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The Endosulfan: Introduction, Impacts, Biotransformation & Kerela Tragedy

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Abstract: Endosulfan, an organochlorine pesticide, is a widely used pesticide globally. Its accumulation causes a great threat to the environment. This pesticide has two isomers, namely, alpha and beta. Both of these isomers degrade into different substrates among which endosulphan sulfate is extremely toxic as compared to others. It is not only hazardous to soil, soil micro flora but also human beings. This lipophilic chemical is water insoluble but it sticks to the soil particles and persist in soil and water for several years. The present review analyzes the impact and biotransformation of this pesticide and highlights its impact on human and animal health.

Keywords: Endosulfan, biotransformation, pesticide, toxicity, organochlorine.

I. INRODUCTION

Endosulfan (alternatively endosulphan) is an insecticide and acaricide. It was introduced to the market in the 1950s and it became a widely used pesticide for decades, continued after most of the other members of the cyclodiene group were removed from the market because of their toxicity, bioaccumulation, and environmental persistence. Endosulfans have poisoned the air, water, soil, and overall environment, posing a significant health risk to all living things. Although endosulfan has been listed in the Stockholm Convention as a persistent organic pollutant to be worldwide banned, it is still in use in some countries [1]

Endosulfan is a combination of two isomers, alpha-endosulfan and beta-endosulfan, with a mixed proportion of 70% and 30%, respectively **[2].** In 2011, endosulfan was added to the Stockholm Convention's list of banned substances. Endosulfan remains a favoured method in many developing nations, including China and India, where an official phase-out was slated to begin in 2016 and last until 2021. In nations like India, the debate over the global eradication of endosulfan as a POP is still going on, and more scientific information is needed for an efficient management of endosulfan [3]

Microbial degradation has long been thought to be a safe and cost-effective way to remove toxins from the environment. Biotransformed products formed during the insecticide's biodegradation, as well as the aftereffects of their transformed metabolites. This is important because the main biotransformed metabolites, endosulfan sulphate and endosulfan, are both toxic and harmful to a wide range of species. [4].

Aerial spraying of endosulfan over cashew plantations was stopped and then banned in kasargaod, kerela, more than 15 years ago. While the environmental effects of the spraying were noticed soon after the operations started in 1976 with the extinction of bees, a local physician noticed the human health effects in the early 1990s thousands of people have been affected [5].

II. ENDOSULFAN

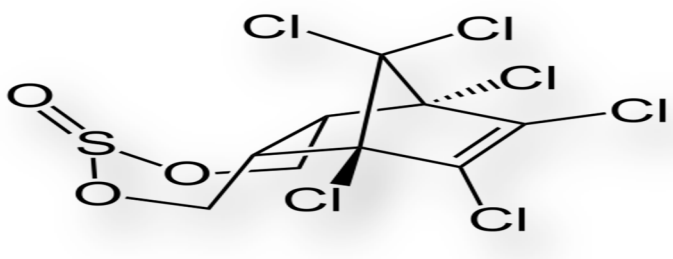

FIGURE 1 : MOLECULAR STRUCTURE OF ENDOSULFAN [1]

Endosulfan is an organochlorine insecticide which was first introduced in the 1950s and is commonly known by its trade name Thiodan .It is a diastereomeric mixture of two isomers i.e. alpha-endosulfan (64-67%) and beta-endosulfan (29-32%).It belongs to the organochlorine group of pesticides, under the Cyclodiene subgroup with chemical formula $C_9H_6Cl_6O_3S$. It has a chemical name i.e 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9ahexahydro6,9-methano-2,4,3-benzodioxathiepin-3-oxide**,** which is an organochlorine pesticide (OCP) that has been widespread used in the worldfor control pest such as aphides, beetles, whiteflies, worms etc. protection of variety of crops, including cereals, fruit, vegetables, tea and some non-food crop like tobacco and cotton. Endosulfan is toxic to non-target animals and humans [1].

Although endosulfan is now off-patent and it is being phased out in many nations around the world, it is reportedly still being used in India and china [6].

Chemical and Physical properties of Endosulfan

- In pure form it exists as colorless crystals
- Slightly soluble in water
- Dissolves readily in xylene, chloroform, kerosene and most organic solvents and is a non-combustible solid
- Mixable with most fungicides and compatible with most pesticides [7].

A. Acute Toxicity of Endosulfan

Acute psychological disorders, seizures, coma, brain oedema, diminished memory, and death may all result from acute endosulfan poisoning. If inhaled, ingested, or absorbed through the skin, endosulfan is extremely toxic and can be fatal. Oral toxicity is more severe than dermal toxicity in the short term.Symptoms of poisoning include hyper activity, excitement, dyspnea (breathing difficulty), salivation, loss of consciousness, diarrhea, anemia, nausea, vomiting,insomnia, blurred vision, cyanosis (bluish discoloration of skin due to want of oxygen), foaming at the mouth, tremor, dry mouth, lack of appetite, irritability, head ache, decreased respiration, loss of memory, haematuria, albuminuria, confusion, dizziness, imbalance and lack of coordination [7].The acute toxicity of Endosulfan (organochlorine) and Diazinon (organophosphate) pesticides to adult amphibians, Buforegularis was evaluated to determine uptake and effect of environmentally relevant concentrations on survival, morphology and behavior [8].

B. Chronic Toxicity of Endosulfan

Exposure through certain conditions of use (e.g. lack of protective equipment), exposure have been linked to congenital physical disorders, mental retardations and deaths in farm workers and villagers in developing countries.The liver, kidneys, immune system, and testes appear to be the key target organs in endosulfan'ssubacute and chronic toxicity. A number of neurotoxicitystudiesanalysis in rats (gavages) revealed that females were more responsive than males [9].

Immunosuppression and neurological problems have been attributed to long-term exposure.At low levels of exposure, endosulfan has been shown to have negative effects on the immune system. Organochlorine compounds have a growing body of evidence that they can function as hormones. These chemicals, such as DDT, PCBs, and endosulfan, may also play a role in the decline in sperm production, a rise in testicular and prostate cancer, and an increase in male sex-related defects [10].

III. IMPACT OF ENDOSULFAN

Pesticides are widely used in modern agriculture, and they are an efficient and cost-effective way to improve yield quality and quantity, ensuring food security for the world's ever-growing population.The existence of high levels of endosulfan in soils posses a risk to terrestrial ecosystems and human health through the food chain. As a result, the effects of endosulfan on the terrestrial biota at environmentally relevant doses are of great concern [11].

In respective to biodiversity and human health. High levels of endosulfan are more likely to persist in soil than other environmental matrixes, such as water and air, because of its lipophilic nature [3].

Endosulfan is ancommon environmental contaminant due to its semi-volatile composition, which renders it resistant to environmental degradation processes. It is hydrophobic, therefore it tends to get absorbed into soil particles, causing it to persist. Endosulfan's slow breakdown often results in the formation of endosulfan sulphate [12]. OCPs accumulate in adipose tissues due to their lipophilic properties, and reach in the organism not only by direct exposure but also through the diet and from the mother to the eggs [4]. Despite the fact that pesticides are beneficial to crop production,however their extreme use may haveserious consequences due to their bio-magnification and persistent existence [13].

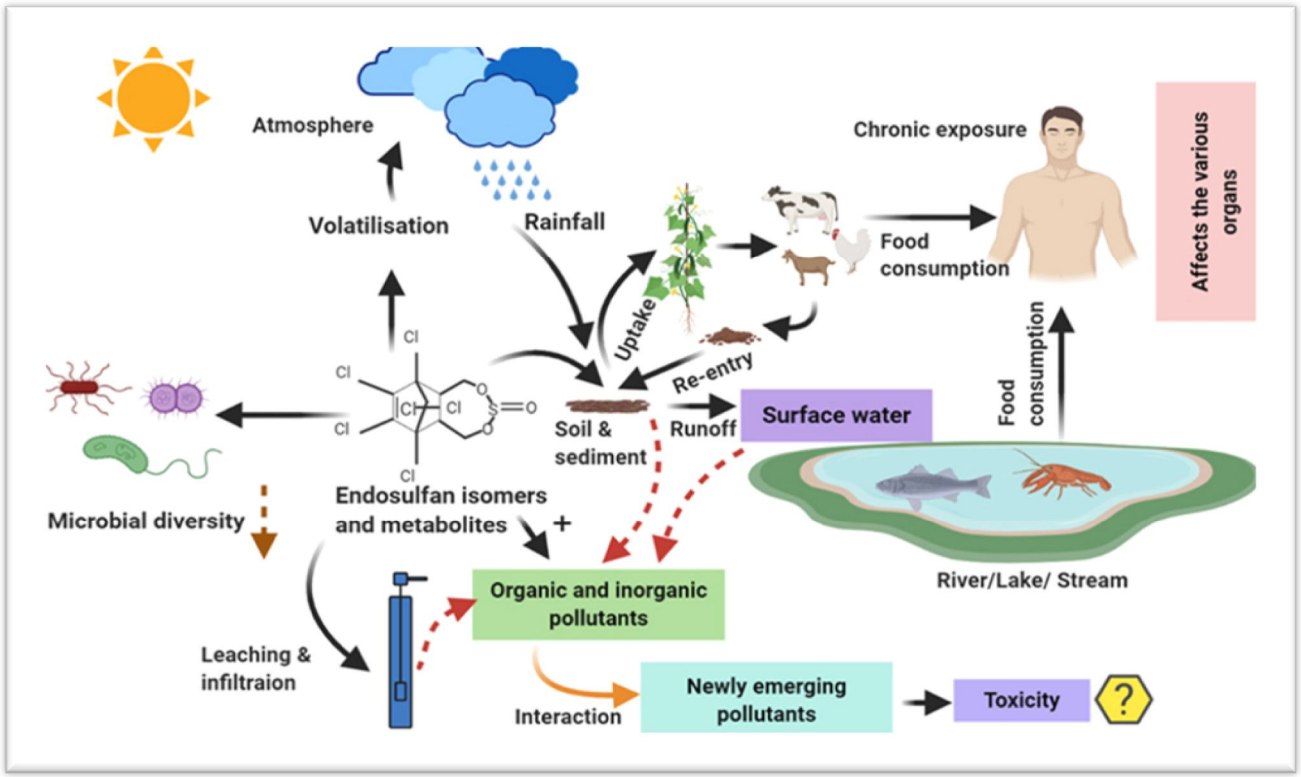

FIGURE 2. Persistence, toxicological effect and ecological issues of endosulfan [14].

A. Impact of Endosulfan on Ecosystem

The species richness of butterfly fauna in endosulfan-affected areas of Kasargaod District, which had caused serious threats to the ecosystem.Butterflies are considered as bio-indicators of a healthy and diversified ecosystem and have an intimate relationship with plants. As endosulfan is persistent and butterflies have a close relationship with plants, they may be directly affected. Endosulfan kill insects by endocrine disruption. Asendosulfan is a broad-spectrum insecticide, it damaged a wide range of organisms, resulting in a 40–70% reduction in diversity in the area. Forest regions with a lot of species (mostly birds and butterflies) as well as places close to the plantation were impacted. As a result, a significant butterfly population had vanished [12].

B. Endosulfan in the Reproductive System of the Aquatic Organism

Endosulfan are used insecticides across the world in the previous decade and their transformed products are causing acute toxicity to crustacean species resulting in ecological impact on aquatic ecosystems [4].

Amphibians and reptiles are experiencing a worldwide decline and the major cause using of OCPs.In oviparous species, one of the most important functions of the oviducts is to provide egg white proteins and eggshell to the ovulated eggs. The relationship between the existence of OCPs that act asEDCs in oviparous species eggs has been explored, as well as eggshell characteristics, which has been showed thatOCPs exposure has a direct impact on maternal oviductal functioning, as evidenced by lower eggshell porosity, which resulted in lower hatching survival at 10 days [4].

The external genitalia (phallus or clitero-penis) of crocodilians are made up of an unpaired organ that is considered sexually dimorphic.The phallus in males acts as a conduit for intromission and insemination into the female cloaca during copulation, while profuse innervation in females indicates the phallus is linked to sex arousal and/or a neuroendocrine response required for successful copulation.It has been found that since the phallus is the hormone-dependent organ, its size may be altered by exposure of EDCs [15].

Agricultural pesticides can reach aquatic habitats by air drift, runoff, and/or leaching during application. The distribution of toxicants in different environmental compartments depends on both their physicochemical properties and environmental conditions that impact the degree of transport, transformation, adsorption, and/or bioaccumulation by the aquatic biota. lipophilic nature,

persistent organic pollutants, including organochlorine pesticides, are able to bioconcentrate and biomagnify through the food chain [16].

C. Impact of Endosulfan on Human Health And Animals

Endosulfan was used to considered a vital pesticide for farming, however, concerns about human health effects and environmental effects of pesticides exposure hasincreased over the past decade, but that organochlorine are still the most commonly used pesticides in India. Negligence during handling of pesticides usually as part of the operator error, lack of information or lack of training can cause a serious health risk for farmers who are the major pesticide users and are regularly exposed to pesticides in many ways. The World Health Organization (WHO) and the United Nations Environment Programme (UNEP) declared that in the developing world people experienced and suffered severe poisoning from pesticide. Endosulfan can have adverse effects on the immune system at low levels of exposure .The short and long term health implications of the use of Endosulfan as a pesticide caused Congenital Birth defects, reproductive health problems, cancers, loss of immunity, neurological and mental diseases [17].

D. Bioaccumulation of Endosulfan in Fatty Tissues

Endosulfan stores easily within the fatty tissues of living organisms. The presence of α-endosulfan, β -endosulfan, and its metabolites in fatty and non-fatty tissues and fluids in higer amount has been found in adipose tissue, Endosulfandiol and endosulfan sulfate were more frequently found in placenta homogenate, human milkand in blood from umbilical cord [18].

Humans can be exposed to endosulfan through inhalation, dietary (fatty food of animal origin), and skin contact. Contaminated food and water are the primary causes of endosulfan contamination in the general population. Endosulfan is quickly absorbed into the gastrointestinal tract and bioaccumulates in fatty tissues due to its lipophilic nature. Since endosulfan accumulates in the human body, it can be passed from the mother to the foetus via the placenta and breast milk[1].

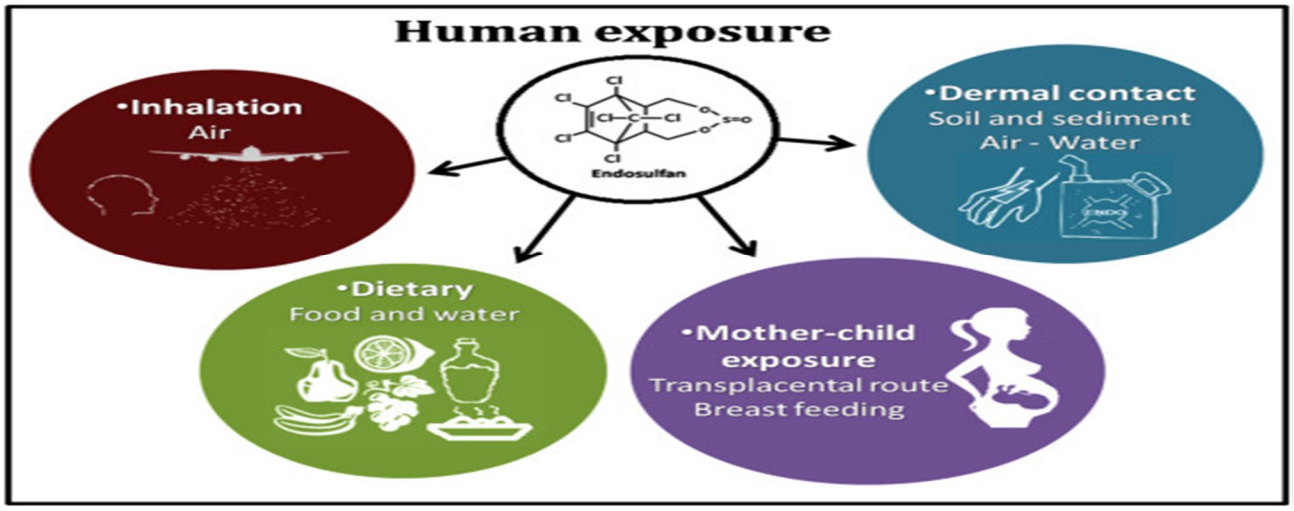

Figure 3. Possible routes of human exposure to endosulfan. Inhalation: air. Dietary: food and water. Mother-child exposure: transplacental route and breast feeding. Dermal contact: soil and sediment, air and water [1]**.**

IV. BIOTRANSFORMATION OF ENDOSULFAN

Endosulfan is degraded readily by soil microorganisms. The rate of degradation depends mainly on soil type, pH, microbiological activity, and temperature [19].Pesticides used on agricultural crops enter the soil's surface, where they are converted into one or more transformed products, either biologically or non biologically. Endosulfan are semi-volatile and persistent compounds. They can be found in a variety of environmental samples due to their different properties.

A. Biotransformation of Endosulfan by Bacteria

Biotransformation of endosulfan by using bacteria has been vastly studied by researchers. Endosulfan will be oxidized into endosulfan sulfate (considered more toxic compound than endosulfan) by oxidation pathway and also hydrolyzed into various other intermediate compounds (considered less toxic) by hydrolytic pathway.

The degradation pathway adopted by bacteria varies from one species to another. Some of them are, the strain *Pseudomonas sp. KS-2P*.The three bacterial isolates *P. spinosa, P.aeruginosa, and Burkholderiacepacia* were able to degrade 90% of endosulfan.*Pseudomonas* bacteria identified as *P. aeruginosa SKL-1*was able to degrade α and βendosulfan into endosulfan sulfate [20]. A endosulfan and endosulfan sulfate were biotransformed into endosulfandiol, ether, and lactone by *Pseudomonas sp. Strain IITR01.*

B. Biotransformation of Endosulfan by Fungi

Endosulfan biotransformation and transformed products produced by various fungal species. *Chaetosartoryastromatoides, Aspergillusterricola,* and *A. terreus* were found to degrade both the isomers of endosulfan,transformed metabolites were endosulfandiol and ether.

Fungal strain *Aspergillusniger ARIFCC 1053* was found to be a suitable bioaugmenting agent for treating endosulfan-contaminated soil. Another fungal strains *Trametesversicolor*and *Pleurotusostreatus* transformed endosulfan into endosulfan sulfate and also into small amount of endosulfanether [4].

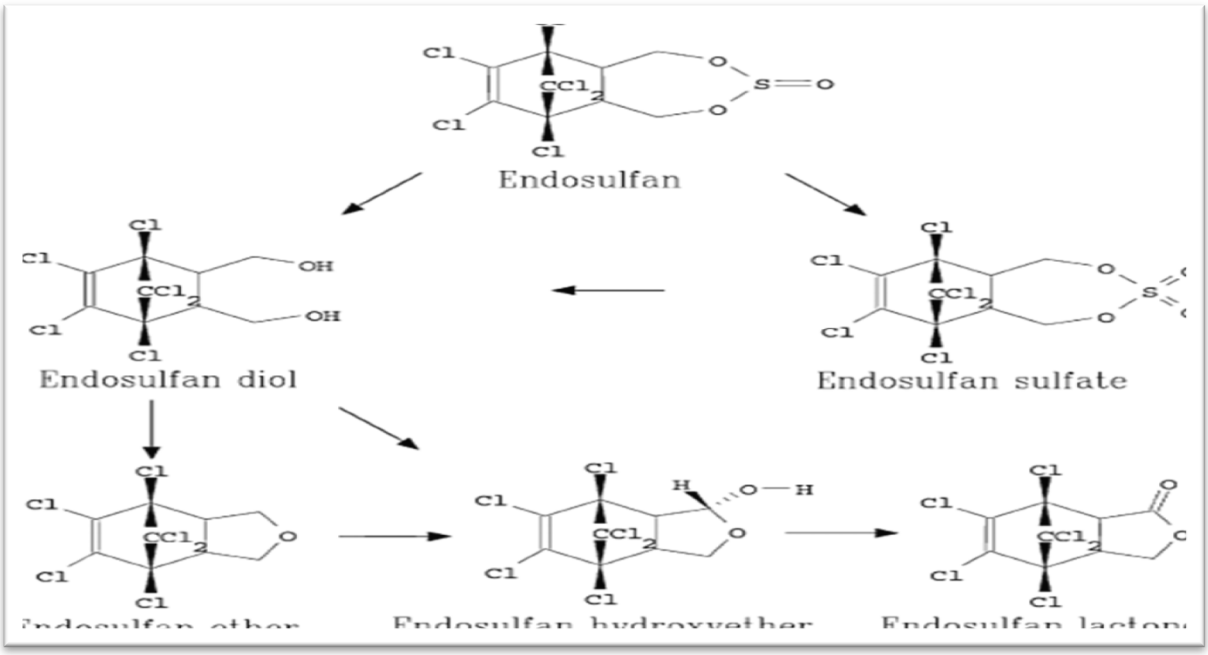

FIGURE 4.SOURCE: METABOLITES OF ENDOSULFAN [20]

V. TRAGEDY OF ENDOSULFAN IN KERELA

The most widely used pesticide in India is endosulfan (Department of Agriculture, Government of India 2009–2010). In the years 1999–2000, the country produced approximately 81,000 metric tonnes of endosulfan. Mental and physical disorders, reproductive failure, hormonal dysfunction, skin rashes, concurrent abortions, and other health problems have all been attributed to the molecule [2].

In Kasargod's Padre Village, residents reported that aerial spraying of Endosulfan in the cashew plantations began in 1976.Usage of endosulfan continuously as a pesticide on cashew plantations in Kerala's Kasargaod district for over 20 years. In other parts of Kerala, this pesticide was applied through aerial spraying or manual pumps to tea plantations, paddy fields, and fruit orchards.It was later discovered to be extremely hazardous to human health andmany illnesses were also triggered by the endosulfan. It poisoned entire populations of insects that are both useful and important. In humans and animals, these ailments included skin irritations, nerve tissue loss, and reproductive and developmental damage.There were records of calves being born with deformed limbs a few years later. Frogs, fish, bee colonies, fireflies, and jackals were all extinct in these regions. Many local children and individuals under the age of 25 were suffering from serious mental illnesses. Moreover, Endosulfan was also used extensively in mango farms.

There were also accounts of animals giving birth to deformed children, and people witnessed the daily deaths of monkeys, reptiles, and tens of thousands of butterflies. In Muthalamada, a 2014 survey found over 150 Endosulfan victims, with 40% of them suffering from chronic illnesses [21].

Later, In 2005, the Kerala government outlawed the use of endosulfan. However, neighbouring countries continued to use them. The Stockholm Convention on Persistent Organic Pollutants (POPs) adopted a global ban on the manufacture and use of Endosulfan [22].

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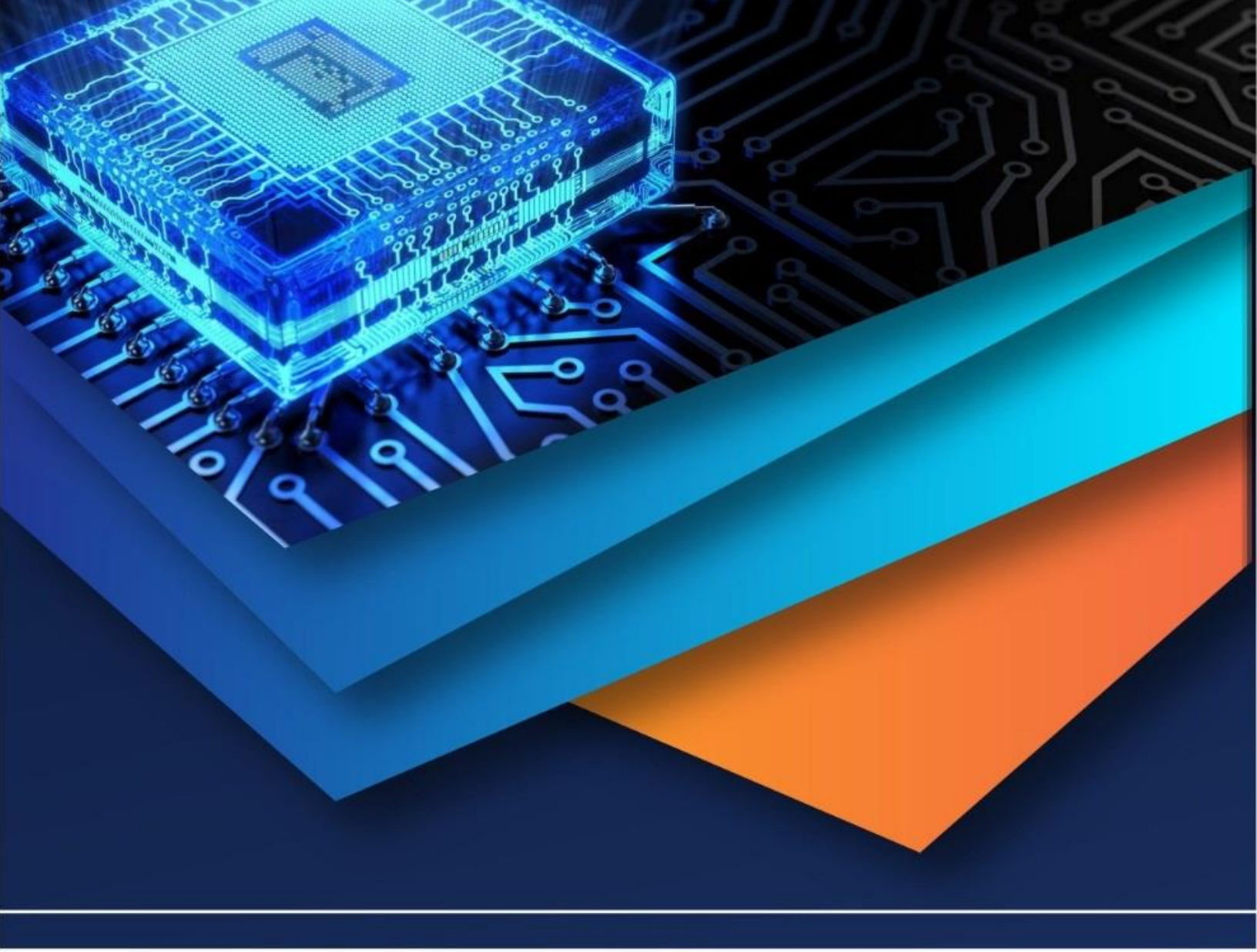

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