Optical Fiber Sensor for Heavy Chemical Detection: An Overview

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Abstract. Heavy metal contaminations such as mercury, lead, arsenic, cadmium, and zinc are becoming more serious and have become a hazard to human health. Due to their non-biodegradable nature, they can easily accumulate in the environment and cause toxicity even at low concentrations. Therefore, detecting the presence of these metal ions requires a highly sensitive sensing method. Traditional detection methods, such as electrochemical analysis, require complicated sample preparation, are costly, and typically require a lengthy measurement period. These days, optical fiber sensors have been acknowledged due to their unique characteristics such as compact size, high sensitivity, low cost, high flexibility, and immunity to electromagnetic interference. An overview of an optical fiber sensor technology for heavy chemical measurement is discussed in this paper. The sensing mechanisms are summarized, as well as the chemical water quality parameters and sensitivities.

1. Introduction

In recent years, the environmental degradation is crucial due to global development and enhancement of population, leads many researchers to investigate the negative impact as well as the solution such as for global warming, climate change, and species extinction [1]. One of the major factors is water source pollution. As we know water is vital source not only for human, but also for major species including animals and plants in the world. Most of developing countries like Malaysia is dependent on the conservative process of collecting water samples and water analysis [2-3]. Based on the river analysis in Malaysia, 150 out of 646 rivers in Peninsular Malaysia have been classified as polluted [4].

Many methods have been reported for water monitoring measurement and still, the most used due to accuracy and reliability is electrical conductivity devices [5]. However, this equipment can be significantly expensive, exhibits high power consumption and requires a professional person to handle the operation. Moreover, this technique is susceptible to electrical interference and does not consider...
other contents that affect water density but do not conduct electricity. Thus, a simple and cost-effective optical fiber sensor is chosen besides other advantages such as being immune to electromagnetic interference, compact size of design, high sensitivity, safe in hazardous environments and high durability against water corrosion [6]. This optical fiber is boosting a large researcher's attraction for wideband amplifiers, pulsed fiber laser from micro- to femtoseconds speed either in bright or dark pulses, and various types of fiber sensor development [7-11].

Thus, in this paper, we discussed various types of an optical fiber sensor for heavy chemical detection that purposely for river water monitoring. The sensitivity for each sensor is also elaborated with the specific heavy chemical such as Mercury (Hg), Nickel (Ni), Plumbum (Pb) and Ferum (Fe).

2. **Heavy chemical effects to human’s health**

The most common heavy metals contaminants found in river water are mercury, lead, arsenic, chromium, cadmium, and zinc. These heavy chemicals are very dangerous to the human body and able to abolish the entire aquatic population. Mercury usually comes from instrument factories, coal burning, cosmetics waste, smelting process and salt electrolysis [12]. It can cause damage to the brain, kidneys and developing fetus. Thus, World Health Organization (WHO) has stated that there should only be 0.006 mg/L of mercury in drinking water [13].

Lead contaminants originate from various paints, cosmetics, hair dyes, gasoline, batteries, smelting, tableware, and coal. The maximum amount of lead that is safe to humans is 0.1 mg/L [13]. Excessive intake of lead can harm humans brain cells, cause mental retardation, brain death and dementia for elderly [14]. Activities such as mining, glass production, arsenic raw materials for pigments and papers can cause arsenic contamination if not properly handled.

WHO stated that the maximum amount of arsenic that can be consumed by humans is 0.01 mg/L at most [13]. Arsenic or arsenic compounds can lead to digestive and cardiovascular illnesses, harm to the nervous system, liver and skin cancer [15]. Chromium can cause numbness of limbs, ulcers, and mental disorders and thus only 0.05 mg/L are allowed in drinking water [13]. Chromium usually originated from cosmetics, leather preparations, tanned leather, chrome-plated metal parts, rubber, and ceramic raw materials [16]. Other contaminants that can be found in river water is cadmium.

It comes from waste activities in freshwater such as coal, mining, smelting and chemical industries and can cause renal dysfunction, cerebrovascular disease, high blood pressure and destroy the bone calcium. Thus, only 0.003 mg/L are allowed to be consumed by humans. Other than that, zinc also can be found amongst the contaminants. Zinc that mostly are from fertilizers, mining, steel processing and coal and waste combustion can cause stomach cramps, skin irritation, vomiting, nausea, anemia, causing respiratory disorder, and damage to the pancreas. It is advised not to take more than 5 mg/L [13].

3. **Optical fiber sensor for heavy chemical detection**

Table 1 shows the various optical sensor methods for different chemical measurements in water. Interferometer-based sensors have been commonly used for heavy metals detection. Z. Q. Tou et al. proposed an interferometer-based sensor using a photonic crystal fiber (PCF) that sandwiched between two single mode fibers (SMF) [17]. Impregnation and encapsulation technique were used to coat polyvinyl alcohol (PVA)/PAA hydrogel film on the PCF surface. 5-amino-8-hydroxyquinoline was modified chemically to allow Nikel ions (Ni$^{2+}$) been sensitive for detection. Then, a thermodynamically stable complex will be produced which decrease the volume gel and increasing the gel of refractive index on the surface of fiber, subsequently interference spectrum is shifted. The result from the experiment showed that the sensitivity of the sensor was 0.214 nm/uM.

Fiber grating utilizes the fiber materials photosensitivity in order to produce phase grating spatial in the core of fiber. The aim is to change periodically the refractive index of the core fiber in the specific grating area. J. Du et al. was successfully to fabricate a long period fiber grating (LPFG) with 25 mm long and 320 um period on normal SMF based on liquefied gas inscribed etch process [18]. Periodic mesoporous organosilica (PMO) films was grafted with selective ligand to perform as Lead ions (Pb$^{2+}$) sensitive films. This PMO will open and harmonize pore structure to allow metal material absorption.
Then, the film refractive index will be harmonizing matched closely to the fiber cladding refractive index, and thus lead concentration is sensitive to be detected. It is revealed that the sensitivity is about 2.072 nm/μM.

Table 1. Various types of fiber sensors and measurements.

| Title & Citation | Method | Sensitivity | Chemical Measurement |
|------------------|--------|-------------|----------------------|
| Poly (vinyl alcohol) hydrogel based fiber interferometer sensor for heavy metal cations [17] | Interferometer based sensor coated with polyvinyl alcohol (PVA)/PAA hydrogel film | 0.214 nm/μM | Ni²⁺ |
| Periodic Mesoporous Organosilica Films: Key Components of Fiber-Optic-Based Heavy-Metal Sensors [18] | Fiber grating-based sensors grafted with Periodic mesoporous organosilica (PMO) films | 2.072 nm/μM | Pb²⁺ |
| Surface Plasmon Resonance based fiber optic sensor for mercury detection using gold nanoparticles PVA hybrid [19] | Localized Surface plasmon resonance (LSPR) optical fiber sensor coated with gold nanoparticles-polyvinyl alcohol (PVA) complex | - | Hg²⁺ |
| Optical fiber-based heavy metal detection using the Localized Surface Plasmon Resonance technique [20] | Localized Surface plasmon resonance (LSPR) optical fiber sensor coated with gold nanoparticles | 0.28 nm/mM | Pb²⁺ |
| A Fiber-optic Sensor Based on Plasmon Coupling Effects in Gold Nanoparticles Core-satellites Nanostructure for Determination of Mercury Ions (II) [21] | Localized Surface plasmon resonance (LSPR) optical fiber sensor coated with gold nanoparticles | - | Hg²⁺ |
| Chitosan/poly(acrylic acid) based fiber-optic surface plasmon resonance sensor for Cu²⁺ ions detection [22] | Surface plasmon resonance (LSPR) optical fiber sensor using Tapering method coated with gold film and chitosan | 0.1184 nm/μM | Cu²⁺ |
| Ratiometric fluorescence sensor for Fe³⁺ ions detection based on quantum dot-doped hydrogel optical fiber [23] | Ratiometric fluorescence sensor coated with thioglycolic acid and graphene quantum dots | - | Fe³⁺ |
Surface plasmonic is a technique occurred between metal and dielectric interface that widely used for monitoring the analytes testing in the biochemical measurements. The plasmonic fiber sensors have many advantages such as high integration capability, small volume, and real-time remote monitoring and detection compared to the conventional method of prism-based plasmonic sensors. D. Raj et al. presented a surface plasmon resonance (SPR) fiber sensor with gold nanoparticles-polyvinyl alcohol (PVA) complex to enhance the sensitivity of Mercury ions (Hg$^{2+}$) [19]. A plastic-coated quartz fiber with 630 um fiber diameter and 600 um core diameter is used for the sensor development. Figure 1 illustrated the schematic diagram of experimental configuration. A sensitive surface area where the cladding is removed at about 3cm was coated by thermal evaporation. The SPR spectrum will be shifted and induced when gold embedded in PVA is contacted to Hg$^{2+}$ ions. The result from the experiment showed the detection limit was 1 μM but no sensitivity result is stated.

A reflection-based localized surface plasmon resonance (LSPR) fiber-optic sensor was demonstrated by P. Dhara et al. in 2019 to detect Pb$^{2+}$ ions [20]. Gold nanoparticles have been immobilized using self-assembling method on the surface of optical fiber with 1,1-Mercaptoundecanoic acid to increase the sensitivity towards Pb$^{2+}$ ions. The heavy metal concentration can be determined using the correlation between LSPR resonance shift wavelength and binding rate. Ethylenedinitrilotetraacetic acid was used to remove the bound of heavy metal ions and the Pb$^{2+}$ ion sensitivity of the sensor was 0.28 nm/mM.

S. Jia et al. proposed using the same method of LSPR fiber sensor for Hg$^{2+}$ ions measurement [21]. This method was based on the gold nanoparticles plasmon coupling effect that linked to a specific Mercury ions and thymine (T)-rich DNA hybridization. The fiber sensing probe is fabricated using a multimode fiber (MMF) with 600 um core diameter of fiber. Electrostatic self-assembly process was used to coat gold nanoparticles on the sensitive area of fiber to allow LSPR excitement. A reflective silver film was produced at the end of the fiber by the silver mirror reaction and then, it will be reflecting the signal light to enable sensing reflection. The result from the experiment showed the detection limit was 3.4 nM whereas the sensitivity was not reported.

A surface plasmon resonance fiber optic based on tapering method for Copper ions (Cu$^{2+}$) measurement was successfully presented by Ding et al. in 2019 [22]. Two identical MMFs were used with a length of 1.6 cm tapering no-core fiber spliced in between of the fibers. A 1.5 cm long of the fiber coreless was spliced in between of the two MMFs using an electric arc splicer before it was heated by a tapering flame equipment to be stretched up to 1.6 cm. A gold film and chitosan were fabricated to coat the outer face of the no-core fiber tapered. The gold films will stimulate the surface plasmon waves and creating the sensitivity of sensor for Cu$^{2+}$ ions measurement. It was observed that low concentrations will give the best sensor performance whereas the increasing concentration cause the decreasing sensitivity. The Cu$^{2+}$ ions concentration was ranging between 0.2 to 50 um to achieve 0.1184 nm/µM sensitivity.
Finally, fluorescence effect sensing concept for heavy metal detection was produced from operationalized molecules on the fiber sensor, in order to develop non-covalent bonding or changes in chemical reaction, and thus photophysical properties change of the fluorescent chromophore was induced. Then, the fluorescence signal changes will be recognized and detect the heavy metal ions. M. Zhou et al. was demonstrated the Cadmium Telluride (CdTe) doped with hydrogel for Ferric ions (Fe$^{3+}$) detection [23]. A green emissive thioglycolic acid capped graphene quantum dots (gQDs) coated the fiber sensitive area to quench selectively Fe$^{3+}$ ions with a red emissive N-Acetyl-lysine capped QDs (rQDs) that immunized against Fe$^{3+}$ ions. By measuring the ratio of fluorescence intensities of two QDs, the detection limit was 14 nM but again no sensitivity result was reported.

**Conclusion**

In this paper, the current research of heavy metal ion sensors based on optical fiber technology was briefly reviewed. Various sensing methods such as Interferometer based sensor, Fiber grating-based sensors, Localized Surface plasmon resonance (LSPR) and Ratiometric fluorescence sensor were presented. Thus, the surface plasmon resonance concept with tapering method achieves the best sensitivity for chemical detection with 0.1184 nm/µM measurement.

Water quality monitoring are essential especially freshwater for the life of human, animals and plants in this world. Therefore, there are many papers on heavy metal ion sensors for monitoring were published, however their sensitivity results of sensor are often neglected and not included. In fact, the sensitivity of the sensors is important to know the sensor’s performance and accuracy. It also will allow other researchers to study and investigate these sensors to make an improvement for the future sensing development.

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