0.07 µg L^{-1}	[79]
Cu^{2+}	1-(2-pyridilazo)-2-naphtol (PAN)	Yellow to red/purple	0.1 mg L^{-1}	[80]

4. Immobilization Methods

The immobilization of ligands on matrix or membranes is one of the essential steps in the production of optical chemical sensors. Immobilization of the ligands occurs through physical or chemical (covalent) bonding methods (Fig. 9)[81]. Physical methods have issues of slow dye leakage, and the produced sensors have a relatively short lifetime. Meanwhile, the chemical techniques have reproducible reactions and a long shelf-life.

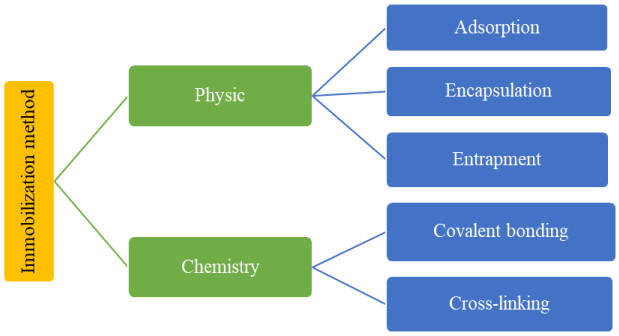

Fig. 9: Classification of ligand immobilization methods[81)]

4.1 Adsorption

Adsorption is a widely utilized technique in immobilizing ligands on sensor membranes. This method involves the physical adherence of the ligand onto the membrane surface through non-covalent interactions such as Van der Waals forces[82)], hydrogen bonding[83)], and electrostatic interactions. The primary advantage of adsorption is its simplicity and cost-effectiveness, as it does not require extensive chemical modification of the ligand and membrane. Furthermore, adsorption preserves the ligand's functionality and bioactivity, ensuring effective interaction with target metal ions.

Unlike other methods that might involve complex covalent bonding processes or the use of harsh chemicals that can denature the ligand, adsorption typically requires milder conditions, preserving the ligand's functionality. Additionally, adsorption allows for a high degree of control over the ligand density and distribution on the membrane, enhancing the sensitivity and specificity of the sensor. However, one notable drawback is the potential for ligand desorption under certain conditions, which can affect the sensor's stability and reusability.

4.2 Encapsulation

Encapsulation is one of the physical immobilization techniques used on the sensor surface. Typically, this method encloses or confines chemical reagents on the sensor surface within a semipermeable membrane. Encapsulation techniques in colorimetric sensors involve embedding the sensing elements in a protective matrix. This approach enhances the stability and functionality of the sensors by safeguarding the active materials from environmental degradation and potential interferences. Encapsulation can be achieved using various materials, such as polymers, including PVC [70,71,73–76,84–86)], cellulose acetate [64,87,88)], polycarbonate[89)], polyvinyl alcohol (PVA)[90–92)], polytetrafluoroethylene (teflon)[93)], sol-gels, or silica matrices which provide a controlled environment for the ligand or chromophore. This protective layer ensures the integrity of the sensor's active components, leading to improved sensitivity and selectivity in detecting heavy metal ions.

The primary advantage of employing the encapsulation technique for immobilizing ligands on membrane sensors lies in the enhanced stability and durability of the sensor. Encapsulation prevents the leaching of ligands, maintaining consistent sensor performance over time. Additionally, it offers protection against harsh environmental conditions, such as extreme pH, temperature fluctuations, and exposure to solvents. This stability is crucial for reliable and long-term monitoring of heavy metals in various applications, including environmental water quality assessment and industrial process control. Moreover, encapsulated sensors often exhibit reduced non-specific interactions, which minimizes false positives and enhances the overall accuracy of the detection process.

4.3 Entrapment

Recently, the entrapment method is a physical immobilization technique that has gained popularity. To trap the reagent inside, this method involves mixing the reagent with a monomer solution, which is then polymerized to create a gel or thin film membrane. The entrapment technique offers several advantages for the immobilization of ligands in membrane sensors. It enhances the stability and longevity of the sensor by protecting the ligand in the matrix, reducing its degradation, and minimizing leaching. This ensures consistent sensor performance over time.

Additionally, the physical confinement helps maintain the biological or chemical activity of the ligand. The localized environment provided by the immobilization enhances the interaction between the ligand and the analyte. It thus improves sensitivity and reduces non-specific interactions, thereby increasing selectivity. Furthermore, the technique is versatile and customizable. It allows the use of different polymers depending on the sensor's requirements. Besides, it enables the incorporation of additional functional groups to enhance sensor performance. Due to the simplicity and cost-effectiveness of the mixing and casting process and its compatibility with various ligands, the entrapment technique is preferred for developing reliable and efficient colorimetric sensors. The sol-gel technique is one of the entrapment strategies that is presently under development. As shown in Figure 10, this process generally entails the formation of sol-gel film at low temperatures and low-cost reaction [94)]. The glass membrane's pores can be made into the desired shape using this technique, which facilitates reactions between the analyte and the internal reagents.

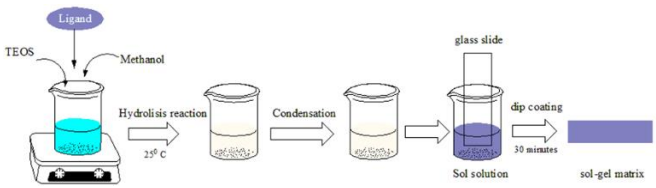

Fig. 10: Schematic of sol-gel matrix preparation

4.4 Covalent bonding

Covalent bonding is a well-known technique for immobilizing ligands on colorimetric sensors. This method involves the formation of stable covalent bonds between the ligand molecules and the sensing membrane, typically using chemical reagents. The immobilization process ensures that the ligand adheres tightly to the membrane surface, increasing the durability and reusability of the sensor. One of the critical advantages of covalent bonding is its robustness. The strong covalent bonds minimize ligand leaching during the sensing process, ensuring consistent sensing performance across multiple uses.

Furthermore, the covalent bonding can induce a more uniform and controlled distribution of the ligands on the membrane surface. It can further improve the sensitivity and selectivity of the sensor towards target heavy metal ions. The general principle behind chemical immobilization techniques is the formation of covalent bonds between reagent molecules and the active or functional groups of supporting materials, such as polymers[81]. This method can be used to create a matrix or membrane that is stable and resistant to leaching[37]. Aish et al.[95] successfully immobilized 2-(2-benzothiazolylazo) -3-hydroxyphenol (BTAHP) with covalent bonding in agarose membrane. The resulting membrane sensor was red with a long shelf life and a detection limit of 3.0×10^{-10} M.

Nazmi and Low[96] developed a novel colorimetric sensor for detecting mercury ions (Hg^{2+}). In their study, they immobilized a specific ligand, dithizone, on a cellulose acetate (CA) membrane through covalent binding. Immobilization was achieved by covalently bonding the C=O group of GA to the OH group of CA and/or NH of CS. This covalent bond not only increased the stability of the sensor but also provided a high sensitivity and selectivity to Hg^{2+} ions. The sensor showed a rapid color change in the presence of Hg^{2+}, allowing easy visual detection. The robustness of the covalent bonds ensures that the sensor can be reused multiple times without significant performance loss. It then demonstrates the practical advantages of this immobilization technique in environmental monitoring and industrial applications.

5. Data Processes

Several sensor materials cannot transmit electromagnetic radiation, and thus, the analysis of the resulting color cannot be done. The paper-based sensor materials can be analyzed using reflectance spectroscopy, as reported by Mizuguchi et al.[97]. They employed solid-phase reflection spectrophotometry to measure the color intensity (reddish-orange) produced by the sensor at a wavelength of 490 nm. The same method was also utilized by Sanchez-Pedreño et al.[98]. The membranes were placed into the manifold, and the reflectance of a heavy metal (Hg) was assessed at a wavelength of 560 nm.

For transparent materials such as sol-gel, PVA, and agarose, color analysis can be conducted using Spectrophotometer UV-Vis[99]. Meanwhile, another technique currently being developed is the use of digital image processing, such as smartphones[100,101] and laser scanner[59,102,103] to analyze the colors produced by sensors. Commonly, the sensor color is captured, and the RGB value is extracted using software, such as Image J, eye dropper, or other mobile Apps. The RGB intensities obtained are then transformed into Abs values by applying the Beer-Lambert law (Eq. 1)[104].

$$R_{B=} \text{-Abs} = \log\left(\frac{I_0}{I}\right) \quad (1)$$

In this case, I_0 is the intensity of white light, which is 255. Abs and I are the calculated Abs and intensity of the analyte solution in the chosen RGB channel at various analyte concentrations, respectively. The RGB values can also be converted using the ED (Euclidean Distance) (Eq. 2)[5]. ED values are calculated by subtracting the RGB values from the center of the sensor in the 'before' and 'after' images.

$$ED = \sqrt{(\Delta R)^2 + (\Delta G)^2 + (\Delta B)^2} \quad (2)$$

6. Conclusion and Perspective

This review briefly covers the recent advancements in the development and application of colorimetric sensors for detecting heavy metal ions in water. These sensors, which work based on color changes to indicate the presence of specific heavy metals, offer a practical solution for monitoring environmental pollution. The paper illustrates the critical role that various materials play in fabricating efficient colorimetric sensors. The materials include agarose, paper-based, sol-gel, and polymer, each offering unique properties and sensitivities towards different heavy metal ions.

The application of colorimetric sensors demonstrates a significant leap in environmental monitoring, offering a cost-effective, portable, and user-friendly alternative to traditional analytical methods. Their ability to provide on-site and real-time detection is precious in resource-limited settings and for rapid response scenarios. Furthermore, these sensors contribute to a better understanding of environmental pollution dynamics, enabling more effective management and mitigation strategies.

Primary heavy metals, including mercury, nickel, cadmium, lead, chromium, and copper, were highlighted due to their significant environmental and health impacts. Sensitive, selective, and easy-to-use methods to detect these metals in aquatic environments are several essential attributes of a sensor, underlining their harmful risks to human health and ecosystems. Sensors employ different immobilization methods and complex reagents, showcasing a diverse range of approaches to detect and quantify heavy metal concentrations. Overall, the

advancements in colorimetric sensor technology present a promising avenue for environmental monitoring, offering a balance between accuracy, efficiency, and accessibility. This progress is vital in addressing the growing concerns over heavy metal contaminations and their impacts on public health and the environment.

Future research in the field of colorimetric sensor technology for the detection of heavy metal ions should focus on enhancing the sensitivity and selectivity of these sensors. The development of multi-analyte sensors capable of detecting multiple heavy metals in complex matrices simultaneously is crucial. Additionally, research should explore the integration of nanomaterials and advanced polymers to improve response times and detection limits. There is also a need for robust, field-deployable sensors with built-in data logging and wireless communication capabilities for real-time monitoring. Finally, efforts to reduce the environmental impact of sensor materials and increase their biodegradability will further align this technology with sustainable practices.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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