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Recent Trends in Chemsensor Evaluation: Techniques, Challenges, and Future Perspectives

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Abstract: Chemsensors have been playing a crucial role in various aspects of biomedical science, analytical and environmental chemistry. The toxic metal ions like Zn, Cd, Cu, Pb and Hg have increased gradually but now have reached an alarming situation, crossing the threshold value. Due to high toxicity of these heavy metals there is an obvious need for a sensor system to detect their presence. Chemsensors prove very promising as the system is rapid, selective, sensible, low-cost, easy-to-use, and has the ability to provide real-time signals.

An evaluation of various chemsensors known to us, proves their potential to serve human kind and therefore a deep and wide angle is required to cover these sensors.Apart from fluorescent, luminescent, optical,conjugate, gas, amide based chemsensors have also been developed. During recent times considerable efforts has been has been devoted to the synthesis of chemical compounds having the capability to sense or trap a particular toxic metal ion. A particular category of such compound being sterically encumbered selenium containing species. Due to large covalent radius and greater polarizability of selenium compared to Oxygen, Nitrogen & Sulfur which greatly influences the complexation properties of these compounds. Selenium containing hosts have been reported to display strong affinities with Hg^{2+} or Ag^{2+}(environmentally toxic metal ions). As confirmed by physicochemical data the presence of multiple soft selenium donor, the flexibility of the arms, steric bulk and open exterior geometry make these molecules potent tool for trapping Hg (II) selectively. Hence such tailored ligand and complexes could serve a great potential for trapping environmentally toxic metal ion and thus has application as sensors. The integration of sustainable materials and self-powered sensing mechanisms further enhances the applicability of chemosensors in real-world scenarios. This paper provides a comprehensive overview of current evaluation techniques, identifies major challenges, and discusses future directions for developing more reliable and efficient chemosensors.

Keywords: chemsensor, organochalcogen, polarazibility,sterically encumbered etc.

I. INTRODUCTION

Till today a great variety of sensors has been synthesized by man, few of which are those that allows us to detect chemical species, this particular type is called a chemical sensor, and is defined by IUPAC as, a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal (1). This device can be either macroscopic (e.g. a pH measuring electrode) or microscopic, it refers to the molecule (or an assembled supra-molecular unit) that could selectively bind the target analyte and furnish information about this binding, therefore acting as a microscopic chemical sensor.

Chemsensor are sensory receptor that transduces a chemical signal in to an action and have vast potential as detecting units and thus are continuously emerging as a tool for industrial, research, scientific and pharmaceutical markets. In this series a particular set of coordination compounds are also emerging as a potent tool in which chalcogen (O, S, Se &Te) containing compounds plays a significant role. Selenium is the element from chalcogen series which is a naturally occurring element considered a link between metals and nonmetals. It is found in nature in small concentration in rocks, plants, coal and fossil fuels (2). One of such sterically encumbered selenium compound, tetrakis(iso-propyl seleno methyl benzene) on complexation with Hg^{2+}, Ag^{2+}, Pb^{2+}& Cd^{2+} showed selectivity towards Hg^{2+} ions though coordination to selenium is not an exclusive feature for mercury. As confirmed by physicochemical data the presence of multiple soft selenium donor, the flexibility of the arms, steric bulk and open exterior geometry make these molecules potent tool for trapping Hg (II) selectively. There is a great potential in designing of sterically hindered organo-selenium molecule to bind environmentally toxic metal ion selectively. Hence such tailored ligand and complexes could serve a great potential for trapping environmentally toxic metal ion and thus has application as sensors. Thus, the most burning issue today of energy and environment are increasing the necessity of those sensors which can detect air pollutants in environment like SO_X, NO_X etc. as well as can be applied for control systems of combustion exhaust from stationary facilities and automobiles.

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II. ANALYSIS OF TOXIC (HEAVY) METAL IONS

There are a number of metal ions that play a vital role in our daily physiological life. Few of them are sodium (Na^+) potassium (K^+), calcium (Ca^{2+}), copper (Cu^+ and Cu^{2+}) and zinc (Zn^{2+}), among others. However, some metal ions such as lead (Pb^{2+}), cadmium (Cd^{2+}) and mercury (Hg^{2+}) are highly toxic and may cause serious health and environmental problems.

Anode stripping voltametry (3) & Surface Plasmon resonance spectroscopy (4, 5) are two of the established technologies for sensitive and selective detection of metal ions and other electrochemically active substances.

Heavy metal poisoning due to various contamination is a matter of serious concern all around the globe. Sample collection and their laboratory analysis is the traditional approach to detect toxic metal ion which suffers from various disadvantages for it being expensive, inconvenient, time consuming and also prone to errors during sample collection, transportation and handling. However today number of portable devices like X- ray fluoroscence, voltametry etc. are there which could help in such detection but again they are not widely used because of technical and other limitations. In developing country like India there has been an urgent need of low cost, easy to use and reliable device which could be used in medical diagnostics, environmental monitoring of heavy metal poisoning.

Mercury being a heavy-metal with environmental and physiological toxicities that are recognizable even at very low concentration. Long-term exposure to this metal leads to permanent deterioration of the central nervous and endocrine system in the human body because mercury passes easily through biological membranes, such as skin, respiratory, and gastrointestinal tissues. Fluorescent probes for detecting metal ion has also been an interesting area of research. Up till now, several types of small organic molecules, oligonucleotides, proteins, DNA and DNAzyme platforms have been examined for potential as Hg^{2+}-responsive groups in fluorescent probes. However, most of these probes shows quenched emission, required the involvement of an organic solvent, and also had limitations on selectivity and sensitivity. Therefore, not all the reported fluorescent probes could successfully detect Hg^{2+} ions in biological samples, only a few probes based on small organic molecules have achieved this goal and give fluorescence images of biological samples. Bo Tang et al have also reported seleno fluorescent probe, an organoselenium fluorescent probe (FSe-1) for mercury, based on the irreversible deselenation mechanism. Here FSe-1 exhibits an ultrahigh selectivity and sensitivity for Hg^{2+} detection due to the strong affinity between Se and Hg (6)

III. EVALUATION OF CHEMSENSORS FOR HEAVY METALS

A. *Fluorescent Chemosensorsfor detection of alkali and alkaline earth metal ions*

The first fluorescent chemsensor for cations was recorded in the year 1867, when Goppelsröder reported that morin (Morin is a pentahydroxyflavone that is 7-hydroxyflavonol bearing three additional hydroxy substituents at positions 2' 4' and 5) forms a strongly fluorescent chelate with Al^{3+}. Initially, most fluorescent chemsensors for cations were based on the coordination interactions between the hosts and the guests. However latersupramolecular chemistry was used in chemsensor designing, Sousa *et al.* reported two naphthalene based chemsensors for the detection of alkali metal ions (Figure 1) using supramolecular chemistry in fluorescent chemsensor design (7).

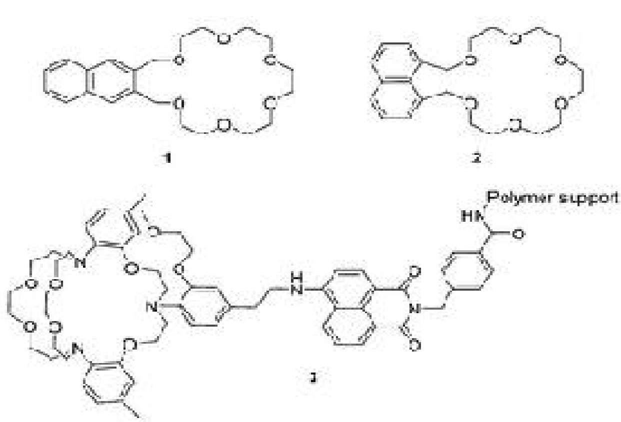

Fig 1 Structures of the fluorescent Chemosensors 1–3

Source : L.R. Sousa, 1977.

B. Fluorescent Chemsensorsfor d-block Metal ions

A part from the above mentioned fluorescent chemsensors for alkali and alkaline earth metal ions, which are all based on coordination interaction there are other set of transition metal ion based fluorescent chemsensors in which chemical reaction is the main basis since these metal ions have the tendency to trigger specific reactions. As known copper (Cu) is the third most abundant and essential transition metal in the human body, as it is involved in various physiological and pathological processes. The structure, mechanism and applications of fluorescent chemsensors for Cu^{2+} has been successfully studied by Shuoliu et al.(8).However earlier in1997, Czarnik and co-workers (9) have reported pioneering work on a rhodamine-B derivative and its ring-opening reaction for sensing copper ion (Cu^{2+}). Mercury (Hg) is one of the most prevalent deadly toxins on earth, which arises from many sources such as gold production, coal plants, thermometers, barometers and mercury lamps etc. Since earlier times, a huge number of fluorescent chemsensors have been developed for the detection of Hg^{2+}. Initially, the fluorescent chemsensors being non-fluorescent due to the PET (Photoelectron transfer) process, however the addition of Hg^{2+} induces an enhancement in fluorescence, whereas other metal ions except for Ag^{+} caused no interference (10).

Apart from fluorescent chemsensors, several groups have designed organoselenium based polynucleatingcentres in which the open coordinating site of selenium is restricted sterically by incorporating allied organic groups(11). The specific orientation of a donor selenium sites in a polynuclear species may also be controlled by a large number of weaker interactions, available due to heteroatoms present in allied organic groups and therefore the organochalcogens may exhibit more diverse behaviour than generally expected (12).The incorporation of selenium atoms substituted at the 1,2,4,5 positions of the central benzene ring leads to architectures which an act as suitable bridging bidentate chelating ligands towards M^{2+} ions. Addition of a solution of Ag(I), Pb(II) and Cd(II) ions to solution of newly synthesized selenium ligands, did not induce any change in the UV-Vis spectra. The complexation process caused notable changes in the absorption spectrum, upon addition of an increasing amount of Hg^{2+} ions. Since, coordination to selenium is not an exclusive feature of mercury, the non-reactivity of species with other metal ions is strange. The flexibility of the arms, steric bulk, open exterior geometry and multiple soft selenium donor sites make these molecules potential candidates for trapping Hg(II) selectively. Both 1:1 complex and 2:1 complex (metal-ligand) were successively formed, which is in complete agreement with physicochemical data. The effects in terms of metal ion, substrate specific response, of the coordinating ligand has been studied by potentiometric and spectroflorometric measurement.

C. Fluorescent Chemosensorsfor Anions

In contrast to the above described cation sensing devices the field of anion sensing is now a relatively mature science in line. Anion (halides, sulphate, dicarboxylate ions etc) plays an important role in biological and industrial processes as well as the presence of anionic pollutants in the environment has driven the need to produce such sensors. Recently, Sessler&coworkers (13) reported two anion induced supramolecular assemblies of expanded porphyrins 4 and 5 (Figure 2). Porphyrins 4 and 5 can form supramolecular polymers with several diacids, which can be used as chemsensors for both anions and organic solvents.

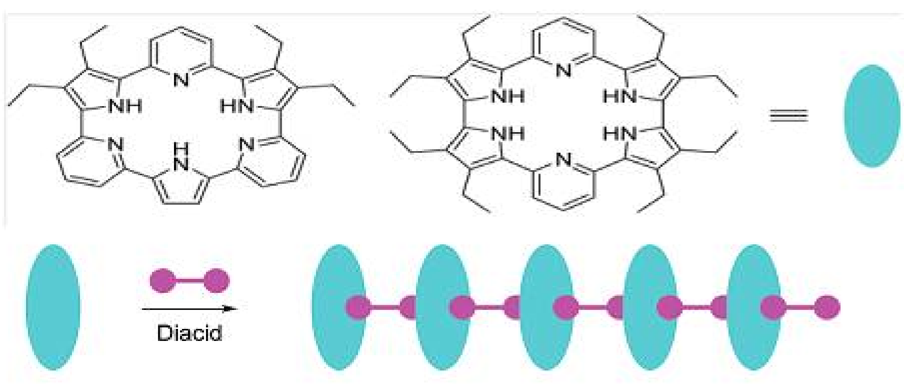

Fig 2 Structures of fluorescent chemsensors 4 & 5 and the schematic illustrates the construction of supramolecular assemblies using 4, 5, and diacids as the building blocks.

Source : J.L. Sessler, J. Am.Chem. Soc., 2015

D. Fluorescent Chemsensorsfor Biomacromolecules

Biomacromolecules are vital for the function of living biological systems. The fluore.scence imaging techniques provides us a powerful tool for studying these biomacromolecules and to completely understand their purpose in these complex biological systems due to excellent spatial and temporal resolution and high molecular specificity. Czarnik carried out pioneering work on anthrylpolyamines to sense polyanions such as heparin, poly-L-glutamate, ds DNA andss DNA in water(14).

- ds : double stranded ss : single stranded

E. Luminescent Chemsensors

Luminescent chemsensors for transition metal ions has been recently studied by Bargossiet. al in which various systems active units and receptors are different as are the target ions: Zn^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ag^{+} and Cu^{2+}. In solution a good selectivity and affinity was observed and the binding is signaled in all cases by pronounced changes in the photophysical properties such as emission wavelength, intensity, and excited state lifetime of the inserted luminophore. The mechanism for signal transduction depends strongly on the chosen receptor and luminophore moieties, and has been investigated in detail by means of steady state and time resolved spectroscopy(15). Luminescent zinc complexes as chemsensors for adenine detection are well known.

F. Optical Chemsensors

Variety of optical chemsensors are known till now. Recently highly sensitive optical chemsensors have been reported, which implement bragg grating structures which though insensitive to chemicals, is made sensitised by effective etching (16). As known silica nanoparticles, silica gel and mesoporous silica are used as supporting platforms to fabricate optical chemsensors because of certain properties like high porosity and expectant adsorption capacity etc similarly, silica-based optical chemsensors are good alternatives to classical instrumental methods for detecting and adsorbing metal ions, due to their effect and lower price. Chromogenic type and fluorogenic type optical probes, such as azobenzene, naphthalimide and rhodamine, are grafted to the surface of silica-based materials by sol–gel reaction, the limit of detection, response time and selective properties of optical sensors are improved sequentially(17).

G. Congugate Sensors

Alternatively known as photoinduced electron transfer (PET) sensors. In such sensorsthere is a nitrogenous ligand or chelator which has sufficient selectivity for the targetedanalyte and then covalently tether this to a fluorophore. When the amine nitrogen of theligand chelator is free they will quench the fluorescence in the solution via photoinducedelectron transfer, sometimes up to 1000 folds. However, when the amine electrons areinvolved in interactions with metal ions or H-bonding with the analyte, quenching doesnottake place and the original fluorescence of the parent fluorophore is restored so theanalyteis signaled by an increase in the fluorescence intensity without any spectral shift,which isconsidered as a major drawback but some advantages of conjugate probes are also known.The fluoroscence of azacrownsquaraine as well as water soluble squaraine is studied alongwith the ion sensing of squaraine based chemsensors in water (18).

H. Amide-based Chemsensors

An simple, efficient and eco-friendly method for the synthesis of amide-based chemsensor(N,N-bis(2-benzamidoethyl)benzamidefrom commercially available material has been developed byBhagat et.al. (19) The application of chemsensor for qualitative and quantitative analysis of metal ions in a various extracted solution using UV-VIS spectroscopy techniques has been proved. This chemsensor helps in the preliminary analysis and detection of Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} metal ions in aqueous and spiked solutions. Such chemsensor has excellent application in forensic chemistry and toxicology for detecting metal poisoning cases.

The syntheses of chemsensors are reported in theliterature by various methods from readily available starting materials (20).Ultrasound-assisted synthesis of diphenylamine-based Schiff base used in the detection of copper(II) ion in aqueous solution,microwave-assistedsynthesis of graphitic carbon nitride quantum dotsand photoluminescent carbon dots synthesis using starch (Tapioca Sago) via solution method at mild condition possess great applications in various fields such as environmental (21), forensic(22),and the biologicalsciences.

Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} shows excellent absorbance in the UV-VIS analysis

It was observedthat metal ions form stable complexes with chemosensorand show visible color change or change in color intensity of aqueous solution. InUV-VIS analysis, absorbance was increased with respect to concentration and it validates the Lambert-Beer's Law.

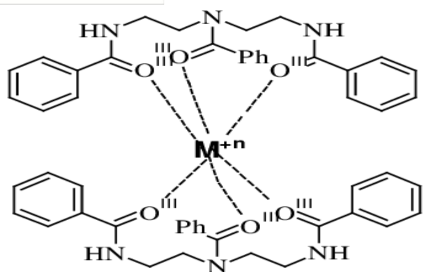

Figure 3 Amide based chemosensor forms coordination complex with metal ions
Source : Section B-Short communication; Bhagat et.al Eur. Chem. Bull. 2019, 8(9), 212-215.

I. Gas Sensors

Alam et al. (2022) provide a comprehensive review of recent advancements in chemoresistive-based heterostructure gas sensors. The study highlights various heterostructure designs, including p–n, n–n, and Schottky junctions, which enhance sensor performance by improving charge transfer mechanisms. The authors discuss the role of metal oxides (e.g., ZnO, SnO_2, WO_3) and 2D materials (e.g., graphene, MXenes, and transition metal dichalcogenides) in increasing sensor sensitivity, selectivity, and stability. The review also delves into the working principles of these sensors, explaining how heterostructures facilitate band alignment and electron transfer, leading to improved gas detection. Despite the significant progress, the study identifies key challenges such as sensor stability, cross-sensitivity, and response drift, which hinder large-scale implementation. The authors emphasize the need for AI-driven sensor optimization, flexible electronics, and miniaturized sensor arrays to overcome these limitations and enable real-world applications. Overall, the review provides valuable insights into the current state and future directions of heterostructure gas sensor technology, making it a crucial reference for researchers in the field (23)

IV. APPLICATIONS

1) Chemsensors have been playing a crucial role in the field of bio-medicinal science, analytical and environmental chemistry by being a molecule that can selectively bind the target analyte and furnish information about this binding. A Highly selective and sensitive detection of inorganic phosphate in aqueous solution and living cells by fluorescent chemsensor is also studied (24).
2) Adulteration, inconsistencies and contamination in food products and beverage samples are detected fast but accurate though chemsensors.
3) Use of chemsensors for the detection of pollutants such as heavy metals or radionuclide are among the main targets since their detection and removal could be envisioned at very low concentrations because of their ability to display specific and strong complexing abilities.
4) Wearable chemsensors in the healthcare system focussed on sweat-based, saliva-based and tear-based analysis (25) makes them a convenienttool for the detection and long-term monitoring of the chemical, biological, and physical status of the human body in real time.

V. CHALLENGES

Despite significant advancements in chemosensor technology, several challenges persist in their evaluation and practical application. One primary issue is achieving the necessary selectivity and ruggedness for effective environmental analysis. Operating chemosensors in natural environments requires robustness, long-term stability, and reliable calibration to ensure accurate detection of analytes in real-time distributed systems (26)

In the realm of fluorescent chemosensors, despite over a century of development, challenges such as aqueous solubility, analyte selectivity, biocompatibility, and labor-intensive synthetic optimization remain prevalent. These issues hinder the practical application of chemosensors in complex biological and environmental contexts (27).

Furthermore, the integration of chemosensors into real-world applications necessitates addressing challenges related to sensor drift and the need for robust calibration algorithms. Continuous monitoring in uncontrolled environments requires calibration algorithms to estimate gas concentrations accurately, and issues like slow dynamics continue to affect real-world performance (28). Addressing these challenges is crucial for the advancement of chemosensor technology and its effective deployment across various fields.

VI. FUTURE RESEARCH DIRECTION

Recent advancements in chemical sensor technology have unveiled promising research directions aimed at enhancing sensitivity, selectivity, and integration with emerging technologies. One notable development is the integration of photonic crystals into chemical sensors. These structured dielectric materials, with their spatially periodic arrangements, offer unique advantages in improving sensor performance. Latest review highlights the construction of photonic crystals with versatile opal or inverse opal structures, emphasizing surface functionality for target recognition and signal transduction. This integration facilitates various sensing principles, including reflection spectra-based sensing, visual colorimetric sensing, fluorescence sensing, and surface-enhanced Raman spectroscopy (SERS)-based sensing (29).

Another emerging area is quantum plasmonic sensing, which leverages quantum technologies to surpass classical sensitivity limits. Quantum plasmonic sensors exploit the enhancement and localization of electromagnetic fields at metal-dielectric interfaces, enabling ultra-sensitive detection capabilities. These sensors hold potential in applications such as blood protein analysis, chemical detection, and atmospheric sensing (30). The convergence of artificial intelligence (AI) with chemical sensing is also gaining momentum. Researchers at Pennsylvania State University have developed an electronic "tongue" that utilizes AI to distinguish between similar substances, such as Coke and Pepsi. This device employs graphene-based sensors connected to a neural network, achieving high accuracy in identifying various liquids. Such AI-integrated sensors could revolutionize applications in food quality monitoring and safety (31). Wearable chemical sensors are advancing toward non-invasive health monitoring. A notable innovation is a self-powered electronic finger wrap that analyzes sweat to monitor health indicators. This device harvests energy from the user's sweat and tracks biomarkers such as glucose and vitamins, supporting personalized healthcare and wellness management (32). Future directions in chemosensor research will likely focus on self-powered sensors (33), bio-inspired designs, quantum-enhanced sensing, and sustainable sensor materials to improve efficiency and reduce environmental impact. With continued innovation, chemosensors are expected to become more cost-effective, user-friendly, and widely accessible, paving the way for their integration into smart cities, personalized medicine, and next-generation analytical devices.

These developments underscore a trend toward integrating advanced materials, quantum technologies, AI, and wearable designs in chemical sensor research, paving the way for more sensitive, selective, and user-friendly sensing solutions in various applications.

VII. CONCLUSION

The field of chemsensors has developed significantly over 150 years. They have covered a diverse area of human interference, be it clinical biochemistry, medical diagnosis, industrial process control, environmental monitoring, tracing selective toxic metal ion etc. Chemosensors have made significant strides in recent years, driven by advancements in nanomaterials, signal transduction mechanisms, and integration with emerging technologies such as artificial intelligence (AI) and the Internet of Things (IoT). These sensors play a crucial role in environmental monitoring, healthcare diagnostics, food safety, and industrial applications due to their high sensitivity, selectivity, and rapid response times.Despite these advancements, several challenges remain, including sensor stability, cross-sensitivity, miniaturization, and real-world deployment under varying environmental conditions. Researchers are addressing these issues by developing hybrid materials, flexible and wearable sensor platforms, and AI-driven data analysis methods.

The present paper highlights few of the important chemsensors used in the area of heavy metal ion detection and their advantages in terms of its easy production, low cost, ease of operation, reliability and good sensor to sensor reproducibility etc. However, operating a sensor in a natural environment poses substantial challenges in terms of ruggedness, long-term stability and calibration. Today, we are witnessing the explosive development in this field of sensors, their applications have covered almost all of the fields. Thebiological and environmental analysis has increasingly stringent requirements imposed by regulatory bodies, so while a current chemsensor may work it may fall short of the required selectivity or sensitivity required for use in a specific practical application in future or so. To meet the upcoming challenges of present and future world we need, and will continue to need an increasing number of chemsensors.

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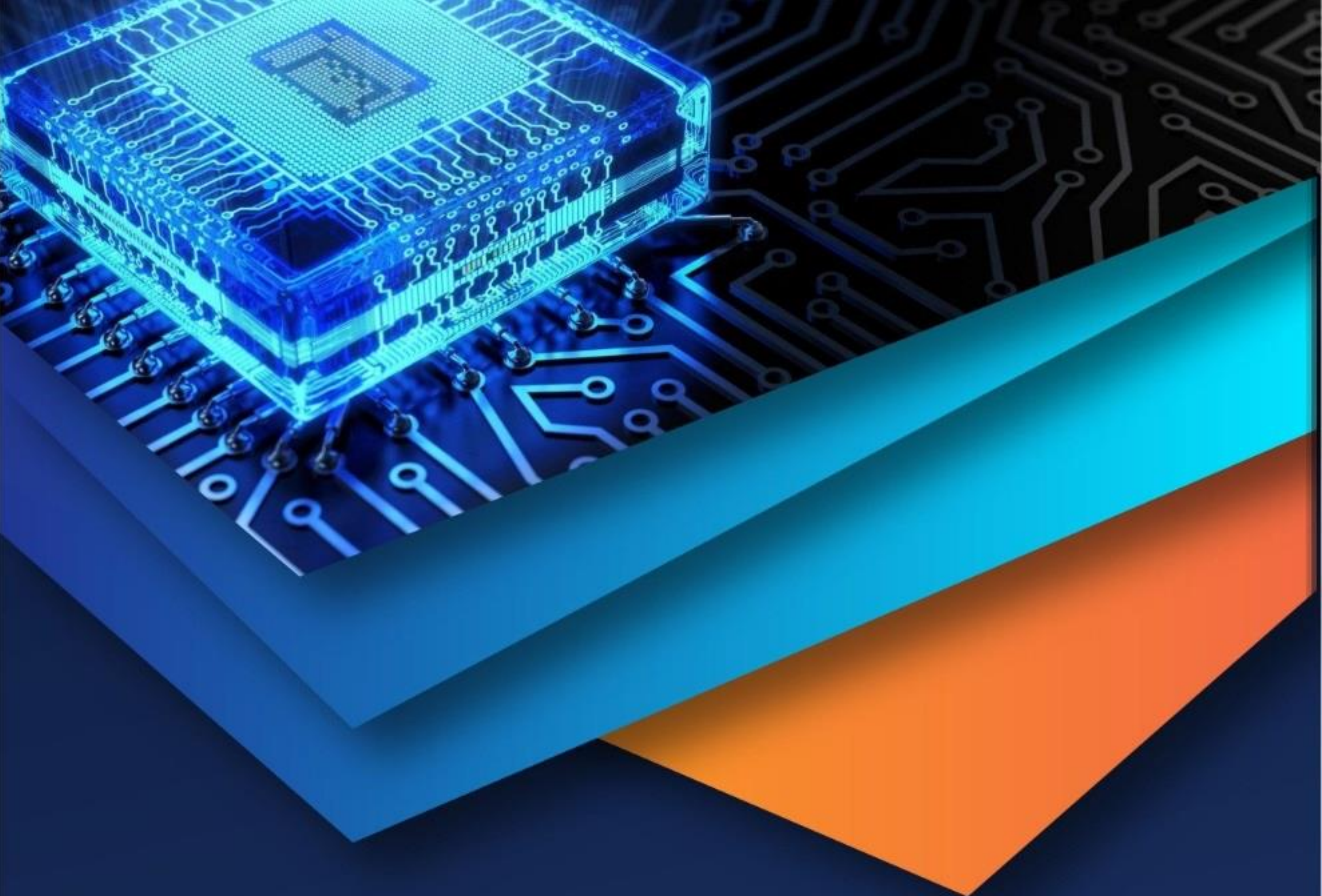

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