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Application of Molecularly Imprinted Polymer (MIP) - Sieve Sensorfor Removal of Mercury in Hospital Wastes

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Abstract: ***Healthcare facilities are under increasing pressure to eliminate mercury. The most common routes of exposure to mercury in the healthcare facility include inhalation of inorganic mercury vapour after a spill or accidental skin contact with mercury. Accidental spills of liquid mercury can increase the levels of mercury in the air or wastewater of a HCFs. Establishing protocols for proper cleanup of spills involving mercury is an on flow challenge in Healthcare Sector where Bio safety and Bioethics are first law to be followed for human safety. Molecularly Imprinted Polymers (MIPs) are synthetic receptors which have very beneficial properties in this regard for cleaning purposes as they are robust, low-cost, have a high specificity, and can even detect their target molecules in complex matrices.These polymers have affinity for the original molecule and have been used in applications such as chemical separations, catalysis, or molecular sensors. These are now finding high potential for removing mercury from the environment.***

Keywords: Health Care facilities, molecularly imprinted polymer, polyesters, semicarbazone, mercury

1. Introduction

The most common routes of exposure in the HCFs include inhalation of inorganic mercury vapor after a spill or accidental skin contact with mercury. Accidental spills of liquid mercury can increase the levels of mercury in the air or wastewater of a healthcare facility. For all these reasons, mercury spills in the HCFs has to be managed properly and effort should be made by adopting principles of reduce, re-use, re-cycle or recovery options or even eliminate the use of mercury in HCFs in a phased manner. [1-3]

Mercury-containing products can be found almost anywhere in the HCFs. Following are the main sources of mercury in health care facilities are Accident & Emergency Department, Dental Department, Endoscopy Department [4-7]. Some of the mercury based instruments used for diagnosis purposes by the health care facilities are as follows:

a) Thermometers (used for measurement of body temperatures);
b) Sphygmomanometers (used for measurement of blood pressure);
c) Dental amalgam;
d) Oesophageal dilators (also called bougie tubes);
e) Cantor tubes and Miller Abbott tubes (used to clear intestinal obstructions);
f) Laboratory chemicals (fixatives, stains, reagents, preservatives);
g) Medical batteries etc.

2. Risk of Mercury to the Environment

Any emission of mercury into the environment, even at very small concentrations, can pose a threat to human health because of mercury's tendency to become concentrated in animal tissue as it moves up the food chain due to ***bioaccumulation.***

Mercury is typically found in many areas in hospitals. Items such as thermometers, sphygmomanometers (blood pressure cuff), thermostats, switches, gauges, batteries, light bulbs, laboratory stains and solutions can all contain mercury. Mercury in broken or outdated equipment is often improperly discarded as red bag waste or trash and sent to the incinerator. Incineration causes mercury vapors to escape into the air, starting a trail of pollution with the smallest creatures at the bottom of the food chain ending with those at the top, like humans. Some rooms and offices may still have supplies of elemental mercury tucked away in a storeroom. This supply, especially if it is forgotten or poorly managed, exists as a potential risk to the environment, patients and employees and can be very expensive to clean up.[8-10]

3. Managing Mercury Practices

Traditional treatment processes are limited in their ability to remove emerging contaminants from water, and there is a need for new technologies that are effective and feasible. A review on recent research results on molecularly imprinted (MIP) and non-imprinted (NIP) polymers was given by Murray and Ormeci which evaluated their potential as a treatment method for the removal of mercury contaminants from wastewater. It also discussed the relative benefits and limitations of using MIP or NIP for water and wastewater treatment. Further, a review on use of advanced polymeric materials for metal ions including mercury was proposed by Shakerain et al.

Molecularly Imprinted Polymers are synthetic receptors containing recognition sites with a predetermined selectivity for various substances, ranging from ions, to neurotransmitters, proteins, and even whole cells [12]. Their specificty and selectivity towards their target molecule is similar to natural antibodies, but MIPs are superior in terms of their long-sterm stability, chemical inertness, and their ability to withstand extremes of pH and temperature .

4. Molecularly Imprinted Polymer

A Molecularly Imprinted Polymer (MIP) is a polymer that has been processed using the molecular imprinting technique which leaves cavities in polymer matrix with affinity to a chosen "template" molecule. Like plastic receptors the imprinted polymer grabs specific chemicals.These are synthetic polymers possessing specific cavities designed for target molecules. They are prepared by copolymerization of a cross-linking agent with the complex formed from a template and monomers that have functional groups specifically interacting with the template through covalent or noncovalent bonds. These work on the simple lock-and-key combinations. Molecular imprinting is, in fact, making an artificial tiny lock for a specific molecule that serve as miniature key. The process usually involves initiating the polymerization of monomers in the presence of a template molecule that is extracted afterwards, thus leaving complementary cavities behind. Subsequent removal of the imprint template leaves specific cavities whose shape, size, and functional groups are complementary to the template molecule. These polymers have affinity for the original molecule and have been used in applications such as chemical separations, catalysis, or molecular sensors.

The surface ion-imprinted poly(ethylene terephthalate)-semicarbazide (PET-SC) modified chelating fibre sieves (Hg-PET-SC) were prepared using Hg(II) as a template and formaldehyde as a cross-linker and showed higher adsorption capacity and selectivity for the Hg(II) ions compared with the non-imprinted fibres (NIP-PET-SC) without a template. The maximum limit of detection values for Hg-PET-SC and NIP-PET-SC were 60.05 µg/l and 24.51 µg/l, respectively using MIP-PET-SC-CNE and NIP-PET-SC-CNE sensors. The selectivity coefficient of Hg(II) ions and other metal ions on Hg-PET-SC indicated an overall preference for Hg(II) ions. Rebinding and cross-selectivity studies were also carried out using various divalent ions as interferents.[13]

Because of their predetermined selectivity, MIPs can be used as ideal materials in Health care sector. Especially, MIP-based composites offer a wide range of potentialities in biomedical waste treatment. But segregation of reusable and non-reusable mercury containing products, its recycling , proper handling and disposal of mercury, mercury-containing equipment, collected mercury spill and laboratory chemicals and establishing protocols for proper cleanup of spills involving mercury is an onflow challenge in Healthcare Sector where Biosafety and Bioethics are first law to be followed for human safety [14]

Taking an idea of using polymer sieves for chelation of Hg, this paper also focuses on the same technique trying to make it useful for treatment biomedical mercury waste management.

4.1 MIP development

Mechanism of formation of Hg^{2+} imprinted polymer has been given in Figure1.

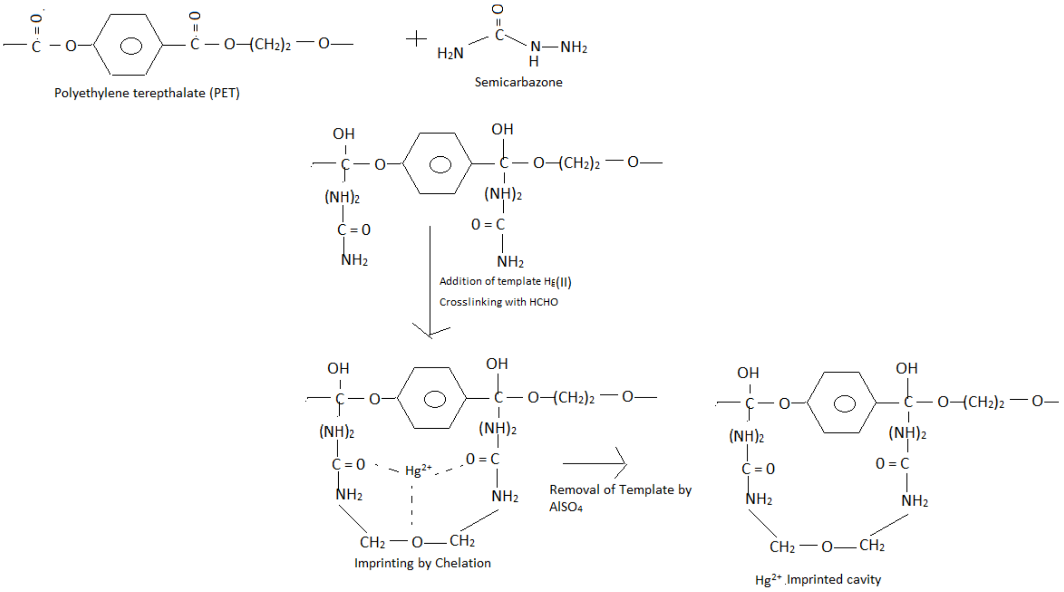
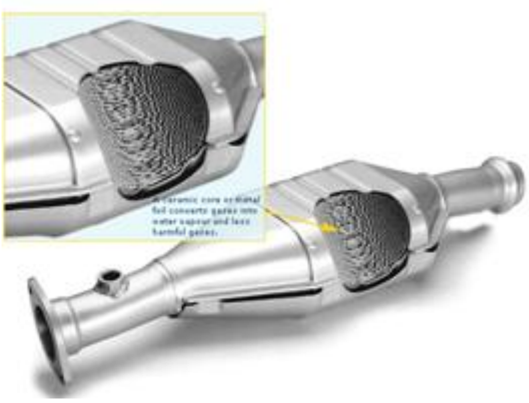


Figure 1: Mechanism of formation of Hg^{2+} imprinted polymer

4.2 MIP as Sieves

Polymers that have been imprinted can then be formed into a variety of materials, including nanoparticles, thin membranes, and gels, which can be used to make a filter.This is because of their porosity and large surface-area (Figures2 and 3). The filter can be applied in many ways[15]. If a membrane is produced to absorb pollutants in a liquid medium, it can be coated on a large surface area screen which can be replaced. For Gases, more surface area is required.Large catalytic converter style filters can be made to maximize contact between the gas molecules and the filter itself [16].

Here, the interior of a sieve has a huge amount of surface area for a relatively little size.



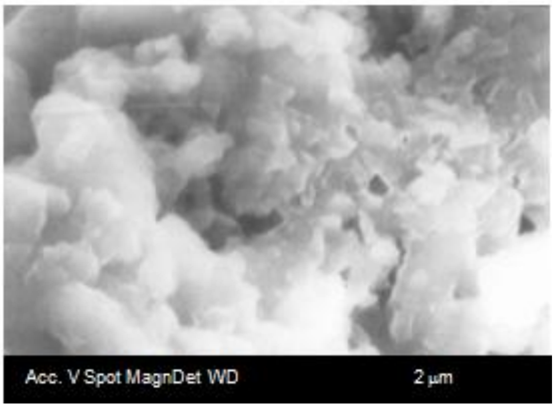


Figure 2: Development of molecularly imprinted sieves**Fig.3.**SEM image of MIP

4.3 Sensor Development

Taking cognizance of difficulty in developing ultra-thin layer coating of MIP (Hg)-film to enhance mass-transfer kinetics on the modified solid-electrodes,, in developing a micro-phase film inwardly exposed and accessible at electrode surface to recapture analyte unhindered, and in enhancing the LOD to ng mL^{-1} range. Carbon nanotube electrodes (CNE) have self-adsorptive characteristics rendering high stability and reproducibility with stable MIP (Hg)-DMF casting solution. Since CNE used was preanodised at +0.4 V (vs. Ag/AgCl), the additional forces allowing firm adherence of film onto a minute mercury drop were coulombic interactions at electrode / film interface through electron-rich functionalities (>C=O, $-NH_2$ and ring nitrogen) in the similar fashion as shown in Fig. 4 and 5. The stability of MIP (Hg) cavities and their molecular recognition characteristics remained unaltered during film coating, template retrieval, and binding-rebinding processes .The preanodisation helped electrocatalytic action of the electrode by generating carbonyl, carboxylate and hydroxyl radical species through consumption of dissolved oxygen of the cell content; and therefore, the catalysedvoltammetric response with this electrode could be feasible even in the absence of supporting electrolyte and deaeration of the cell content [17].

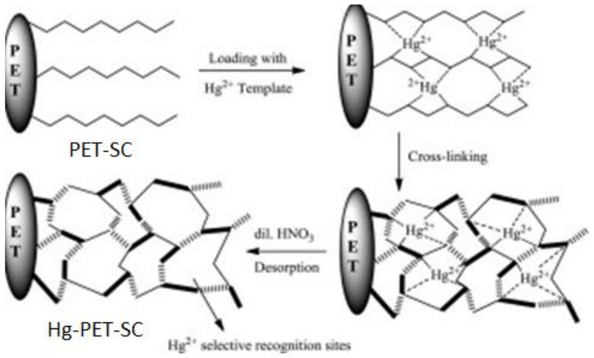


Figure 4: Graphical representation of MIP- sieve sensor: Absorption and Desorption

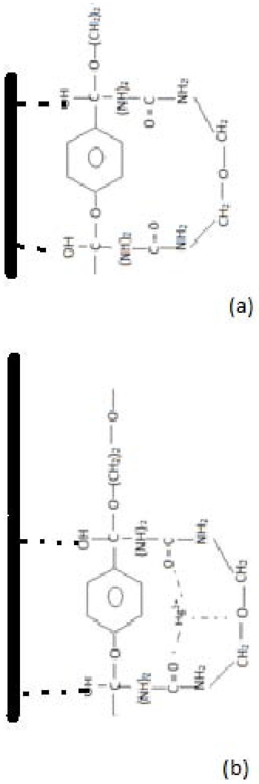


Figure 5: (a) MIP (Hg) coated CNE (b) MIP-Hg rebinded-CNE

Voltammetric Detection

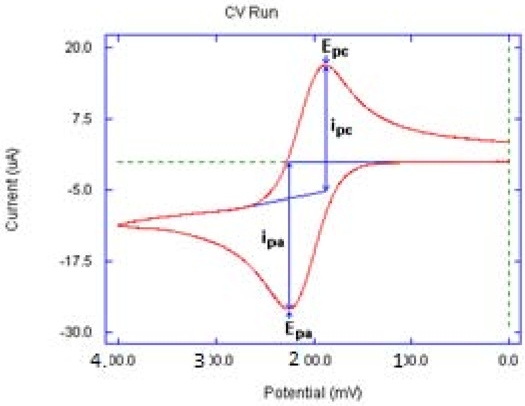


Figure 6 (a): Cathodic stripping cyclic voltammograms of Hg with MIP (Hg)-modified CNE. Hg accumulation potential: +0.8V (vs. Ag/AgCl); MIP (Hg) concentration:

450 µg mL^{-1}; deposition time of polymer: 30s; accumulation time of analyte: 60s;

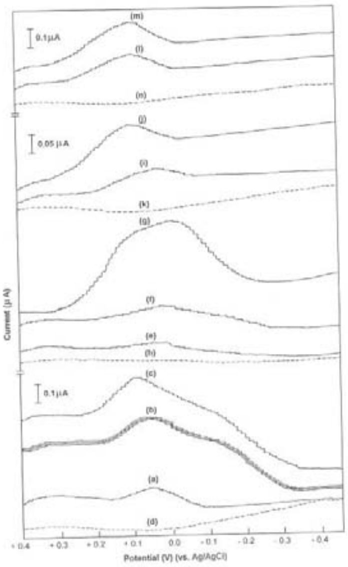


Figure 6 (b): DPCSV measurement of Hg with MIP(Hg)-modified CNE in aqueous samples [various Hg concentration (µg mL^{-1}): DPCSV with NIP(Hg)-modified CNE

Optimisation of analytical parameters for cyclic as well as differential pulse cathodic stripping voltammetry was adopted from Prasad et al., As could be seen from CV runs (Fig. 6(a)), in stripping mode at 300 mVs^{-1}, obtained at MIP(Hg)-modified CNE sensors, confirm the reproducibility of the modification process.

5. Rebinding and Cross-selectivity Studies

The rebinding and cross- selectivity studies were carried out with sieves using MIP as well as NIP coating using bivalent Ca^{2+} and Mg^{2+} ions.

The diluted water sample when passed through MIP-sieve rebinded Hg^{2+} selectively which was confirmed by Mercury Test Kit for Drinking Water (Boris'),

The cross-selectivity studies, showed very good selectivity of MIP forHg^{2+}, but not that for Ca^{2+} and Mg^{2+} ions, as shown in this figure. To confirm this, separate confirmatory tests for Ca^{2+} and Mg^{2+} ions using NaOH and further proceeding with EDTA titrations were performed.

However, there was a chance of false positives using NIP sieve as is shown in figure7.

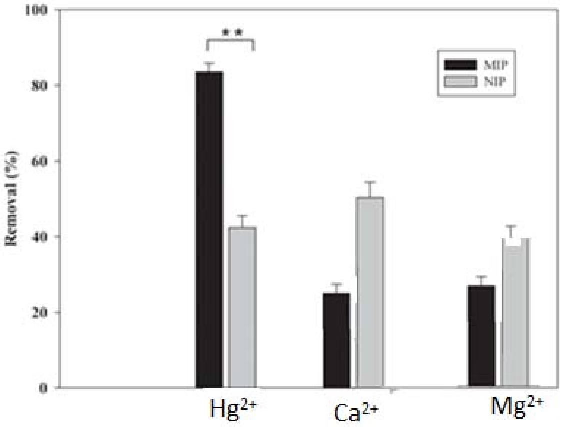


Figure 7: Rebinding and cross-selectivity studies using MIP/NIP with other metal ions

The maximum adsorption capacity values were found out using Boris' mercury test kit for Hg-PET-SC – CNE and NI-PET-SC – CNE were 60.05 µg/l and 24.51 µg/l, respectively.

6. Conclusion

The selectivity coefficient of Hg (II) ions and other metal ions on Hg-PET-SC indicated an overall preference for Hg (II) ions. However, there is the problem of false positives. Proper management of Hospital Pollution is still a challenge.

This process is reliable and cost-effective. But the sludge disposal is however hazardous and still a problem to be solved as it is non-biodegradable.

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