Mercury Detection in Marine Environment using Electrospun Nanofibers as Colorimetric Sensor

Dr. Blesslin Sheeba, Dr. V. Nandagopal, Dr. P. Rajalakshmy, T. Kesavan and Aneesh Kumar A. G.

1 Professor, Department of ECE, R.M.K. Engineering College, Kavaraipettai 2 Professor, Department of Electrical and Electronics Engineering, Er. Perumal Manimekalai College of Engineering and Technology, Hosur 3 Assistant Professor, Robotics Engineering, Karunya Institute of Technology and Sciences, Coimbatore, 4 Assistant Professor, Sri Krishna College of Engineering and Technology, Coimbatore, 5 Deputy Manager, VVM Core, Reliance Pro& Prop ManSer Ltd.

1 tbs.ece@rmkec.ac.in, 2 nandhu050577@gmail.com, 3 rajalakshmy@karunya.edu, 4 kesavant@skcet.ac.in, 5 aneeshisin@gmail.com

Abstract. Potable water from sea/ocean is becoming contaminated at a fast rate and there is need for monitoring this rate of contamination. There are a number of pollutants that cause contamination, harming aquatic and marine environment. Detecting this water pollutant has become a major concern in recent year and this paper proposes a novel solution to identify specific pollutants (Arsenic and Chromium) in water. Nanomaterials have been identified to have higher sensitivity, quick recovery, faster response and ease of design when compared to other materials used. The proposed work uses electrospun nanofibers to detect the presence of mercury which is a heavy metal ion, in marine water. Electrospun nanofibers exhibit many features like easy functionalization, porous nature, large surface area, quick response and enhanced selectivity and sensitivity. To detect mercury ion, an electrospun nanofiber-based sensing platforms is devised and the observations are recorded.

Keywords: Materials, Sensor, Nanofiber, Water pollutants, Biological contaminants, Heavy metal ions

INTRODUCTION

Survival of humankind depends on the balance of ecosystem. However, human beings have been disturbing this balance of nature in the venture to drive economic and industrial growth. One such driving force of nature which is deeply affected by us is water. There are various water pollutants that corrupt the water bodies and thereby affect potted water that is used by us. Detecting this water pollutant has become a major concern in recent year and this paper proposes a novel solution to identify specific pollutants (Arsenic and Chromium) in water. Research has shown that due to high surface to volume ration, nanomaterials are highly favoured in detecting these pollutants are hence used in sensor fabrication [1, 2]. Nanomaterials are found to be highly sensitive because of the exposed surface atoms, which are large in number. To manufacture the sensor material, nanofiber which can be easily fabricated and manipulated to produce sensors is used [3]. Moreover, his method is also economical to use as it involves non-expensive instruments are require conventional microelectronics manufacturing devices for fabrication purpose. Nanofibers of different composition, size and shape offer exquisite and unique catalytic, optical, physic-chemical and electronic properties. Depending on the types of pollutants, the detection method using nanofiber will vary. There are three
broad classifications of water pollutants namely Heavy metals, biological contaminants and organic compounds. The Sensors built using nanofibers will play a crucial role in monitoring water pollution.

1. LITERATURE SURVEY

A metal that is available in abundance in earth’s crust is Iron (Fe), occurring in many oxidation states where Fe(III) and Fe(II) are the common content found in water. In neutral pH, FeHCO₃, Fe²⁺ and Fe(OH)₃, are the species observed in water. Living organisms require iron to function normally. However overload of Iron as well as deficiency of iron will cause harmful effect on animals, plants and human being alike. Lead is one of the naturally occurring elements on earth, detected in low concentration in water and soil [4]. Pb occurs in two oxidation states namely 2 and 0, where Pb²⁺ is in a more reactive form. When compared with other heavy metals like Cd, As and Hg, Pb is found in very low concentration in deep aquifers. Drinking water is contaminated by lead from various sources like household paint, vehicle exhausts and industrial wastes. When human beings are exposed to lead for a prolonged period of time, it will affect major body organs such as reproductive system, heart, haematopoietic, gastric and neurological system. It has also been identified in [5] that Pb has harmful effects on pregnant women resulting in miscarriages. Persistent bio accumulative toxin, Mercury (Hg), is observed less toxic in nature. However, when they present in water, the aquatic environmental bacteria will form methyl mercury from the mercury present, which is said to be highly toxic [6]. Mercury is accumulated in water through alkali processing, coal fired power plants and other harmful spills from industries. Mercury is also found in the volcanic eruptions which form sediments on the earth [7]. Similarly, Cadmium is also present in very low concentration which increases due to continuous use of phosphate fertilizers present in Cd, industrial waste water disposal, seepage from hazardous waste site and mining activities [8]. Now-a-days, well water is the primary cause of arsenic poisoning is over use of well water which will lead to damaged blood vessels, reduced production of RBC and WBC and sensation of ‘pins and needles” in feet and hands [9].

2. EXISTING WORK

2.1 Heavy Metal Ions Detection:

As the usage of electronic goods has scaled up dramatically over the past two decades, so have the induced heavy metal ions (HMI) pollution into the water. This has led to polluting the water environment, endangering living organisms and human beings who consume this water [10]. Exposure to HMI for a prolonged time will result in chronic or critical damage to the gastrointestinal system, reproductive system, immune system, central nervous system and the brain [11]. Fertilizers are identified to be the major source of HMI along with household electronic waste and chemical water from industries. The highest concern with HMI is that they have the ability to accumulate inside living organisms without any sign of degradation or decay with time. Chromium (Cr), Arsenic (As), Mercury (Hg), Cadmium (Cd) and Lead (Pb) are considered to be the heavy metals which are extremely toxic. When these HMI are consumed by living beings, they will cause severe health effect, despite their dosage.

Food, water and air are three major sources through which human beings are exposed to HMI. Hence detection of these heavy metals plays a crucial role in developing means to eradicate the detected HMI. Environmental Protection Agency (EPA), World Health Organisation (WHO) and European Union have identified the permissible limit in which they can be present in water and have deemed it as a priority substance that needs to be continuously monitored. The Table 1 gives the permissible limits of contaminants according to international standards. X-Ray Fluorescence Spectrometry (XRF), inductively coupled plasma mass spectroscopy (ICP-MS) and atomic absorption spectroscopy (AAS) are some of the spectroscopic techniques which are used to detect HM in water [12, 13]. These techniques can detect every low HMI concentration and are said to be highly sensitive. However, they are not economical as they require high end instrumentation. Colorimeter, Raman
spectroscopy, electrochemical sensing and optical methods which are comparatively less intensive HMI detection techniques are preferred [16].

Table 1 Permissible heavy metal contaminants level in marine and drinking water

| HEAVY METAL | DRINKING WATER (μg/l) | Aquatic fresh water (μg/l) | EPA |
|-------------|-----------------------|---------------------------|-----|
|             | WHO                   | EPA                       |     |
| Lead (Pb)   | 10                    | 15                        | 82  |
| Cadmium (Cd)| 50                    | 100                       | 570 |
| Chromium (Cr)| 3                     | 5                         | 1.8 |
| Mercury (Hg)| 6                     | 2                         | 1.4 |
| Arsenic (As)| 10                    | 10                        | -   |

3. ORGANIC CONTAMINANTS

Industries are the major sources of organic contaminants in water resources. Large quantities of aromatic hydrocarbon solvents and gasoline are released into the ocean and there are also reports on occasional oil spillage which will greatly affect water environment. Moreover, research shows that oil spillage will result in ground water contamination and aquatic life loss [14]. Chlorinated and aromatic hydrocarbons, insecticides, pesticides and volatile organic compounds are some of the common contaminants according to EPA. A common sensor that is sensitive to the analyte that is monitored is the sensors built based on Surface enhanced Raman spectroscopy. SERS sensing technique is also highly reviewed as a choice for detecting organic contaminants. SERS sensors are highly effective due to the optimum size offered by nanofibers for occurrence of surface plasmon resonance. In [15], Chamuah et al. depicted SERS using PVA fibers coated with gold. As depicted in the Figure 1, this is used as the substrate for SERS. Thiacloprid, quinalphos and deltamethrin are the three types of pesticides detected using this method. The sensitivity of nanofibres can be further increased by doping the material with TiO2 enhancing their organics detection activity.

Figure 1. SERS using PVA fiber coated with gold
4. PROPOSED METHODOLOGY:

The proposed work works on electrospun nanofibers to detect the presence of Hg$^2+$ and Cu$^2+$ ions in marine environment. The electrospun nanofiber is fabricated with rhodamin B derivative or pyrine derivative. The diagram shows fluorescent electrospun nanofibers fabrication process. Based on the synthesis, immobilization, electrospinning, sensor application and characterization, results have been recorded and observations have been made. Initially, poly (HEMA-co-NMA) is prepared followed by synthesis of rhodamine derivatives to sense Hg$^2+$. Electrospinning is used to fabricate the nanofibers using copolymers. This is followed by stability enhancement through cross linking. Three steps are involved in immobilizing the functional probe.

- The first step involves freeze drying the fibers followed by using hydroxyl groups to immobilize the fiber surface.
- The second step is exposing penta-fluorophenyl methacrylate amine-containing spirolactam (PPFMA) to surface grafting process which will trigger atom transfer.
- Finally surface fibers are incorporated with RhBN2 in a mercury-responsive probe known as Fiber-g-RhBN2 which serves as an excellent agent to identify the concentration of Hg$^2+$. 

Mercury contamination in estuaries and coastal regions are considered to be crucial as these contaminants can be transmitted to river waters which further carry them into the ocean. Studies show that reactive Hg deposits faster than elemental Hg thereby contaminating estuaries. In proposed work, FNFM materials are used to identify the level of Hg present in the water deeming it fit or unfit to be used by human beings. Polyacrylonitrile (PAN) nanofibers are used to prepare FNFM (Fluorescent NanoFibrous Membrane) which is highly sensitive. To detect the presence of mercuric ions (II), surface immobilization is carried out. This processed PAN nanofiber is used to detect Hg$^2+$ ions present in the water. It is found that this nanofiber has the ability to identify Hg$^2+$ in minimum concentration as required by WHO.
5. RESULTS AND DISCUSSION:

Based on the experimental analysis, it is found that the electrospun nanofibre has excellent selectivity towards Hg²⁺ when compared with the other heavy metal ions such as Pb²⁺, Na⁺, Mg²⁺, K⁺, Fe²⁺, Cd³⁺, Cd²⁺, Cu²⁺ and Zn²⁺, including PL intensity enhancement. It is found that Hg²⁺ is detected to have maximum and minimum limits at 10⁻²M to 10⁻¹M and 10⁻⁷M to 10⁻⁶M respectively. The EDTA is used to reverse fluorescence such that it can be used for a minimum of four cycles. Fig.4 shows the relative trend graph of P3.1.0 ES nanofiber.

Figure 4 a) Relative trend graph (I/I_{max}) of P3.1.0 ES nanofibers.
Figure 4 b) Reversibility of the Hg2+-dependent “on–off–on” fluorescence intensity profile of P3-1.0 ES nanofibers

Fig.4 b. indicates the effect of reversibility of Hg2+ in terms of intensity of fluorescence using P3-1.0.

Figure 4 c) Variation in the PL spectra of P3-1.0 ES nanofibers in aqueous solutions with different molarities of Hg2+ ions from 0 M to 10⁻³ M.

The variation in the PL spectra for the varying molarities of Hg2+ is observed in Fig.4.c.

6. CONCLUSION AND FUTURE SCOPE

Water is the basis essential for human existence and hence it is of utmost importance that its level of purity is monitored and saved from contamination. In order to prevent and remove these pollutants and implement remediation techniques, we need to diagnose and assess the type of pollutant and its concentration in water. Nanomaterials are found to be advantageous owing to their higher sensitivity, quick recovery, fast response, ease of design and field utilization. Nanofibers serve as a viable and attractive material for monitoring water pollutants as futuristic sensing devices. There has been good progress in the development and design of colorimetric sensor platforms because of the unique features offered by electrospun nanofibers which led to optimized detection of Hg2+ ions. This proposed work focuses primarily on the detection of a single ion presence in the marine surface and
there is still need for detecting other heavy metal ions. Hence efforts need to be taken in the future to couple the advantages of functional probes and electrospinning to develop an advanced calorimetric sensor that is capable of differentiating and identifying a group of metals that may lead to harmful effects when present in marine water.

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