Fiber Optic SPR Sensor for Detection of Pb Ions utilizing Molecular Imprinting

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1. Introduction

The presence of heavy metal ions in contaminated water is creating lots of heath damage in livings species in last few decades. Most commonly used heavy metal ions are Cu^{+2}, Ni^{+2}, Pb^{+2}… etc. Taking into account of above, the detection of lead ions (Pb^{+2}) ions in contaminated water is important [1]. Molecular imprinting is a method used for the selective identification of templates. It creates binding sites or nano cavities in polymer which has complementary shape and size of the templates and recognizes the template molecule by key and lock model [2]. It has been used along with surface plasmon resonance (SPR) for the confirmation of the binding of templates with the polymer. SPR is a phenomenon which allows the real time detection of bimolecular interaction with the help of a p-polarized light. A sharp dip in transmittance spectra at a particular wavelength, called resonance wavelength, has been observed while satisfying resonance condition in SPR. If there exists a change in the dielectric nature of sensing medium, then a shift in resonance wavelength has been observed [3]. By measuring the shift we can observe the binding of template molecule with the polymer because the binding of template with the polymer produces the variation in the dielectric nature of the polymer.

In the present study a preliminary study on the fabrication and characterization of a fiber optic sensor for the detection of Pb^{+2} ions utilizing SPR and molecular imprinting has been reported. To fabricate molecularly imprinted polymer (MIP), $Pb(NO_3)_2$ is used as template molecule. When template molecule near the vicinity of the MIP, it binds with the imprinted sites which causes the shift in resonance wavelength is recorded while recording the SPR response of the fiber optic probe. The proposed sensor operates in the concentration range of 10^{-9} M to 10^{-4} M of Pb^{+2} ions. The proposed sensor has various advantages such as low cost, fast response and capability of online monitoring and remote sensing.

2. Probe fabrication and Experimental Setup

For fabrication of fiber optic probe, 1cm long portion of a 17 cm long plastic clad optical fiber has been uncladed by a sharp blade. The unclad portion is then cleaned by acetone and methanol several times. Then the unclad portion is coated by a 40 nm thick Ag film using thermal evaporation method. The MIP having Pb^{+2} as template is coated over Ag thin film using dip coating method. For the preparation of MIP, Pb^{+2} ions are used as template, methacrylic acid (MAA), trimethylolpropanetrimethacrylate (TMPTM), 2,2-azo-bis-isobutyronitrile (AIBN) and acetonirile (ACN) is used as functional monomer, cross-linker, reaction initiator and solvent respectively. The removal of template from the polymer is performed by washing of probe by 0.1 M HNO_3 several times. Finally probe is left overnight for drying. Solutions of Pb^{+2} ions having concentration range from 10^{-9} M to 10^{-4} M are prepared in de-ionized water for the characterization of probe.

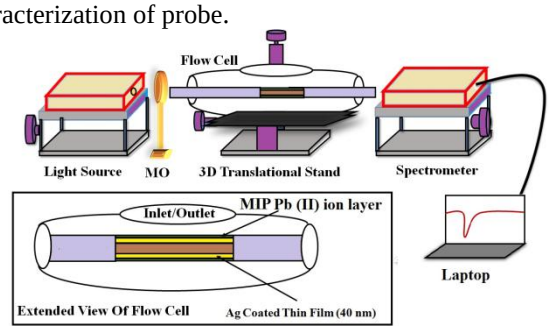

Fig.1 Schematic diagram of experimental set-up

Fig. 1 shows a schematic of experimental setup used for characterization of probe. A polychromatic light source is used for launching the light into the input end of the fiber. At the output end of the fiber probe a spectrometer is used to record the transmitted spectrum, which is interfaced with a laptop.

3. Results and Discussion

To characterize the fiber optic probe, the Pb^{+2} ion solutions of concentration range from 0M to 10^{-4}M are poured into the flow cell and their respective SPR response has been recorded one by one. SPR response shows a shift in resonance wavelength as the concentration of Pb ions increases. This shift in resonance wavelength is due to the binding of Ni ions to the imprinted binding sites present in the MIP. The shape and size of the binding sites is complementary of template which causes which is responsible for the selective binding of Pb ions with the polymer. This binding causes the change in the dielectric nature, thus refractive index of sensing region (MIP). The change in refractive index is recognized by the shift in resonance wavelength in SPR spectra.

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