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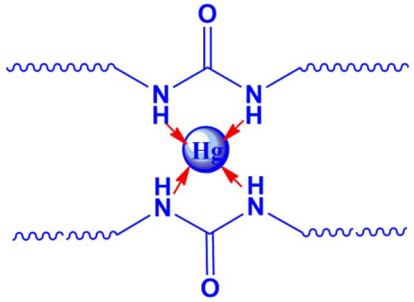
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A Detailed Perceptive on the Ecofriendly Polymer based Mercury Sensors

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Abstract: ***Investigation of mercury poison in aquatic environment is an immense area of research interest to the scientific community due to its role in chemical, industrial, food and toxicity. Most of the energy generation and metal refining power plants release mercury in to the aquatic environment and slowly converted to methyl mercury by bacterial action, which can induce serious neurological disorders to humans by consuming these sea foods. We report an ecofriendly amide polymer based sensor which acts as a sensor to trace mercury present in water, which makes the water free from such kind of toxic ion by simple binding. The sensor is prepared in such a manner that consists of a peculiar urea group on either end of the polymer. The metal-ion binding are analyzed through monitoring with nuclear magnetic resonance spectroscopy which clearly shows the shift for various anions to the core of the sensor. The solid- state demonstration of the cation guests by this versatile receptor could be useful in alkali-metal salt separation technology. Qualitative binding of mercury to the sensory group used to understand the solution-state behavior of ligand in the presence of this ion. Furthermore, targeting the binding of contaminant ion from dilute solution must be combined with UV-Visible spectroscopy to remove or concentrate the resultant complexes contaminants from the remaining solution. The addition of mercury to the aqueous solution of the polymer results in quenching of the absorption peaks which is directly proportional to the binding efficacy. Finally, the methodology provides a simple path for the sensing of toxic ion for on a large scale application. Compared to small molecule, polymers chains with multiple recognition elements can increase both the binding efficiency and recognition selectivity for specific analyses.***



Keywords: amphiphilic, ion sensors, toxicity, UV-Visible, receptor, absorption.

I. INTRODUCTION

Environment pollution essentially due to hazardous heavy metals and minerals (Cu, Cr, Ni and Hg) is an important communal problem due to its high toxic and nonbiodegradable properties. Recovery of such kind of toxicity from water is very complicated and creating more crucial issue due to their tendency to accumulate in body organs and providing prompt harmful effects to natural resources. Therefore it is essential to develop some novel techniques to selective removal of metal ions which are also eco-friendly and cost-effective to build a sustainable society. The entrapment of such crucial metal ions could be detected by several older technique including chemical precipitation, reverse osmosis, ion exchange, electrochemical treatment techniques adsorption, extraction, membrane filtration, irradiation and coagulation. Adsorption method is regarded as one of the most promising methods to trace heavy metal ions and have more predictable importance in environmental valuation. Macromolecules are very effective in analyzing the binding nature of heavy metal ions especially mercury. Due to its linking units and better swelling nature it can incorporate huge number of metal ions with it. Various polymers including branched, linear and amphiphilic block copolymers play a vital role and cost effective in tracing the metal ions from water resources. Researchers develop a huge number of various polymers with different architectures for such kind of projects. Wu and Cui recently reported a ultrasensitive microelectrode array based on shrinkable polymer to trace heavy metal mercury ion with simple fabrication and low cost.

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This methodology is very effective to detect ultra-low concentrations mercury ions and the heat-shrinkable film-based microelectrode arrays construction method can be applied to many fields. Abdi et al; reported a surface plasmon resonance sensing detection of mercury and lead ions based on poly(pyrrole-chitosan) conducting polymer composite. Thakare et al analysed a simple synthesis of highly selective and fast Hg(II) removal polymer from aqueous solution based on polymerizing aminothiophenol. Shirzadmehr et al; reported a new nano-composite potentiometric sensor containing an Hg^{2+} ion imprinted polymer for the trace determination of mercury ions in different matrices for the successful determination of trace amount of mercury. Sarkar et al; proposed a low-cost prototype device based on silver nanoparticle-impregnated poly(vinyle alcohol) (PVA-Ag-NPs) nanocomposite thin film for mercury detection.

Stimuli responsive polymers are the one that are highly effective with respect to the environment and also that can change their volumes drastically in response to various external physical and chemical stimuli. Currently, polyethylene glycol (PEG) and its aqueous solutions represent interesting solvent systems for solvent replacement, and may stand comparison to other newly favored systems such as ionic liquids, supercritical carbon dioxide and micellar systems. PEG's are chosen as most effective and ecofriendly in respect to other polymers due to inexpensive, biodegradable, non-halogenated and having low toxicity. The polyethylene glycol (PEG) is one of the water soluble polymers with high solubility and also acts a amphiphilic in nature after specific modifications to improve the permeability of ions in to the polymer recognition group.

In this work, we report a highly efficient, low-cost amide based polymer sensor capable of exhibiting a high selectivity for Hg^{2+} in the background of a wide range of competing heavy metal ions. We have utilized a bifunctional polymer matrix, which forms homogeneous thin film on a glass substrate. The sensing mechanism is found to be based on entrapment of Hg^{2+} on the polymer cage were the -NH -CO linkage form bonding with the mercury ions from water resources and acts as a mercury sensor. The possible interaction between mercury ions within the polymer matrix has been examined by NMR and UV-Visible studies. To the best of our knowledge, this is the first simple and inexpensive portable sensor and prototype device for Hg^{2+} ion detection in environmental water samples with very high selectivity even in the presence of other relevant transition metal ions.

II. MATERIALS

Polyethylene glycol 1500, Phenyl isocyanate, deutrated chloroform ($CDCl_3$) and deutrated dimethyl sulfoxide (DMSO d6) were purchased from Aldrich and used as received without further purification. Tetrabutylammonium chloride (TBACl), tetrabutylammonium fluoride (TBAF), tetrabutylammonium nitrate (TBAN) and tetrabutylammonium acetate (TBAAc) were purchased from Alfa Aesar chemicals and used as received. Dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) were purchased from Aldrich and SRL chemicals and distilled, before use wherever applicable.

III. INSTRUMENTATION

^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer. For NMR, DMSO d6 and CDCl3 were used as solvents, TMS as internal standard. IR spectra were recorded with a JASCO FT/IR-460 plus spectrometer, using KBr discs. The mass spectrum was performed using a GC-MS mass spectrometer (WATERS) with electrospray ionization. UV-Visible absorption spectra were measured on a Shimadzu UV-Visible 2550 spectrophotometer in the wavelength range of 200-800 nm at RT.

A. Synthesis of butyl -1-cyanoethylcarbonotrithioate

A 250 ml 3-neck round bottom (RB) flask (fitted with septum and reflux condenser with N2 bubbler) was charged with Poly(ethylene glycol) bis(3-aminopropyl) terminated in 15 ml of dimethyl formamide. The temperature of the mixture was maintained between 0 and 5 ºC.

Phenylisocyanate was added over 10 min to the RB flask and the mixture was stirred for 6 hrs. After the mentioned time period, the reaction mixture was filtered, washed with dichloromethane twice. The crude product of butyl -1-cyanoethylcarbonotrithioate as a yellow color solid. Yield of CTA: 85% 1H NMR (400 MHz, CDCl3, δ, ppm): 4.9 (q, 1H, -S-CH carbon), 3.4 (t, 2H, -SCH2 carbon, 1.8 (d, 3H, -SCH3 carbon), 1.7 (quintet, 2H, -CH2 carbon), 1.45 (sextet, 2H, -CH2 carbon), 0.95 (t, 3H, -CH3 carbon). 13C NMR (100 MHz, CDCl3, δ, ppm): 219.8 (C=S), 119.0 (C=N), 37.5 (S-CH2), 32.0 (CH2 carbon), 22.0 (–CH2 carbon), 16.0 (S-C(CH3) carbon), 13.0 (-CH3) carbon).

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IV. RESULTS AND DISCUSSION

The metal binding sensor is prepared by means of coupling reaction by reacting polyethylene glycol based colorimetric receptors and phenyl isocyanate in the presence of polar solvent at room temperature for the selective recognition of mercury. The detailed synthetic procedure and characterization data are given in the experimental data. The ^{1}H NMR spectra of the obtained sensor in DMSO d6 shows five prominent peaks at 8.63, 7.44, 7.28, 6.95 and 3.48 ppm respectively. These peaks corresponds to protons from the –NH, -CH, -(CH2)n groups and proves the structure elucidation of the synthesized sensor. The GC-MS mass spectrum of the sensor (shown in the Supporting Information) provides additional evidence for the structure. The synthesized polymer sensor are mediated in such a way that it is neither totally hydrophobic nor hydrophilic and deviated from completely water soluble nature. In addition it behaves as a amphiphilic character. Since poly(ethylene glycol) is covalently binded to phenyl isocyanate it should enhance the property of efficacy. Further the material is less toxic the environment and water sources and hence it is more suitable for aquatic environment. Therefore the synthesized sensor is more suitable for metal ion recognition which also possesses a reorganized bipedal cleft with amide NH protons suitable for the recognition.

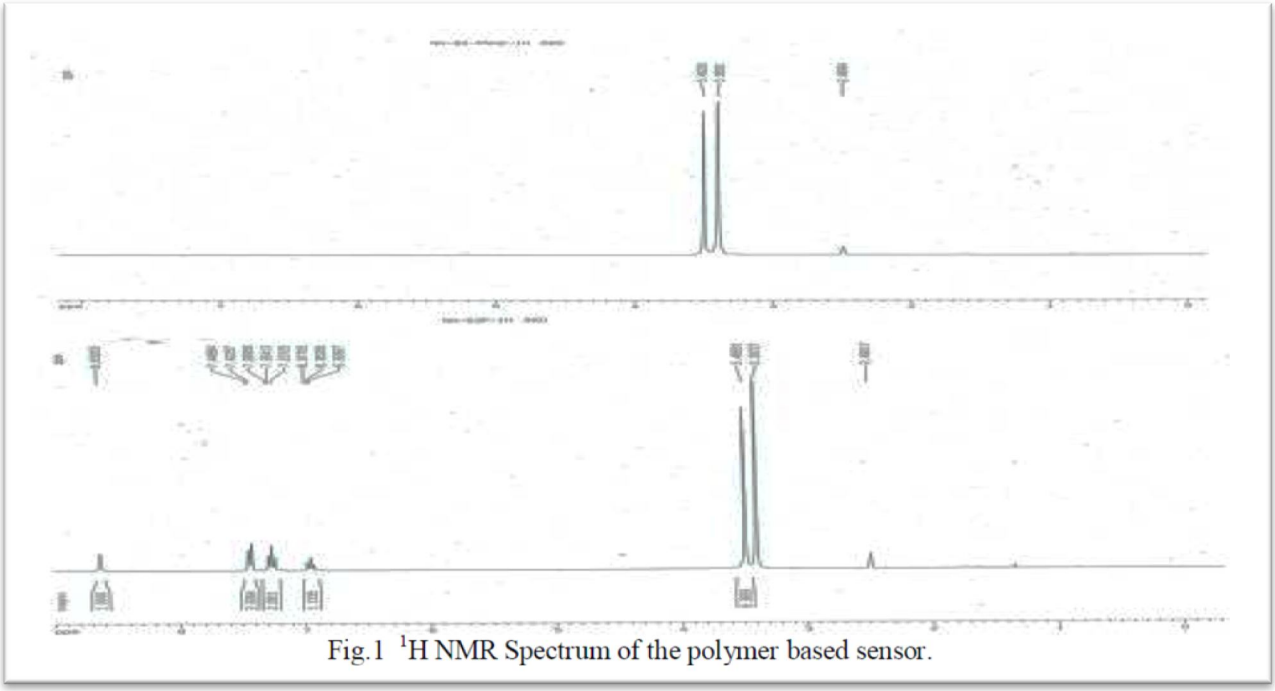


Fig.1 ^{1}H NMR Spectrum of the polymer based sensor.

Qualitative ^{1}H NMR experiments were performed with mercuric chloride to understand the solution-state behavior of the sensor (figs 1 and 2) in the presence of this metal ion. The addition of the sensor to the solution of mercuric chloride in DMSO-d6 results in a downfield shift of 1.22 ppm for the free chloride resonance, indicating the participation of the ion in hydrogen bonding with -NH of the receptor. The metal ion prefer to bind with the –NH group rather than –CH group as shown in fig.3 due to the affinity of the metal ion to the amine residue. The increased steric hindrance also has an effect on the solution phase binding. These results illustrate that the mercury with higher atomic size bind effectively with the polymer. The sensor binds mercury too strongly which can be measured by means of ^{1}H NMR methods. In general the binding affinity for any anion with the selected sensor is necessarily in the order of F- > Cl- > PO3- > Br- >NO3- > AcO^{-}. However in the case of metal ions the methodology is totally different from anion binding. The amide link holds the mercury in cage and withstands it for a longer period unless quenching is done. Even though the NMR observation of peaks shift is less either by up field or downfield, the information greatly helpful to predicts the binding of metal ion to the particular sensory group. The polymer is colorless and transparent in nature however by the addition of mercuric chloride the intensity of colour increase and turns to yellow which simply implies the bonding between the sensory amine groups with the mercury

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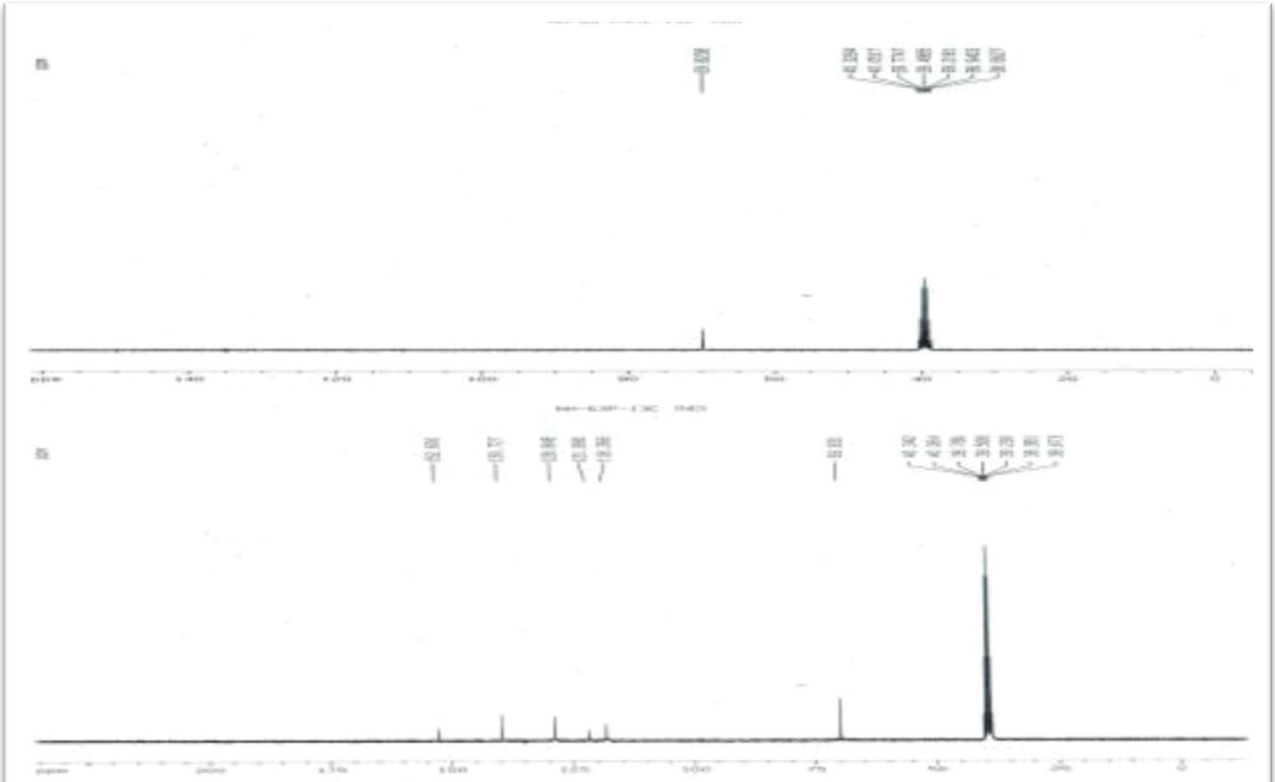


Fig.2 ^{13}C NMR Spectrum of the polymer based sensor.

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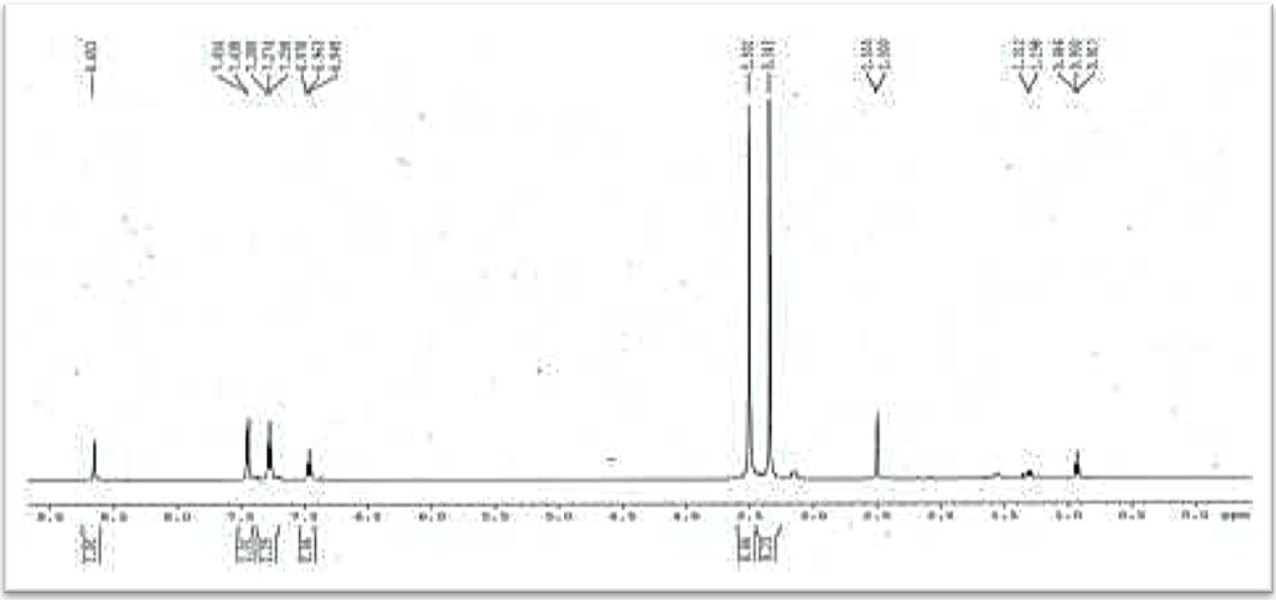


Fig 3. NMR spectrum of binding of metal ion with polymer

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The UV-Vis. Absorption spectrum is recorded for the polymers and its interaction with metal ions at the concentration of 10^{-5} mol/L (with respect to the molecular weight of the polymer) is shown in figure 4. The absorption spectra of the homopolymer and its binding interactions with metal ions are successfully monitored by UV-Vis. spectroscopy. The absorption band for the homopolymer shows two peaks. The one at around 320 nm is weak in intensity in compared to while that around 260 nm is broad and highly intense and is due to the large blue shift of the absorption from the polymer group.

The binding interactions were carried out in solution state using metal cation such as mercuric chloride. The binding interaction shows similar absorption bands but with shift in absorption regions and also there is an increase in peak positions. The binding efficiency of the polymers is monitored successfully by using different equivalents of metal ions which are shown in figure.

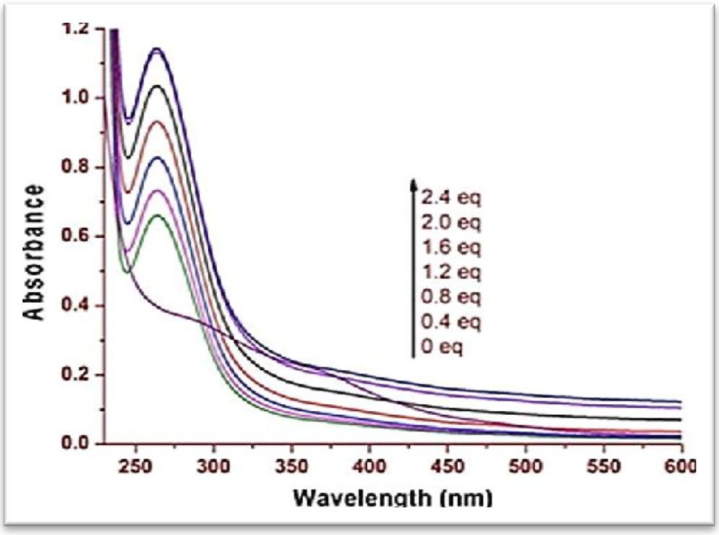


Fig 4. UV-Vis. Measurements on the interactions of polymer [1 $X10^{-4}$m) in water with mercury at different equivalents.

The binding interactions were carried out in solution state using metal cation such as mercuric chloride. The binding interaction shows similar absorption bands but with shift in absorption regions and also there is an increase in peak positions. The binding efficiency of the polymers is monitored successfully by using different equivalents of metal ions which are shown in figure. The spectra shows hyperchromism effect and the efficiency is more and better binding ability is reported at the equivalent of 1.2 as shown in figure 4. The enhanced binding efficiency is observed for mercury ion, which implies that amine is more pronounced to interact with mercury compared to other functional groups.

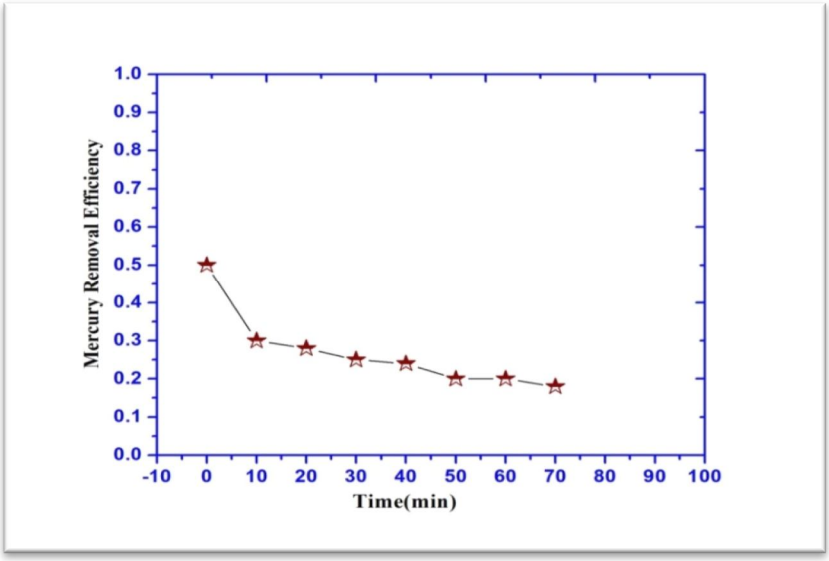


Fig. 5. Plot of mercury removal efficiency of the polymer vs. time in min.

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The mercury removal efficiency is monitored for the polymer sensor at different time period. The results obtained are shown in the figure 5. From the results it can inferred that at zero time the removal efficiency is 0.5 which implies that initially the addition of mercuric chloride to the aqueous solution of the polymers result in binding of the mercury to the polymer through amine linkage. Further monitoring that the efficiency of the binding is not increased much and it is almost nearer to zero time which implies that the binding of mercury is efficient with the proposed polymer sensor.

V. CONCLUSION

In this manuscript, we report a PEG based amide sensor for tracing toxic elements exclusively mercury. The anionic sensor prepared through polyethylene glycol which should considered being eco-friendly by reacting it with phenyl isocyanate in a polar medium without the necessity of any catalyst. The synthesized polymeric sensor is also confirmed through NMR and mass spectroscopic techniques. The polymeric sensor acts like an amphiphilic moiety that could be used for tracing mercury and the binding nature can be monitored through proton NMR and UV-Visible spectroscopy. The spectra shows hyperchromism effect in UV-Visible measurements and the efficiency is more with better binding ability at the equivalent of 1.2. The enhanced binding efficiency is observed for mercury ion, which implies that amine is more pronounced to interact with mercury compared to other functional groups. This method paves the way for the efficient removal of toxic elements exclusively mercury from water resources through eco-friendly media which is more helpful to the environment and also to reduce water pollution.

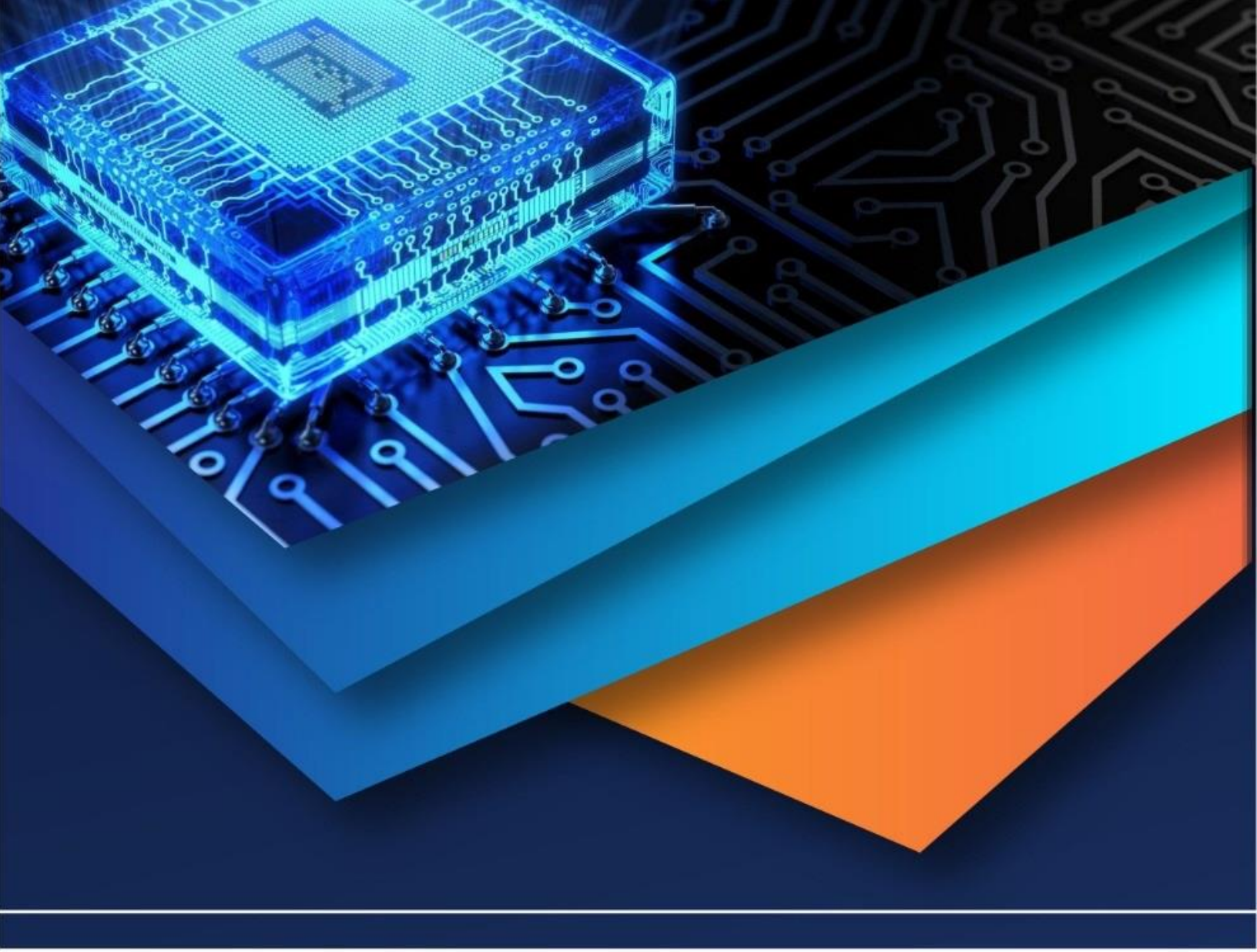
VI. ACKNOWLEDGEMENT

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