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Pivotal Adsorption of Heavy metal ion by Marvelous Carbon Nanomaterials Impregnated with Nanometal synthesized from Agro-waste Cauliflower Leaves

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Abstract: Nanoparticles, with a diameters upto100nm, exhibit a heightened surface-to-volume ratio which allows a greater participation of active surface atoms, fostering improvements in material properties and enhancing implementation. The current work involves acquisition of abundantly, non-edible, and easily available agro-waste cauliflower leaves; pyrolyzed in an inert atmosphere at particular temperature to generate carbon materials. Additionally, the material is activated by using definite concentration of alkali solution followed by impregnation of copper metal and processed with annealing to obtain a desire adsorbent carbon nanomaterial. Adsorption of heavy metal ions [Ag(I)] at pH 6 gives significant result of 96% verified by ICP-AES analysis. Characterization as well as morphology of adsorbent was examined through SEM and HR-TEM. Moreover, XRD revealed the presence of graphitic and amorphous carbon whereas BET prominently explained the specific surface area, pore volume and porosity of the synthesized carbon nanomaterial impregnated with copper nanometal.
Keywords: Cauliflower leaves, heavy metal ions, agro-waste, carbon nanomaterials, Ag (I),

I. INTRODUCTION

The availability of clean, safe and sufficient amount of drinking water is becoming more scarce worldwide (Conde-Gonzalez, *et.al.*, 2016). $AgNO_3$ customarily use in electroplating, photography to sensitize film, mirror production to create reflective layer on glass, laboratory testing for various analytical purposes, staining of DNA, RNA and protein in Gel electrophoresis, various ink formulation industries, textile industry for dyeing and printing etc. (Omri and Benzina, 2012). However significant amount of Ag (I) ion is released as effluent at an alarming rate leading to toxicity in living organism due to its bioaccumulation in aquatic ecosystem, which is ultimately harmful to human being via food-chain. (Chaoqun *et.al.*, 2020).

The excessive exposure to silver ion can lead to argyria, a condition where skin turns bluish-gray due to the deposition of silver particles. (Njewa *et.al.*, 2022). Long-term ingestion or exposure to high concentration of silver can also potentially cause other health issues such as damage to the liver and kidneys. Beyond gastrointestinal symptoms, neurological manifestations encompass tremors, seizures, and the onset of coma. (Tewari *et.al.*, 2023).

The escalating adoption of silver particles for commercial applications is undeniably heightening the environmental and population exposure to silver. The renewed interest in silver is propelled by the surge in antibiotic-resistant bacteria and the escalating incidence of hospital-acquired bacterial infections. The confluence of these factors underscores the imperative to scrutinize the potential consequences of widespread silver particle utilization on both ecosystem and public health. (Chaloupka *et.al.*,2010 and Conde-Gonzalez *et.al.*, 2016).

Properties possesses by silver like malleability, ductility, thermal, lustrous and highest electrical conductivity along with anti-microbial characteristic, making it versatile material with diverse applications. Silver is deemed of particular economic significance in a wide array of applications. (Omri and Benzina, 2012). Therefore, the extraction of silver from waste water can be economically converted into valuable product.

Several methods are employed for the removal of heavy metal ion like membrane filtration, chelation, biological methods, cyanidation process, electrochemical recovery, solvent extraction precipitation, ion exchange and adsorption. (Bisht *et.al.*, 2017, Mukherjee *et.al.*, 2023 and Vazquez *et.al.*, 2014).

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The integration of nanotechnology specifically the utilization of carbon nanomaterials impregnated with copper nanometal (Cu-CNMs) synthesized from agro-waste through adsorption technique, stands out as a comprehensive and leading-edge solution for the sustainable, highly efficient and economically viable to eliminate heavy metal ion from waste water.

In recent years most of the researchers have tried to synthesize carbon materials to expunge Ag (I) ion from waste water by using different sources and precursor like chitosan (Jintakosola and Nitayaphatb, 2016), petroleum pitch, zeolites, lignite, fruits peels, fly-ash, potato peel, (Njewa *et.al*., 2022), coir pith (Kavitha and Namasivayam, 2007), etc. but they have certain drawbacks. Moreover, vegetable waste, a crucial category of residues, are generated abundantly in food and beverage operations, wholesale markets and agricultural practices. In addition, cauliflower leaf is rich in cellulose and lignin, making it suitable for the synthesis of caron nanomaterials (CNMs), a highly effective adsorbent, due to its porous structure and expansive surface area, rendering it well-suited for various application in future. (Ge *et.al*., 2020)

The worldwide production of cauliflower is more than 20 million tons annually. The crop is cultivated across 3.8 million hectares in nearly 150 different nations, with China and India playing significant roles as major contributors to this agricultural production. (Ansari *et.al*., 2016 and Kumari, *et.al*., 2020). The leaf of this vegetable being unpalatable, often considered as waste product; due to its high moisture content, can be gainfully utilized as a potential adsorbent for the elimination of silver metal ion from waste water. Improper disposal of this waste creates public nuisances, emphasizing the importance of incorporating it into enormous adsorbent preparations for effective solid waste management. (Yadav *et.al.*, 2019).

The main objective of the present study highlights preparation of Cu-CNMs from cauliflower leaves and assess its adsorbing capacity for the removal of silver metal ion from waste water; SEM, HRTEM, XRD and BET were also investigated in order to have a clear understanding about the morphology, porosity and specific surface area of CNMs.

II. EXPERIMENTAL TECHNIQUES

All the chemicals involved in the study are of Analytical grade reagent. Double distilled water is accompanied as solvent and also for all dilution purpose.

A. *Synthesis of Cu-CNMs from cauliflower leaves*

The work includes collection of cauliflower leaves from nearby local market, were pyrolyzed by maintaining an inert atmosphere using argon gas at a temperature of 500°C to generate carbon material. Activation of carbon material is carried out by using NaOH solution followed by impregnation of copper metal. Finally, annealing is accomplished to synthesize Cu-CNMs at a temperature of 550°C in the presence of CO_2 gas. The prepared material is highly porous along with exclusive specific surface area which will be a remarkable adsorbent for adsorption of heavy metal ion from wastewater**.**

B. *Adsorption of heavy metal ions*

Initially 1000ppm stock solution of Ag(I) metal ion was prepared by adding appropriate amount of $AgNO_3$ salt in double distilled water. Then working standard solution of 10ppm was prepared by diluting stock solution to particular volumes.

Further, the experiment of adsorption was carried out by adding suitable amount of adsorbent in 10ml of working standard solution at room temperature. Then the solution was kept inside digitally controlled shaker machine for 30 minutes, filtered and used.

Finally, concentration of the Ag(I) ions in the filtrate was detected by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) [Make: SPECTRO Analytical Instruments Gmbh, Germany; Model: ARCOS, Simultaneously ICP Spectrometer having wavelength range130nm to 770nm with the resolution of 9 picometer. R.F. Generator maximum of 1.6KW and 27.12MHz.]

The percentage adsorption of Ag(I) metal ion was determined by knowing the initial (C_i) and final (C_f) concentration of solution using the following relationship. (Mukherjee *et.al.*, 2023)

Percentage adsorption = $\frac{Ci-Cf}{Ci}$ x 100

III. RESULT AND DISCUSSION

A. *Influence of pH on Cu impregnated CNMs – Ag(I) metal ion interaction*

It is well-known that parameter pH plays a critical role in the process of adsorption of heavy metal ion on adsorbent by affecting the surface charge of the synthesized Cu-CNMs and the degree of ionization of the heavy metal ions (Ansari *et.al*., 2016). The adsorption of Ag(I) metal ion increases suddenly from 3 to 6 pH units followed by slight decrease until reaches pH 8 and then sharp decrease is revealed in the uptake of Ag(I) which is in agreement with the nature of curve shown in Fig. 1.

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However, there is an existence of electrostatic force of attraction between the protonated group of Cu-CNMs and the Ag(I) ion at lower pH and when the solution reaches beyond 8 pH unit, precipitation of silver hydroxide increased drastically attributing the presence of more hydroxyl group (Jintakosola and Nitayaphatb 2016). Hence adsorption of Ag(I) on the adsorbent was at optimum pH range of 5-6.

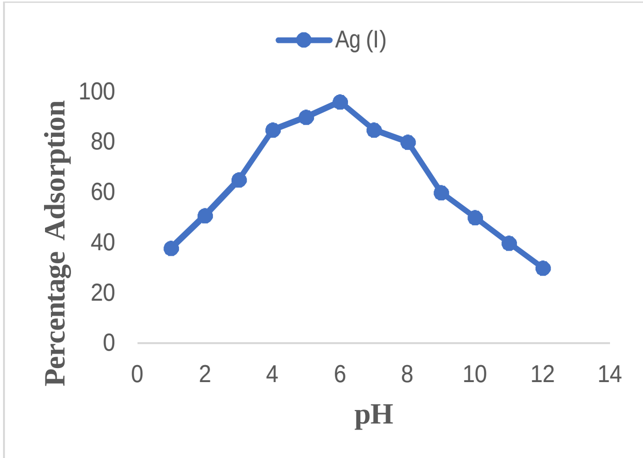

Fig.1 Effect of pH on adsorption of Ag(I) by synthesized Cu- CNMs
[Initial concentration of Ag(I) is 9.65mgL^{-1}]

B. Capacity of adsorbent on adsorption of Ag(I) metal ion

Cauliflower leaves as an adsorbent plays an effective role in removal of heavy metal ion at various stage. Table :1 clearly depicts enormous adsorption of Ag(I) metal ion where the other parameter like dosage amount of each adsorbate was 0.1g and optimum pH 6 of solution was maintained.

Table :1 Effect of different stage of adsorbate on percentage adsorption of Ag (I) ion

Adsorbent at various stage	Percentage adsorption
Raw cauliflower leaf powder	65.08%
Pyrolyzed carbon material	78.82%
Alkali treated carbon material	85.31%
Cu doped CNMs	96.25%

C. Characterization of Carbon Nano Materials

1) Scanning Electron Microscopy (SEM) [Make: FEI and Model: QUANTA 200]

The surface morphology of Cu-CNMs synthesized from agro-waste cauliflower leaves was studied by using SEM provides a vital information. (Gupta *et.al.*, 2018). Fig. 2(a) represent the surface characteristic at magnification of 10000x which has significant numbers of tubular pores and cavities along with the distribution of impregnated copper nano metal having size range of 25-85nm. Fig. 2(b) under magnification of 15000x shows that coarse edges of the material persisting the thickness range of 90-130nm.

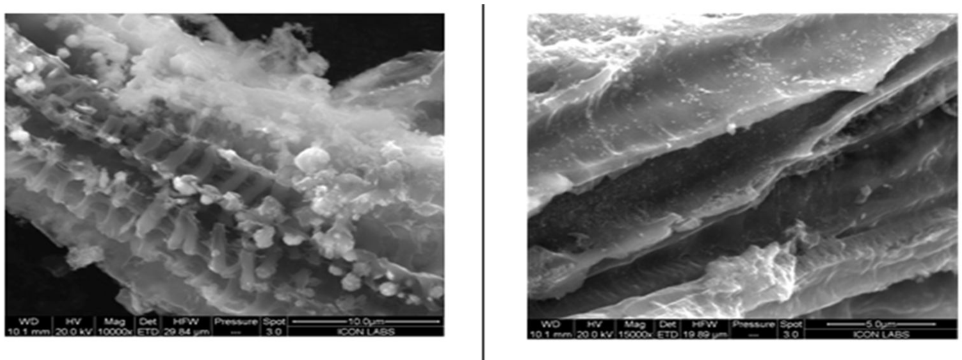

Fig. 2(a) Fig. 2(b)

Fig. 2 (a) and (b) are Scanning Electron Microscopy (SEM) micrograph of Cu-CNM

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2) High-resolution Transmission Electron microscopy (HRTEM) [Make: FEI and Model: TECNAI]

The TEM images in Fig. 3(a) and (b) clearly suggest that presence of copper nanoparticles embedded on the surface on synthesized CNMs. The diameter of isolated Cu nanoparticles ranges 10nm -15nm and also there are very few loosely clusters of Cu nanoparticles whose average diameter ranges approximately 20-80nm. (Ayyappan *et.al*., 1997).

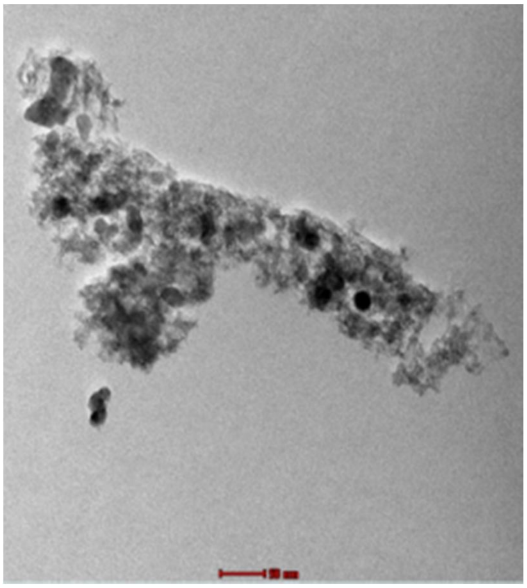

Fig. 3(a)

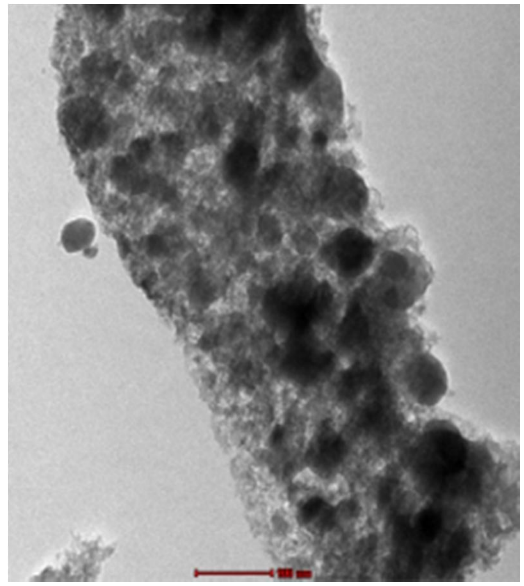

Fig. 3(b)

Fig. 3 (a) and (b) illustrates HRTEM images of Cu nanoparticle on synthesized CNMs

3) X-Ray Diffraction (XRD) [Make: PANalytical, The Netherlands and Model: EMPYREAN]

The ability to control shape, size and morphology of particle plays a keen role in synthesis of nanoparticle. The XRD characterization of the sample demonstrate a high crystallinity level at 2θ in degrees with diffraction angles of 36.28°, 43.36°, 50.58° and 74.82° corresponding to index lines at (111), (111), (200) and (220) respectively confirms the presence of Cu nanoparticle having face centered cubic lattice pattern. (Theivasanthi and Alagar, 2010, Usman *et.al*., 2012 and Thakar *et.al*., 2022). The broad peak at 24.18° whereas sharp intense peak at 29.38° shows the typical structure of graphene oxide and crystalline graphite respectively. (Siburian *et.al*., 2018).

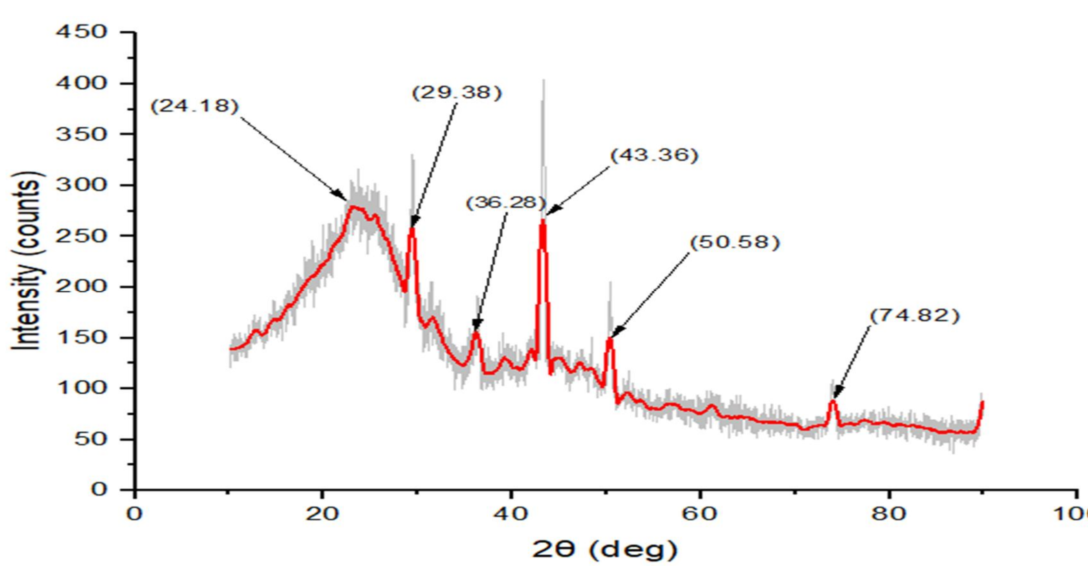

Fig. 4 XRD diffraction pattern of copper nanoparticles impregnated on CNMs

4) BET [Make: SMART INSTRUMENT; Model: SMART SORB 93]

The specific surface area investigated through Brunauer-Emmett-Teller (BET) of Cu-CNMs synthesized from agro-waste cauliflower leaves was found to be $435.54 m^2 gm^{-1}$ and well-developed total pore volume of $0.2814 cm^3 gm^{-1}$. This result illustrates impregnation of copper nanoparticle increases the porosity; presence of extensive surface area helps in good agreement of adsorption of heavy metal ion by adsorbent Cu-CNMs**.**

IV. CONCLUSION

The current study presented the synthesis of copper impregnated CNMs from agro-waste cauliflower leaves results a promising option for adsorption of heavy metal ion from waste water. The scientific data obtained through SEM, HR-TEM, XRD and BET explains the surface characteristic and morphology of carbon material. From ICP-AES scrutiny of adsorbent has a requisite site for adsorption of Ag(I) at pH 6 with the efficiency of 96%. Hence a waste material is converted into a valuable resource which not only minimizes environmental impact but also offers cost-effective solutions.

V. ACKNOWLEDGEMENT

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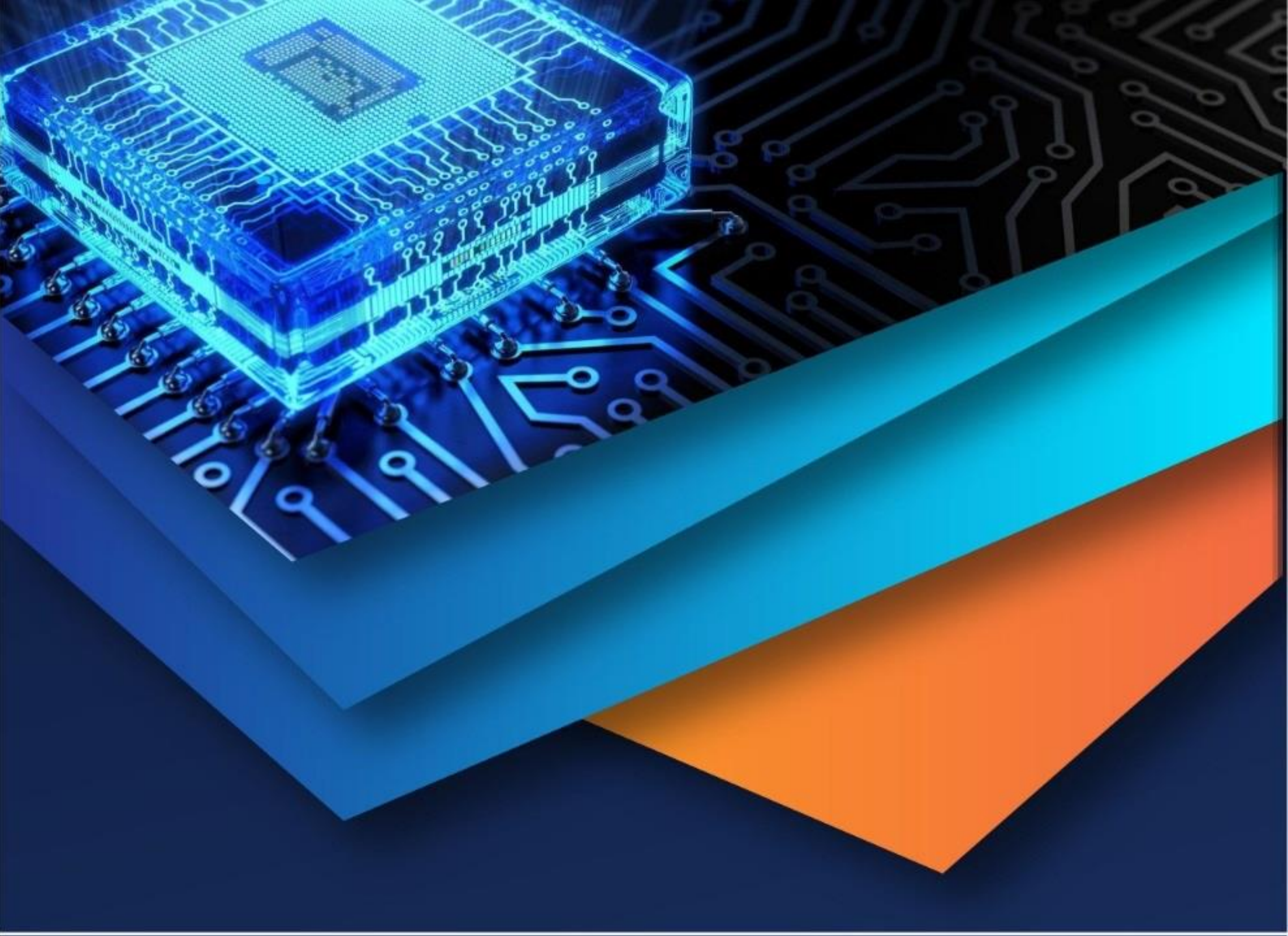

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