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Bio-sorption of Hexavalent Cr (VI) from Aqueous Solution using *Pterocarpus Santalinus* L. F. and *Tectona Grandis L.F.* as Bio-sorbents

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Abstract: Today the growth of industries is rapid, and the problems caused by them are long lasting. The effluents released from industries pollute- land, air, water and create environmental imbalances, also these effluents contain heavy metals which are harmful to living beings. Heavy metals are essential for the growth of living beings when taken in minor quantities and are harmful when they exceed their limit.

There are several techniques for the removal of heavy metals like adsorption, reverse osmosis, chemical oxidation, ion-exchange method etc. Among them adsorption is widely preferred as it is economical where low-cost adsorbents like biological wastes, agricultural wastes and micro-organisms can be used. Present work focuses on the removal of hexavalent chromium from aqueous solution using Pterocarpus Santalinus L.F (red sandalwood leaves) powder and Tectona Grandis L.F (teak leaves) powder as bio-sorbents. All the experiments were conducted in batch mode at room temperature and the effect of various parameters like contact time, initial metal ion concentration, pH and adsorbent dosage on metal ion removal were studied and the results were interpreted.

Langmuir and Freundlich isotherms were studied, and the obtained data were tabulated. Samples were analyzed using Shimadzu UV-1900 spectrophotometer at 540nm wavelength.

Keywords: Heavy metals, Batch mode, Adsorption, Chromium, Pterocarpus Santalinus, Tectona Grandis.

I. INTRODUCTION

Living beings along with minerals and vitamin requires small quantities of metals for their growth. These metals are quintessential to maintain various biochemical and physiological functions in living organisms when they are consumed in low concentrations whereas they become toxic on exceeding their limit. The sources of these metals into our body are through the food we take or the water we drink or the air we inhale. The most well-known metals found in wastewater are arsenic, cadmium, lead, nickel, zinc, cobalt, copper, chromium, iron, molybdenum, selenium etc. These days we are facing a serious issue of water and food contamination which is gradually deteriorating the health of people and having a negative impact on the environment and the ecology. The primary reason for the release of these heavy metals into the surroundings are due to soil erosion, volcanic eruptions, mining, industrial effluents, sewage discharge, pesticides, and herbicides and many more (Monisha Jaishankar et al;2014). This work mainly focuses on the removal of hexavalent chromium from aqueous solution. Chromium is released into the atmosphere by burning of coal, cement industries, incineration operations, tanneries, and textile industries. Chromium in its trivalent form is useful in human vascular and metabolic systems whereas hexavalent chromium is dangerous as it can cause kidney failure and liver damage.

A. Bio-sorption

Bio-sorption is a technique in which sorbent is of biological origin and it is regarded as a simple, cost-effective, and environmentally friendly process for removing pollutants (Enrique Torres 2020). Pollutants naturally bind to biomass and therefore they can be removed by simple techniques. The biomass used in this sorption process can be alive or dead. The pollutants binds to the surface of the dead biomass either physically, chemically or by ions based on the surface area of sorbent and it does not require any external driving force. Living biomasses like bacteria, microorganisms reacts with the sorbent and undergo various biochemical reactions thus making the process more complicated (Velásquez L.et al 2009).

B. Bio-sorbent

Bio-sorbents are biological materials that are used to remove contaminants from a solution in a passive manner. Agricultural wastes, algae, bacterial wastes, and industrial wastes are examples of biomaterials. They've gotten a lot of positive response because they're made from renewable resources, are inexpensive, biodegradable, and don't produce secondary contaminants after they've been used up (Adewale Adewuyi 2020).

Many natural materials have been proposed as potential bio-sorbents for water pollution remediation. Inactive or dead microbial biomass, as well as living microbes, can be used as these materials.

II. MATERIALS AND METHODS

A. Chemicals

All the chemicals used in this work are of analytical grade. $K_2Cr_2O_7$ is taken as the source for Cr (VI). Stock solution of 1000mg/L is prepared by dissolving 2.828g of potassium dichromate in 1000ml of distilled water.

Further concentrations of working samples were obtained by diluting the stock solution. 0.1N H_2SO_4, 0.1 N NaOH are used to maintain desired pH of the solution.

B. Bio-sorbent Preparation

The adsorbents used this work are red sandalwood leaf powder and teak leaf powder. Both the leaves are collected from Sri Venkateshwara University College of Engineering, Tirupati and they are repeatedly washed with water for several times to remove the dirt and sun dried.

The dried leaves were ground to fine powder using domestic mixer. Experiments were conducted by washing and drying the adsorbents before the start of the experiment to further remove the color and impurities present in it and the results were compared. The samples were analyzed using Shimadzu UV-1900 Spectrophotometer at a wavelength of 540nm. pH of the samples was measured using Hanna pH meter. All the experiments were conducted at room temperature.Experiments were conducted for varying concentrations (50- 250 mg/L), varying time (10-120 min), varying pH (2-10) and dosage of adsorbent (0.1- 1 g). The adsorption capacity is the quantity of adsorbate that can be taken up by adsorbent per unit mass of adsorbent and can be calculated using the below equation

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

Where q_e is the adsorption capacity of the adsorbent (mg/g), C_o is the initial metal ion concentration (mg/L), C_e is the equilibrium metal ion concentration (mg/L), V is the volume of the sample taken (L), m is the mass of the adsorbent (g). The percentage removal of the metal from the solution is given by

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

III.EXPERIMENTAL RESULTS

The adsorption experiments were conducted by varying concentration (50- 250 mg/L), time (10-120 min), pH (2-10), adsorbent dosage (0.1-1 g). 50 ml metal solution of desired concentration, pH, and adsorbent dosage are taken in a 250 ml conical flask and placed in the mechanical rotary shaker of fixed rpm and rotated for desired time. The obtained samples were filtered and analyzed within short duration after filtration**.**

A. Effect of Contact Time

The experiment was carried out for 120min, and the results obtained were shown in figure 1. The samples were removed from the rotary shaker for every 10 min of time gap and analyzed. The percentage removal gradually increased from 80.67 at 10 min to 90.83 at 120 min when RSWL powder was used, while using teak leaf powder the removal percentage for the first 10 min is 83.33% and at the end of 120min 88.4% was obtained.

Maximum adsorption occurred during the first 10 min of the experiment due to the availability of surface area. Once the available surface area was occupied the metal ion cannot penetrate further and hence equilibrium was attained (S Karunakaran et al; 2021).

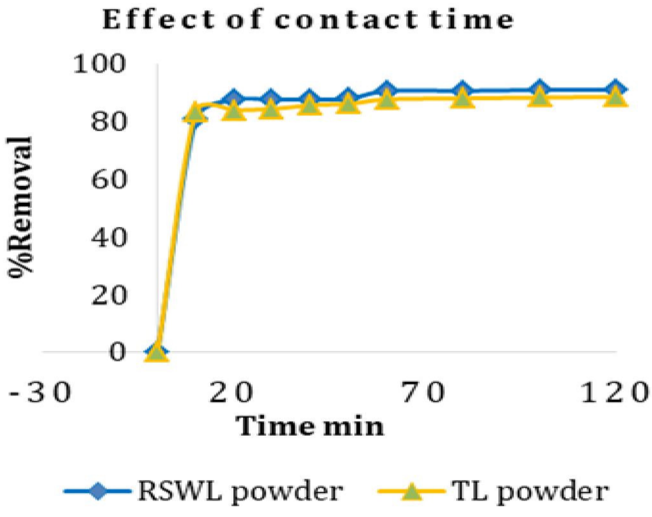

Figure-1: Effect of contact time
Conditions: concentration- 100mg/L; pH- 2; dosage- 0.5g

B. *Effect of Initial Metal Ion Concentration*

With the increase of initial metal ion concentration, the percentage removal of chromium is decreased due to the increase in number of active sites available for adsorption. Whereas adsorption capacity was increased gradually due to increase in driving force (P. King et al. 2006). Maximum removal percentage of Cr (VI) was observed for 50mg/L i.e., 91.91 and 93.068 for RSWL powder and teak leaf powder respectively. Maximum adsorption capacity for RSWL powder was found to be 15.365mg/g while for TL powder it is 15.845mg/g. the obtained results were shown in figure 2.

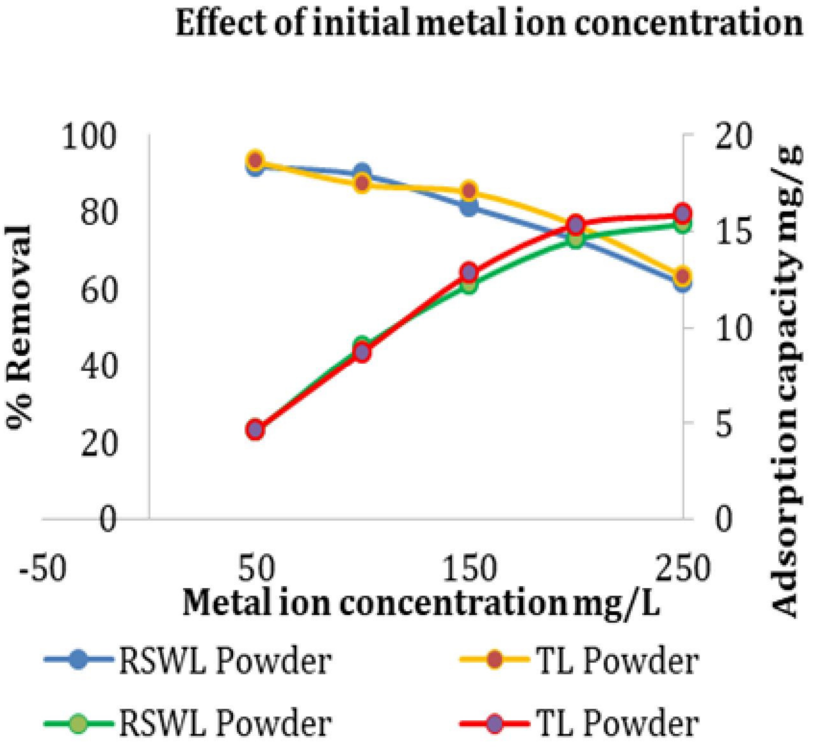

Figure-1: Effect of initial metal ion concentration
Conditions: pH-2; dosage- 0.5g; time- 120 min

C. Effect of pH

pH is an important parameter in adsorption as it has major impact on the removal of metal ions from the solution. It has effect on solution chemistry as well as site dissociation. The percentage removal of metal was found to be 90.44 at low pH of 2 when RSWL powder was used. As the pH is increased from 2 to 10 the percentage removal is decreased from 90.44 to 56.89 as shown in figure 3. The adsorption capacity at pH 2 was found to be 9.045 mg/g and at pH 10 it is 5.689 mg/g. This high adsorption capacity at low pH is due to the surface positive charge of the adsorbent and as the pH increases the adsorbent takes surface negative charge. When TL powder was used the percentage removal was found to be 85.33 and 69.11 at pH 2 and 10 respectively. The maximum adsorption capacity of 8.533 mg/g was observed at pH 2 when TL Powder was used.

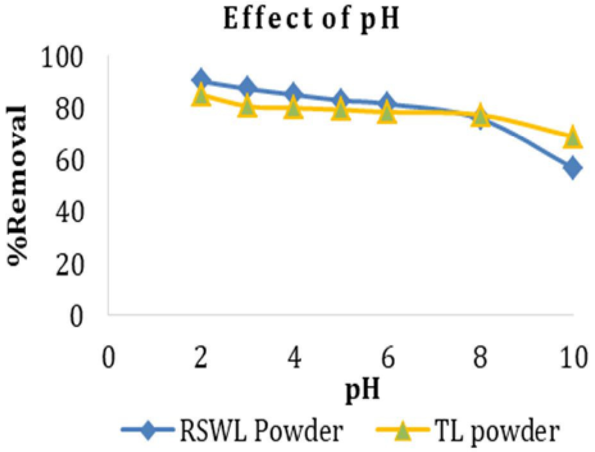

Figure-3: **Effect of pH**

Conditions: concentration- 100mg/L; dosage- 0.5g; time- 120min

D. Effect of Adsorbent Dosage

Adsorbent dosage is an important factor that affects the adsorption capacity of adsorbent (S. Vilvanathan and S. Shanthakumar 2014). Dosage is varied from 0.1g to 1g where maximum removal is obtained when 0.5 g of adsorbent was used. This is due to the availability of maximum number of active sites for adsorption. When small amount of adsorbent was used the active sites for adsorption are not sufficient and the adsorption rate will be low. Maximum adsorption was attained when 0.5g was used and after that a decline in the removal percentage was observed as the pores are blocked and no more adsorption takes place. Maximum removal of 90.44%, 85.33% was observed for RSWL powder and TL powder respectively. Adsorption capacity was found to be 9.044 mg/g and 8.533mg/g for RSWL Powder and TL powder respectively. The obtained results were shown in figure 4.

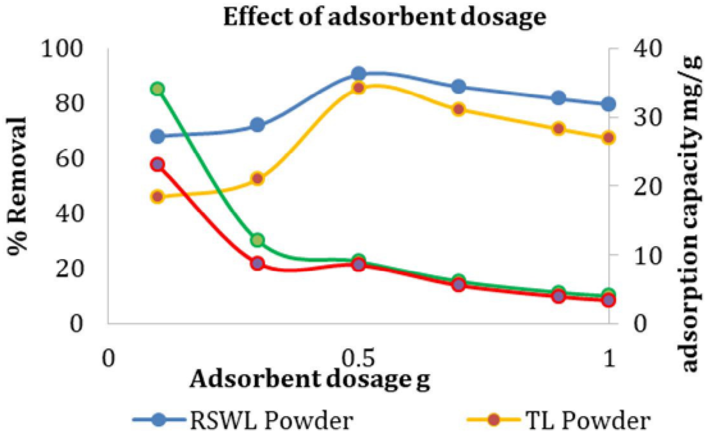

Chart 2: Effect of dosage

Conditions: concentration-100mg/L; time- 120 min; pH-2

E. Langmuir Isotherm

Langmuir isotherm model assumes that there are finite number of active sites that are evenly distributed across adsorbent's surface. There is no interaction between adsorbed molecules because these active sites have same affinity for adsorption of monomolecular layer (Vijaykumar et al. 2012).

Linearized equation for Langmuir model can be written as

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (3)$$

Where C_e is equilibrium concentration (mg/L), q_e is adsorption capacity (mg/g), q_m is maximum monolayer adsorption capacity (mg/g), K_L is Langmuir constant (L/mol). The Langmuir isotherms for the adsorbents is shown in figure 5, figure 6

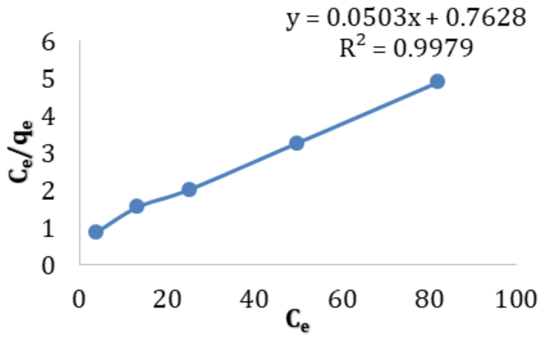

Figure- 5: Langmuir isotherm RSWL Powder

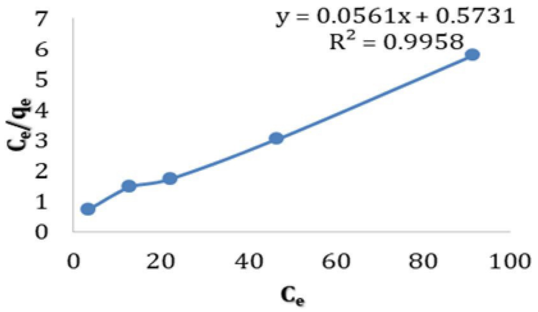

Figure- 6: Langmuir isotherm for TL Powder

F. Freundlich Isotherm

The Freundlich isotherm model is not limited to formation of monolayer and can be used for adsorption on heterogeneous surface with interaction between adsorbed molecules. This model also assumes that as the adsorbate concentration increase the concentration of adsorbate on adsorbent surface also increases (Vijaykumar et al. 2012).

The linearized form of Freundlich equation is given as

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \qquad (4)$$

Where K_F is sorption capacity (Freundlich constant), 1/n is sorption intensity and that indicates capacity of adsorbent/ adsorbate system, q_e is adsorption capacity (mg/g), C_e is equilibrium concentration (mg/L). The Freundlich isotherms for the adsorbents are shown in figure 7, figure 8.

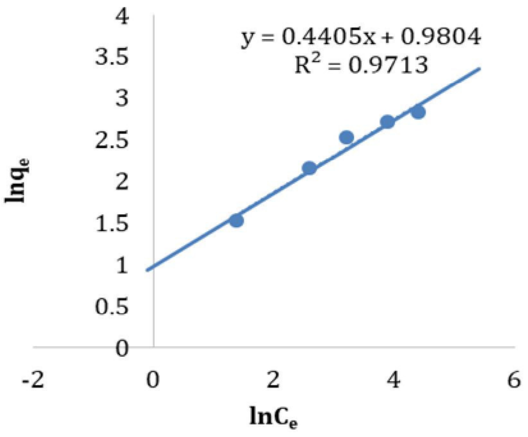

Figure-7: Freundlich isotherm of RSWL powder

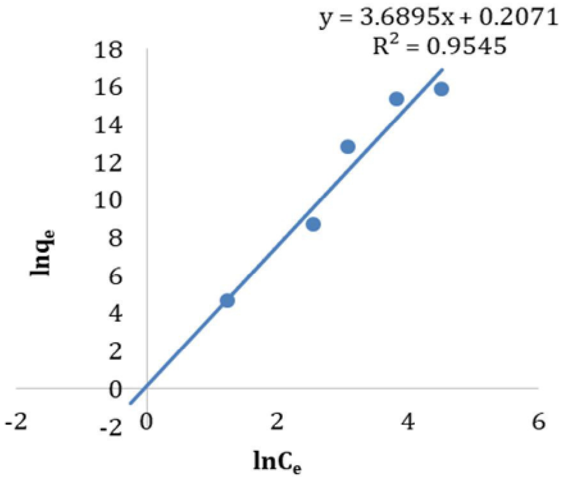

Figure- 8: Freundlich isotherm of TL powder

	RSWL Powder	TL Powder
Langmuir		
q_{max} (mg/g)	19.881	17.825
K_L	0.0659	0.0979
R^2	0.9979	0.9958
Freundlich		
1/n	0.4405	3.6895
K_f	2.666	1.23
R^2	0.9713	0.9545

Table- 1: Data for isotherms

IV. CONCLUSION

The results obtained shows that both the adsorbents are effective in removing chromium (VI) ions from the metal solution. Effects of contact time, initial metal ion concentration, pH, adsorbent dosage on removal were studied, and the data was interpreted. Maximum removal percentages were achieved at pH 2, when 0.5g of adsorbent was used. Langmuir and Freundlich isotherms were studied, and the obtained values are tabulated.

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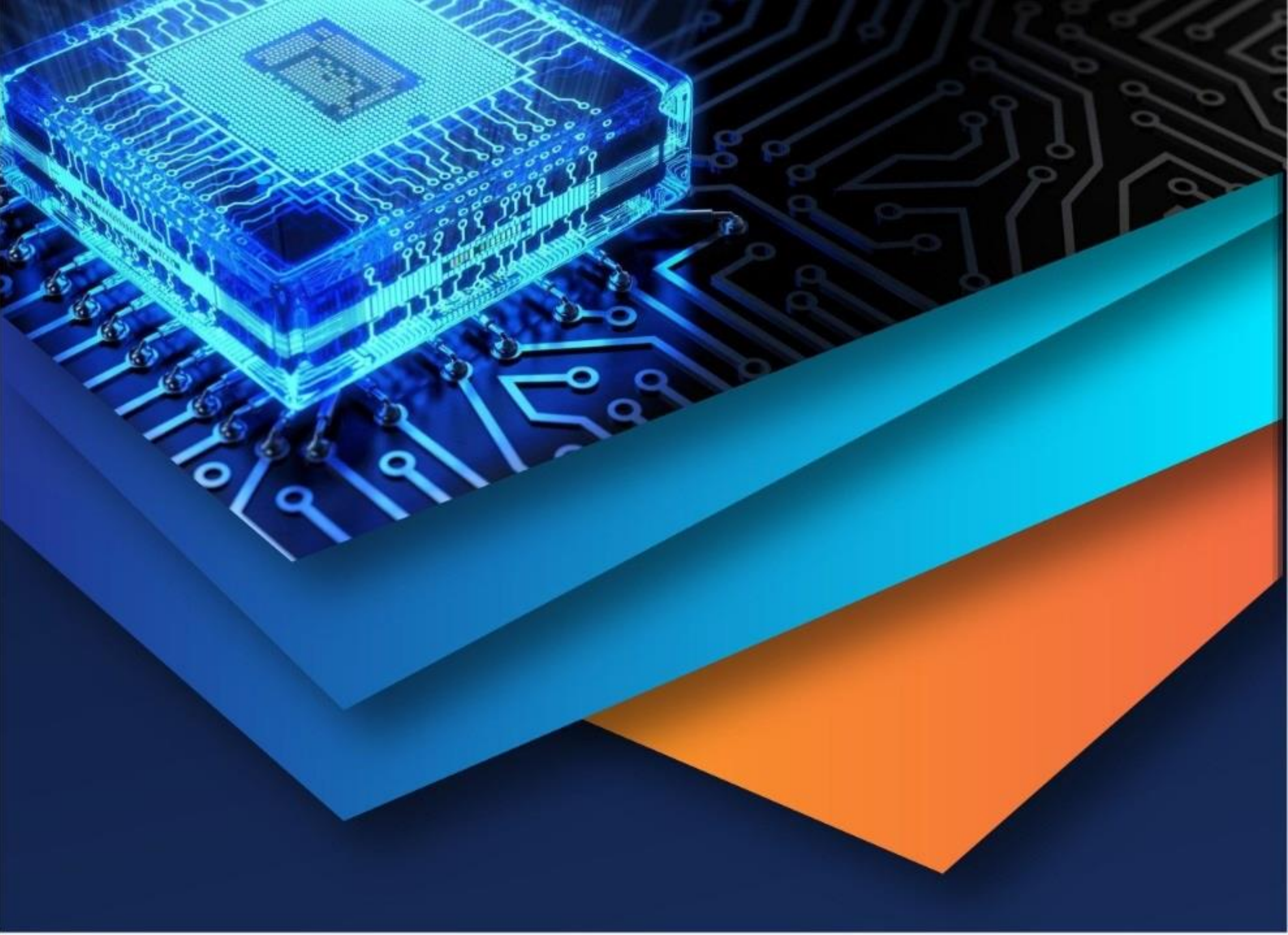

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