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# Defluoridation of Groundwater by Different Biomaterial and Geomaterials: A Review

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***Abstract:*** ***Fluoride (F-), the 13th most common chemical in the earth's crust, is widely known for its health benefits at low concentrations but is a public health threat to many drugs. Fluoride is one of the anionic toxins which is found in overabundance in groundwater because of geochemical response or anthropogenic exercises. The overabundance of fluoride in drinking water influences bone and teeth as well as each tissue and organ of the body. The World Health Organization has set a limit of 1.5 mg/L for fluoride in potable water. More than 260 million people worldwide drink water containing high levels of fluoride. The prevalence and high levels of fluoride in drinking water in many parts of the world have led to research and mitigation efforts to address the increasing health problems associated with this fluoride. this survey Paper talks about the different biomaterials and geomaterials utilized as adsorbents, for example, Zirconium oxide (Pan nanofibers), Moringa Oleifera, activated carbon, Magnesia / Chitosan composite, Neodymium, Natural soil, Mentha longifolia, Brick powder, Tamarind seed, Activated titanium-rich bauxite, and their productivity on fluoride expulsion from groundwater. Numerous strategies and materials are utilized in fluoride expulsion from groundwater in which different types of materials act differently.***
***Keywords: Fluoride, Defluoridation, Geomaterials, Biomaterials, Groundwater, Water treatment, Adsorption, Human Health.***

## I. INTRODUCTION

Groundwater is used worldwide in local and modern storage and water supplies. According to WHO Association, about 80% of human diseases are caused by water. Once groundwater is contaminated, its quality cannot be recovered and resources need to be developed to ensure it. Unadulterated water is scant and isn't effectively accessible by any means. Safe drinking water is an essential need of each person.

1) *Fluoride:* It is a rare component that doesn't happen in the basic state of nature on account of its high reactivity. It represents about 0.3g/kg of the world's outside and exists as fluorides in a few minerals of which are fluorspar, and cryolite. fluoride is an ordinary constituent of water and its focus fluctuates relying on the water source. WHO principles and BIS, 105000,1991 allows just 1.5/L as the upper passable cut-off for fluoride in drinking water for the Indian setting. The fluoride level in water in India goes from 2-29 ppm. By and by, 17 states are endemic for fluorosis, 70-100% of areas in Andhra Pradesh, Gujrat, and Rajasthan. 40-70% regions in Bihar, Delhi, Haryana, Jharkhand, Karnataka, Maharashtra, MP, Orissa, Tamil Nadu, UP, and 10-40% regions in Assam, Jammu, and Kashmir, Kerala, Chhattisgarh, West Bengal.
2) *Defluoridation;* Defluoridation of groundwater is one of the significant healing measures to tackle the high fluoride issue in drinking water. It is characterized as the descending change of fluoride particle fixation in the public drinking water supply so the degree of fluoride is kept up at the typical physiological restriction of 1ppm to forestall dental caries with the least chance of causing dental fluorosis.

### *A. Effects of Fluoride on Human Health*

The effects of fluoride on human health are dependent on the concentration of fluoride in water.

| Fluoride conc. (mg/lit) | Source | Effects |
|---|---|---|
| 1 | Water | Prevention of dental caries |
| 2 | Water | Prevention of dental caries |
| 3 to 6 | Water | Osteoporosis |
| 8 | Water | 10 % Osteoporosis |
| 20 to 80 | Air & Water | Crippling skeletal fluorosis |
| 50 | Food & Water | Changes in thyroid |
| 100 | Food & Water | Defective development |
| >125 | Food & Water | Changes in Kidney |
| 2500 | Acute dose | Death |

Table 1 – Biological Effects on Human Health.[2]

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## II. OBJECTIVE

The objective of this review study is to identify the properties of different biomaterial and geomaterial adsorbents and study the best methods and materials for Defluoridation. Defluoridation measures have social, financial, political, conduct, and natural ramifications, particularly in a non-industrial nation like India. Hence, it gets important to cut down the fluoride focus inside the admissible furthest reaches of 1.5 mg/L as per Indian guidelines. Innovative strategies for defluoridation ought not to be restricted to the labs, rather should discover their approach to be useful in the field.

## III. METHOD

### A. *Adsorption*

Adsorption is the property of a strong substance to draw in and hold to its surface a gas, fluid, or substance in arrangement or suspension. Adsorption is a mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase. The adsorbate is a substance that is removed from the liquid phase and transferred to the solid phase. The adsorbent is the solid, liquid, or gas phase onto which the adsorbate accumulates.

#### 1) *Factors Affecting Adsorption*

*a)* Temperature
*b)* Pressure
*c)* Surface Area
*d)* Activation of solid adsorbents
*e)* Agitation
*f)* pH
*g)* Characteristics of adsorbent
*h)* Dose of adsorbate and adsorbent

Adsorbate: the substance that is adsorbed on the floor.
Adsorbent; the substance on which floor the adsorbate is adsorbed.

#### 2) *Advantages of Adsorption Techniques*

*a)* High selectivity of adsorbents.
*b)* Low expense in establishment and support subsequently financial contrasted with different strategies for fluoride evacuation procedures.
*c)* High proficiency, high profitability of fluoride expulsion, and can eliminate up to 90 percent of fluoride.
*d)* Easy post-treatment after adsorption.
*e)* Adsorption units are straightforward in their activity and plan.
*f)* Eco-friendly.
*g)* Lack of slime creation.
*h)* It is relevant in the evacuation of fluoride even at low focuses.
*i)* This strategy is likewise famous because of the wide scope of accessibility of adsorbents.
*j)* The adsorption strategy is proficient and can eliminate particles from a broad assortment of PH to a lower extra focus than precipitation.[1]

## IV. MATERIALS USED

### A. *Moringa olifera (Bio Material)*

The use of the Moringa oleifera seed powder as a bio adsorbent for the removal of fluoride is feasible. The alkali-treated Moringa oleifera seed powder was found better than acid-treated Moringa oleifera seed powder for fluoride ion removal. The removal by adsorption increases as the pH value increases. The removal by adsorption was found to be optimum at an adsorbent dose of 400 mg/lit. 5. The optimum contact times were 2 hrs and 2.5 hrs for 212 µ and 600 µ respectively.[2]

### B. *Activated carbon prepared from banana peel and coffee husk (Biomaterial)*

The use of activated carbon shows that thermally treated adsorbents prepared from the coffee husk and banana peel are suitable for the removal of fluoride ions. The operational parameters such as adsorbent dose, contact time, pH, and initial fluoride concentration were found to have an effect on the adsorption efficiency.

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At the optimum operation conditions, the adsorbents prepared from banana peel and coffee husk exhibited the highest fluoride removal efficiency of 85 and 86 %, respectively, for 10 mg/L of initial fluoride concentration. Application to the real water sample also resulted in removal efficiency ranging from 80 to 84 %. In terms of time and the adsorbent dose required, a coffee husk was observed to be much more effective than a banana peel. The process of adsorption follows Langmuir adsorption isotherm and pseudo-second-order rate equation in both cases.[3]

*C. Magnesia / chitosan composite (Bio Material)*

The adsorbent namely MgOC composite was prepared to remove fluoride from drinking water which possesses an appreciably higher DC than magnesia. The DC of both sorbents is not influenced by the pH of the medium. The DC of the MgOC composite was not affected in the presence of co-anions except bicarbonate ion. The sorption process follows Freundlich isotherm. The thermodynamic parameter values indicate that the fluoride removal process is spontaneous and endothermic in nature. The kinetics of the MgOC composite follows pseudo-second-order, particle and intraparticle diffusion models. The results of the field trial indicate that both sorbents can be effectively used to remove fluoride from water. However, the treated water was found to be alkaline in nature when both sorbents were used as the Defluoridating medium. Among the two adsorbents, MgOC composite is biocompatible, biodegradable, cost-effective, shaped into any desired form which possesses higher DC with minimum contact time and can be used as a promising sorbent for fluoride removal.[4]

*D. Neodymium / Modified chitosan (Bio Material)*

A new adsorbent was studied for the removal of fluoride ions from synthetic solutions. The method is simple and has shown great potential for the removal of fluoride ions. The main conclusions that can be drawn from the study are given: (1) The treatment conditions were optimized: pH value was 7, the water temperature was at 323 K, and particle size was 0.10 mm. (2) A salt rejection against the water containing 20 mg L−1 of fluoride ions was 98.15% at the dosage of adsorbent was only 2.0 g L−1. 500 mg L−1 of chloride, 500 mg L−1 of sulphate, and 50 mg L−1 of nitrogen of nitrate in water respectively, had no significant effect on the removal rate of fluoride. (3) The equilibrium sorption data were fitted reasonably well for the Langmuir isotherm model. The maximum equilibrium sorption was 22.380 mg g−1 at 303 K. (4) Sorption dynamic study revealed that the sorption process followed a pseudo-second-order equation; the sorption process was complex, and both the boundary of liquid film and intra-particle diffusion contributed to the rate-determining step. (5) The used adsorbents could be regenerated by 4 g L−1 of sodium hydroxide in 24 h. [5]

*E. Natural Soil (Geomaterial)*

The treatment of fluoride-rich waters by using natural materials shows that there is a significant variation in the FTIR spectrum before and after treatment. The variation is noted in the OH region of the spectrum, indicating adsorption and variation in bonding strength. The sites with Fe-OH and Al–OH bonds present in the red soil play a main role in controlling the efficiency of fluoride removal. Fluoride removal is effective in near-neutral conditions. The competitiveness of the OH- and F- ions can be attributed to the change in the pH of the solution. The effective removal of fluoride is maintained for a longer period and decreases with time after the occupation of the active sites. Though the rate of flow is higher at the initial stages the removal was effective due to the availability of more active sites. Subsequently, the rate of flow was lesser and still the removal was found to be effective due to the increase in the contact time between the adsorbent and the liquid. The regeneration of the medium after the experiment for about 9,213 min was attempted and found to be effective, this also helps in the field for the daily backwash of the column after the treatment and helps to regenerate itself. The results obtained indicate this as a possible method for the removal of Fluoride for an effective rural water supply scheme. Further due to its control over the rate of water flow, column experiments are proved to be an easy method for transferring the technology to the field. This method requires no power supply since water moves down by the gravitational force hence it becomes more cost-effective and easier to handle by the local community as a suitable green and clean technology for rural drinking water supply in Fluoride affected areas.[6]

*F. Mentha longifolia (Mint) (Bio Material)*

Results demonstrate that these minimal-effort bio adsorbents could be productively utilized for the evacuation of fluoride over an extensive variety of fixations. Treated biosorbents are seen to be effective for the uptake of fluoride particles somewhere around 2.0 and 10.0 pH. Fluoride removal for a given bio-adsorbent size increased with time attaining equilibrium within 1.5 h. The rate of fluoride removal is observed to be a component of adsorbent dosage and time at a given introductory solute concentration.

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It expands with time and adsorbent dosage; however, higher initial solute fixation will diminish the time and adsorbent dosage. The biosorbents absorption method follows the Langmuir isotherm, which comprises statistical and empirical data estimated from the Isotherm equation. The adsorption capacity of treated biosorbents is studied by varying the initial concentration of fluoride ions between 2 and 15 mg/L. With the largest particle size of 1.4 mm, the amount of fluoride ions adsorbed is found to be 95%. With the smallest particle size of 600 µ for an initial fluoride ion concentration of 10 mg/L, 90% adsorption is observed. Small particle size provides more active surface area and hence such results. Treated biosorbents can be removed effortlessly. There is no compelling reason to recover the depleted biosorbents as they are accessible bounteously, effortlessly, economically and locally. This system is financially perceptive, environment friendly and straightforward and can be embraced in provincial and also urban foundations consistently. Water filtration systems are frequently costly or inadmissible for the situations where they are generally required. The developed technique reported in this study has the advantages of high fluoride removal capacity, ease of operation, and economic, environmentally friendly and thus making this approach most desirable to people, especially in rural areas with high groundwater fluoride contaminations.[7]

*G. Brick Powder (Biomaterial)*

A new adsorbent BP was studied for the removal of fluoride from synthetic as well as from two groundwater samples of different fluoride concentrations. The conclusions drawn from the above study are given below: (1) Adsorption of fluoride on BP from an aqueous solution was found to be a first-order reaction and the mechanism of fluoride removal on adsorbent was found to be complex. The surface adsorption as well as intra-particle diffusion contributes to the rate-determining step. The Defluoridation capacity of BP can be explained based on the chemical interaction of fluoride with the metal oxides under suitable pH conditions. (2) The optimum pH was found to be in the range of 6.0–8.0 for maximum adsorption of fluoride, which makes it very suitable for use in drinking water treatment, especially in rural areas. (3) Presence of others ions in groundwater did not significantly affect the Defluoridation process thereby indicating that BP is a selective adsorbent for fluoride. Comparisons of BP and CAC reveal that BP is an economical adsorbent for the removal of fluoride due to greater and easy abundance as compared to CAC, and it can work on natural pH while CAC can work on acidic pH. [8]

*H. Tamarind Seed (Bio Material)*

The adsorption process of fluoride ion on Tamarind seed does exhibit first-order kinetics and Langmuir-type behaviour and is influenced by many experimental conditions. Remarkably, fluoride removal is favoured at low temperatures and neutral pH. The decrease in sorption capacity at high temperatures is suggestive of an exothermic reaction caused apparently by electrostatic and hydrogen bonds between fluoride ions and the adsorbent. Desorption of fluoride to the extent of 90% from fluoride-loaded Tamarind seed with 0.1 mol l21 HCl reveals the involvement of weak forces. The extension of sorption finding with the laboratory fluoride solution compared to the field water sample is quite agreeable and consistent. Further, household and column Defluoridation methods have been developed. Therefore, from the present study, it emerges that Tamarind seed has the potential to be an efficient defluoridating agent in its powder form, for application in domestic and macro-level treatment systems. Future study is, however, required to immobilize/condition the leachable polysaccharide in Tamarind seed powder, although it is harmless, and to remove testa from Tamarind seed before the kernel is pulverized into powder.[9]

*I. Activated Titanium-rich bauxite (Bio-Material)*

The present study suggests that TRB, containing mainly gibbsite and anatase with a minor amount of goethite, could be thermally activated for the removal of excess fluoride in contaminated water. The optimum temperature of thermal activation for maximum adsorption capacity is found between 300 and 450 ◦C. Although the uptake of fluoride is dependent on contact time, adsorbent dose, pH, and concentration of adsorbate, pH remains the most important factor. The optimum pH for maximum uptake is found between 5.5 and 6.5. The maximum adsorption capacity is found to be 3.8 mg/g at pH ∼ 6 with an adsorbent dose and initial fluoride concentration of 1 g/L and 10 mg/L, respectively. Adsorption of fluoride is fairly rapid in the first 10–15 min and thereafter increases slowly to reach the equilibrium in about 1.0–1.5 h. The adsorption followed first-order kinetics and the data fitted reasonably well to Langmuir and Freundlich isotherm models. The adsorption of fluoride is not greatly affected by the presence of common interfering ions indicating the selectivity of the material towards fluoride adsorption. The competitive effect of interfering ions may be minimized by proper selection of operating pH and fluoride can be removed to the desired level (<1.5 mg/L) from contaminated water using an appropriate dose of activated bauxite.

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Nearly complete desorption of fluoride from loaded bauxite is achieved at pH 11.1 indicating the possibility of reuse. The obtained results would be useful for considering the TRB as an adsorbent for the removal of excess fluoride ions from drinking water.[10]

## V. CONCLUSION AND DISCUSSION

They considered the adsorption of fluoride for different portions of adsorbent, starting convergence of fluoride in water, contact time, and pH, and found that for the ideal measurement of 6 mg/L, the adsorption is the most extreme. They likewise found that adjustment in pH has any effect on Defluoridation. From their investigations, they, in the long run, inferred that the recorded biosorbents can go about as a superior minimal-effort adsorbent for Defluoridation. [1-10]

The adsorption of fluoride on various adsorbents for enhancement of conditions like adsorbent measurement, pH, contact time, and fluoride-eliminating proficiency is recorded in Table II and Table III.

Table II: - Bio-Materials (Adsorbents)

| Sr. No | Name of Adsorbent | pH | Adsorbent dosage(g/L) | Contact time (Hr) | Removing efficiency (%) | References |
|---|---|---|---|---|---|---|
| 1 | Moringa Oleifera | 1 – 10 | 0.5 to 4 | 0.5 to 3.5 | 39 to 51 | S.S. Mokashi 2013 |
| 2 | Activated carbon prepared from banana peel and coffee husk | 6.32 | 5 to 20 | 13 | 80 to 84 | T. Getachew 2014 |
| 3 | Magnesia/Chitosan composite | 10 – 10.6 | 1.0 | 1 | 91 | C. Sairam Sundaram 2008 |
| 4 | Neodymium-Modified chitosan | 5-9 | 0.2 – 2 | 1 | 90 | Ruihua Yao 2008 |
| 5 | Mentha longifolia (Mint) | 2 – 10 | 10 | 1.5 | 90 | V.Sunitha 2018 |
| 6 | Brick powder | 6-8 | 10 – 60 | 1.2 | 48.73 – 56.4 | Asheesh Kumar Yadav 2015 |
| 7 | Tamarind seed | 3-6 | 4 | 2 | 90 | E. Subramanian (2010) |
| 8 | Activated titanium-rich bauxite | 5.5 – 6.5 | 1.0 | 1.5 | 98 | Nigamananda Das 2005 |

Table III: - Geo-Materials (Adsorbents)

| Sr. No | Name of Adsorbent | pH | Adsorbent dosage(g/L) | Contact time (Hr) | Removing efficiency (%) | References |
|---|---|---|---|---|---|---|
| 1 | Red soil | 7.69 | 2 - 3 | 1.5 | 95 | S. Chidambaram 2013 |
| 2 | Charcoal | > 4 | 20 | 2 | 85 | Sanghratna S. Waghmare 2015 |
| 3 | Clay | 5.5-6.5 | 30 | 3 | 92 | Sanghratna S. Waghmare 2015 |

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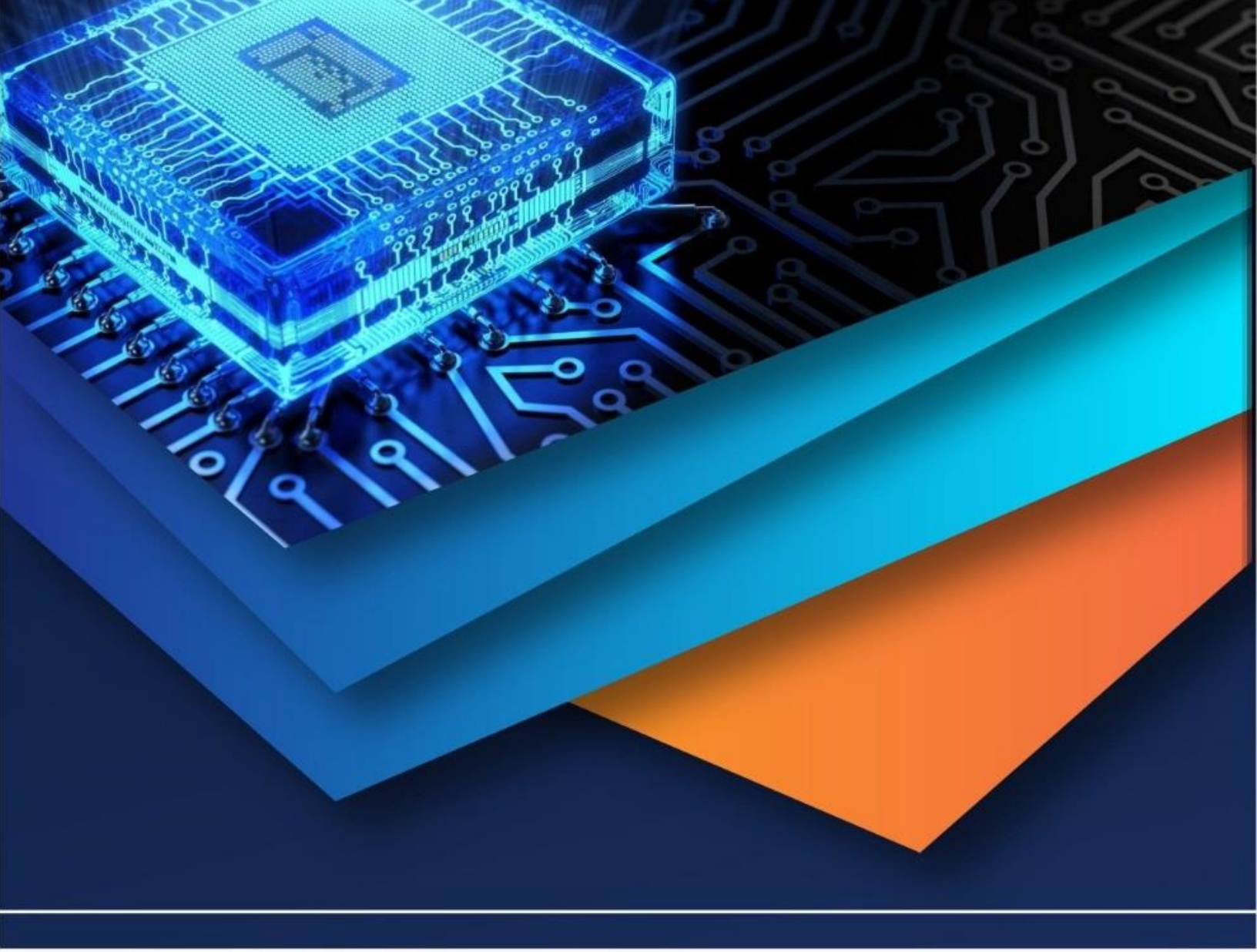
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