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Chlorine As a Disinfectant in Water Treatment

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Abstract: Disinfection of treated water is a necessary process. For this, chlorine and its products are widely used. During the treatment process, chlorine is added to drinking water as elemental chlorine, sodium hypochlorite solution or dry calcium hypochlorite. When applied to water, each of these forms "free chlorine", which destroys pathogenic organisms. If adequate water treatment is not readily available, the impact on public health can be devastating. Worldwide, about 1.2 billion people lack access to safe drinking water, and about 2.4 billion people lack sanitation. As per WHO, 3.4 million people die from water-related diseases. Drinking water chlorination will remain a cornerstone of disinfection. This is because of the wide range of benefits provided by chlorine. However, alternative disinfectants including ozone and UV radiation are available, all disinfection methods have unique benefits, limitations and costs. So, an engineer has to consider all the pros and cons of a disinfectant method properly before deciding the one to adopt.
Keywords: Disinfection, Gaseous Chlorination, Sodium Hypochlorite, Calcium Hypochlorite, Ultraviolet, Ozone, Chlorine dioxide

I. INTRODUCTION

The treatment and distribution of water for safe use is one of the greatest achievements of the twentieth century. Before cities began routinely treating drinking water with chlorine, cholera, typhoid fever, dysentery and hepatitis A killed thousands of people. Meeting the goal of clean, safe-drinking water requires a multi-barrier approach that includes: protecting source of water from contamination, appropriately treating water to consumers' taps.

During the treatment process, chlorine is added to drinking water as elemental chlorine, sodium hypochlorite solution or dry calcium hypochlorite. When applied to water, each of these forms "free chlorine", which destroys pathogenic organisms. In addition to controlling disease-causing organisms, chlorination offers a number of benefits including

A. Reduces many disagreeable taste and odour.
B. Eliminates slime bacteria, moulds and algae that commonly grow in water supply reservoirs, on the walls of water mains and in storage tanks
C. Removes chemical compounds that removes unpleasant taste
D. Helps remove iron and manganese from water

Risks of Waterborne Diseases: If adequate water treatment is not readily available, the impact on public health can be devastating. Worldwide, about 1.2 billion people lack access to safe drinking water, and about 2.4 billion people lack sanitation. As per WHO, 3.4 million people die from water-related diseases. Even where water treatment is widely practiced, constant vigilance is required to guard against water-borne disease outbreaks.

A striking example occurred in May 2000 in the Canadian town of Walkerton, Ontario. Seven people died and more than 2300 became ill after E. Coli and other bacteria infected the town's water supply. A report published by the Ontario Ministry of the Attorney General concludes that, even after the well was contaminated, the Walkerton disaster could have been prevented if the required chlorine residuals had been maintained.

The challenge of Disinfection By-products (DBP): In early 1970s, EPA scientists first determined that drinking water chlorination can develop a group od DBP known as Trihalomethanes (THMs), including chloroform. A report by the International Programme on Chemical Safety (IPCS 2000) strongly cautions:

"The health risks from these by-products at the levels at which they occur in drinking water are extremely small in comparison with the risks associated with inadequate disinfection. Thus, it is important that disinfection not be compromised in attempting to control such by-products."

The Future of Chlorine Disinfection: Despite a range of new challenges, drinking water chlorination will remain a cornerstone of disinfection. This is because of the wide range of benefits provided by chlorine. However, alternative disinfectants including ozone and UV radiation are available, all disinfection methods have unique benefits, limitations and costs. So, we need to consider all the pros and cons of a disinfectant method properly before deciding the one to adopt.

II. HISTORY OF CHLORINATION

Chlorine was first discovered in Sweden in 1744. At that time, people believed that odours from the water were responsible for transmitting diseases. In 1835, chlorine was used to remove odours from the water, but it wasn't until 1890 that chlorine was found to be an effective tool for disinfecting; a way to reduce the amount of disease transmitted through water. With this new discovery, chlorination began in Great Britain and then expanded to the United States in 1908 and Canada in 1917. Today it is the most popular method of disinfection and is used for water treatment all over the world.

III. LITERATURE SURVEY

An estimated 5.6% of household in the middle- and low-income countries, or 67 million people, report that they usually treat their water with bleach or another source of chlorine at home before drinking it (Rosa et al., 2010).

At doses of a few mg/l and contact time of about 30 minutes, free chlorine inactivates more than 99.99% of enteric pathogens, the notable exception being Cryptosporidium, which the Global Enteric Multicentre Study (GEMS) found to be highly prevalent in young children with moderate-to-severe diarrhoea (Sow et al., 2016).

In a systematic review of 1 intervention studies of point-of-use water treatment with chlorine, Arnold and Colford (2007) reported that the intervention significantly reduced the risk of stored water contamination with Escherichia coli. They also reported that the intervention reduced the risk of child diarrhoea. A major finding of their review, however, was an attenuation of the intervention's reduction of child diarrhoea in longer trials. The authors noted that this could be attributable to seasonal variations in microbiological performance or to user fatigue that may be more acute for interventions such as chlorine that adversely impact water aesthetics (taste and odour).

A taste test for acceptability thresholds of NaOCl and NaDCC in Bangladesh found that they were below the doses most chlorine treatment products are designed to provide (Crider et al., 2017).

Recent multi-arm randomized controlled intervention trials in rural Bangladesh and Zimbabwe with 24- and 18-month follow-up periods, found no effects on diarrhoea or child growth of household chlorination and safe storage (Luby et al., 2018; Humphrey et al., 2019).

Notably, the trial in Bangladesh did find an approximately a $1 - \log_{10}$ reduction in faecal contamination in household stored water from the safe storage intervention (Ercumen et al., 2018).

The diminished effect of chlorine and other disinfection interventions overtime has been contrasted with filter interventions, leading some investigators to conclude that this absence of sustained effect after adjusting for possible reporting bias, raises questions abou t the suitability of scaling up chlorine interventions at the household level until further efforts to secure long-term uptake can be shown (Hunter et al., 2009).

A. Action Of Chlorine

When chlorine is added to the water following reactions take place:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

The hypochlorous acid dissociates into hydrogen ions (H^+) and hypochlorite ions (OCl^-) as indicated below:

$$HOCl \rightarrow H^+ + OCl^-$$

It is the hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) which accomplish disinfection of water. The undissociated hypochlorous acid is about 80 – 100 times more powerful disinfectant as compared to hypochlorite ions. This chlorine existing in water as hypochlorous acid, hypochlorite ions and molecular chlorine is defined as free available chlorine.

Both the above-mentioned reactions depend on pH of water. When pH value of chlorinated water is above 3, the hydrolysis reaction is almost complete and chlorine exists as hypochlorous acid. As the pH value increases more and more, hypochlorous acid dissociates to form hypochlorite ions. Up to pH of 5.5 hypochlorous acid remains undissociated, while at pH> 9.5 all the hypochlorous acid is dissociated to form the hypochlorite ions. For pH between 6 to 8, there occurs a very sharp change from undissociated to completely dissociated hypochlorous acid with 96% to 10% HOCl, with equal amount of HOCl and OCl^- ions at pH 7.5.

Combined available chlorine: The free chlorine can react with compounds such as ammonia, proteins, amino acids and phenol that may be present in the water to form chloramines and chloro-derivatives which are known as combined chlorine. This combined chlorine also possessing some disinfecting properties but not as much as the free available chlorine. Since these reactions are usually not 100% complete, some free available chlorine exists along with combined chlorine.

1) *Chlorine is applied to water in three forms.*

They are as under:

a) Chlorine gas
b) Sodium Hypochlorite
c) Calcium hypochlorite

2) *Advantages*

a) Highly effective against most pathogens
b) Provides a residual to protect against recontamination
c) Easily applied, controlled and monitored
d) Strong oxidant meeting most peroxidation objectives
e) Operationally, the most reliable
f) Most cost-effective disinfectant

3) *Limitations*

a) By-product formation
b) Oxidises bromide to bromine, forming brominated organic products
c) Requires transport and storage of chemicals

B. Chlorine Gas

Chlorine gas is a greenish-yellow gas. It is toxic. It is lethal at concentrations as low as 0.1% air by volume. Introducing chlorine to water plays a very effective role for removing almost all pathogenic microorganisms. It can be used both as primary and secondary disinfectant. Chlorine can be used as liquid or gas form. It is a very strong, oxidising agent. Both the forms (liquid and gas) can be stored and used from gas cylinders under pressure. The chlorine cylinders can be 68 kg in weight. The system at which free chlorine is supplied at a concentration of 0.3 – 0.5 mg/l is an ideal system. Chlorine gas may be fed directly to the point of application to the water supply or chlorine gas may be first dissolved in a small flow of water and the chlorine-water solution is fed to the point of application to the water supply.

The first method of application of chlorine is less satisfactory because of poor diffusion of chlorine in water. Further it is found that at low temperatures (<10ºC) crystalline hydrates of chlorine are formed, and hence when the chlorine is directly fed through pipelines and if temperature falls down, choking of pipes leading chlorine may take place. There is also a possibility of corrosion in pipes and valves resulting from accumulation of undissolved chlorine gas. As such only the second method of application of chlorine is used.

1) *Advantages*

a) Lowest cost of chlorine
b) Most effective
c) High quantity of free available chlorine

2) *Limitations*

a) Hazardous gas requiring special handling and operator training
b) Additional regulatory requirements

C. Sodium Hypochlorite Solution

Sodium hypochlorite is used as bleaching agent, mostly to bleach papers or textiles and as a disinfectant in solution. The solution, also known as liquid bleach, contains 10 – 15% of the available chlorine, but rapidly loses its force in storing process. Regular controlled environment is needed as the solution is greatly affected by pH, light and heavy metals. NaOCl solution is a corrosive liquid with high pH (pH = 12). So general precautionary measures for dealing with corrosive fluids should be used such as avoiding metal contact, including stainless steel. This solution may contain chlorate formed due to product degradation in the process of manufacturing and storing. By reducing the degradation of NaOCl, formation of chlorate can also be reduced by avoiding high temperatures, reducing light exposure and limiting storage time. Spill containment should be provided for the storage tanks.

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1) Advantages

a) It has the same effectiveness as the chlorine gas.
b) As compared to chlorine gas, sodium hypochlorite reduces the hazards in storing and handling.
c) No hazardous chemicals are used in on-site generation. Only softened water and high-grade salt (NaCl) is used.

2) Limitations

a) NaOCl can be commercially supplied or generated on-site, the latter being safer due to handling reasons. In on-site generation, salt is dissolved with soft water to make a concentrated brine that is subsequently diluted and passed through an electrolytic cell to form NaOCl. Hydrogen is also produced in this process, and needs to be vented because of its explosive nature.
b) Higher chemical cost than chlorine gas.
c) It has a corrosive nature and lacks stability.
d) Limited shelf-life
e) Potential to add inorganic by-products

D. Calcium Hypochlorite

Calcium hypochlorite or bleaching powder is chlorinated lime, $Ca(OCl_2)$. When it is added to water it dissociates into calcium and hypochlorite ions. These hypochlorite ions combine with hydrogen present in water to form hypochlorous acid.

$$Ca(OCl_2) \rightarrow Ca^{++} + 2OCl^-$$
$$H^+ + OCl^- \rightarrow HOCl$$

This process is known as hypo-chlorination.

Bleaching powder contains about 30 – 35% of available chlorine. It is very unstable compound as it goes on losing its chlorine content when exposed to atmosphere so it requires very careful storing.

1) Calcium Hypochlorite Can Be Added To The Water By Two Ways

a) By mixing calcium hypochlorite powder in a mixing device and then injecting it into the water stream.
b) By immersing chlorine tablets using tablet chlorinator.

Mostly the dosage ranges from 0.5 – 2.5 kg per million litres of water. Different factors account for optimum disinfection that might include temperature, alkalinity, and nitrogen content.

2) Advantages

a) Being solid, bleaching powder is safer and easier to handle than chlorine gas.
b) It has great stability when stored in dry place.
c) Moe stable than sodium hypochlorite, allowing longer storage

3) Limitations

a) Contamination or improper use of bleaching powder may lead to explosion, fire or release of toxic gases.
b) If it is exposed to even very small amounts of water, it can react violently to produce toxic gases, heat and spatter. The powder is to be added in water, not the other way around.
c) Exposure to heat can cause bleaching powder to decompose rapidly, which may lead to explosion and intense fire.
d) Higher chemical cost than elemental chlorine

E. Alternative Disinfectants

Disinfectants alternative to chlorine can be broadly classified in two categories. They are as mentioned below:

1) Chlorine Based Alternative Disinfectants

a) Chloramines: These are the chemical compounds which are formed by reaction of chlorine with ammonia in water. This reaction is as mentioned below:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$
$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$$
$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$$
$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$$

Since chloramines are very weak disinfectants they are used as secondary disinfectant i.e., as residual disinfectant. They provide durable residual for long distribution lines and for instances where free chlorine demand is high.

- *Advantages*
- Reduce the formation of THMs
- Don't oxidise bromide to bromine
- More stable residual than elemental chlorine
- Excellent secondary disinfectant
- Lower taste and odour
- No by-products are formed
- *Disadvantages*
- Weak disinfectant
- Require shipment and handling of ammonia or ammonia compounds
- Ammonia is toxic to fish and may pose problems for aquarium owners
- Cause kidney problems if not removed from water

b) Chlorine Dioxide: Chlorine dioxide (ClO_2) is generated on-site at water treatment facilities. In most generators sodium chlorite and elemental chlorine are mixed in solution, which instantaneously forms chlorine dioxide.

$$2NaClO_2 + Cl_2 \rightarrow 2NaCl + 2ClO_2$$

Since chlorine dioxide gas is unstable, it is commonly generated at the point of its use by the introduction of sodium chlorite solution into the chlorinator discharge line. However, the aqueous solution of chlorine dioxide is stable. Chlorine dioxide has an oxidising capacity 2 ½ times that of chlorin. Further, it is most effective in the removal of taste and odours, particularly those which are caused by phenolic substances and algal growths. It is also reported to be more effective than chlorine as a bactericide and as a sporicide. Chlorine dioxide characteristics are quite different from chlorine. In solution it is a dissolved gas which makes it largely unaffected by pH but volatile and relatively easily stripped from solution. Chlorine dioxide is also a strong disinfectant. It produces residual but it is rarely used.

- *Advantages*
- Effective against Cryptosporidium
- Up to five times faster than chlorine at inactivating Giardia
- Disinfection is only moderately affected by pH
- Will not form chlorinated by-products
- Doesn't oxidise v=bromide to bromine
- More effective than chlorine in treating taste and odour
- Selective oxidant used for manganese oxidation and targeting some chlorine resistant organics
- *Limitations*
- Highly volatile residuals
- Requires on-site generation
- Requires high level of technical competence and monitoring equipment
- Occasionally poses unique odour and tase problems
- High operating cost

2) Non-chlorine Based Alternative Disinfectants

a) Ozone: Ozone is a faintly blue gas of pungent odour. It is an unstable gas which tends to breakdown to normal oxygen O_2 and nascent oxygen (O). the nascent oxygen is very effective in oxidising the organic matter and it is very powerful in killing bacteria. It is generated on-site at water treatment plants by passing dry oxygen through a system of high voltage electrodes. The mixture of ozone and oxygen produced by the ozone generator is introduces in the water to be treated by injecting or diffusing it into a mixing chamber. The dosage of ozone is about 2 – 3 ppm to obtain residual ozone of 10 ppm and the contact period is about 10 minutes. When water is treated by ozone, it first reacts with chemical impurities present in the water. Once this ozone demand of water has been satisfied, free residual ozone in water kills microbes and the disinfection is achieved.

- *Advantages*
  - Strongest disinfectant available
  - produces no chlorinated THMs
  - Effective against spores at high concentrations
  - Efficiency unaffected by changes in temperature and pH value of water
  - Bactericidal action is more rapid than chlorine
  - Doesn't impart offensive taste and odour to water

- *Limitations*
  - Process operation and maintenance requires high level of technical competence
  - Provides no protective residual
  - Higher operating and capital costs
  - Difficult to control and monitor
  - Ozone more costly than chlorine

b) *Ultraviolet Radiation:* UV rays, generated by a machine which contains mercury-vapour lamp enclosed in a quartz globe. These lamps commonly use 220 V DC supply. When UV radiation penetrates the cell wall of an organism, it damages genetic material and prevents the cell from reproducing. It is effective on both active bacteria and spores. The destructive power of these rays begin in blue-green region of the spectrum with a wavelength of 0.490µ and increases in effectiveness to 0.149µ.

- *Advantages*
  - Effective in inactivating most viruses, spores and cysts
  - No chemical generation, storage or handling
  - No by-products produced

- *Limitations*
  - No residual
  - Low inactivation of some viruses (reovirus and rotavirus)
  - May require additional treatment steps to maintain high-clarity water
  - Requires large surface area of water.

IV. COMPARING ALTERNATIVE DISINFECTION METHODS

Up until the late 1970s, chlorine was virtually the only disinfectant used to treat drinking water. Chlorine was considered an almost ideal disinfectant, based on its proven characteristics:

1) Effective against most known pathogens
2) Provides a residual to prevent microbial re-growth and protect treated water throughout the distribution system
3) Suitable for a broad range of water quality conditions
4) Easily monitored and controlled
5) Reasonable cost

More recently drinking water providers have faced an array of new challenges, including:

a) Treating resistant pathogens
b) Minimising disinfection by-products
c) New environmental and safety regulations

To meet these new challenges, engineers must design unique disinfection approaches to match each system's characteristics and source water quality. While chlorination remains the most commonly used disinfection method by far, water systems may use alternative disinfectants. No single disinfection method is right for all circumstances, and in fact, water systems may use a variety of methods to meet overall disinfection standards and to provide residual protection throughout the distribution system.

V. CONCLUSION

Although we have a number of alternative disinfectants to chlorine, still chlorine is widely used worldwide because of the following reasons:

1) *Potent Germicide:* Chlorine reduces the level of many disease-causing microbes in drinking water to almost immeasurable levels.
2) *Taste and Odour Control:* Chlorine disinfectants reduce many disagreeable tastes and odours. It oxidises many foul-smelling algae secretions, sulphides and odours from decaying vegetation.
3) *Biological Growth Control:* Chlorine disinfectants eliminate slime bacteria, moulds and algae that commonly grow in water supply reservoirs, on the walls of water mains and in storage tanks.
4) *Chemical Control:* Chlorine disinfectants destroy hydrogen sulphide and remove ammonia and other nitrogenous compounds that have unpleasant tastes and hinder disinfection.
5) *Residual Disinfection:* We require a residual level of disinfection of water in pipelines to prevent microbial re-growth and help protect treated throughout the distribution system.

Although chlorine has several limitations such that it imparts bad taste and odour to water and produces DBPs; it is still in use due to the above-mentioned advantages. All the disinfectants have their own pros and cons which are to be kept in mind while deciding the disinfectant method for the particular water treatment system.

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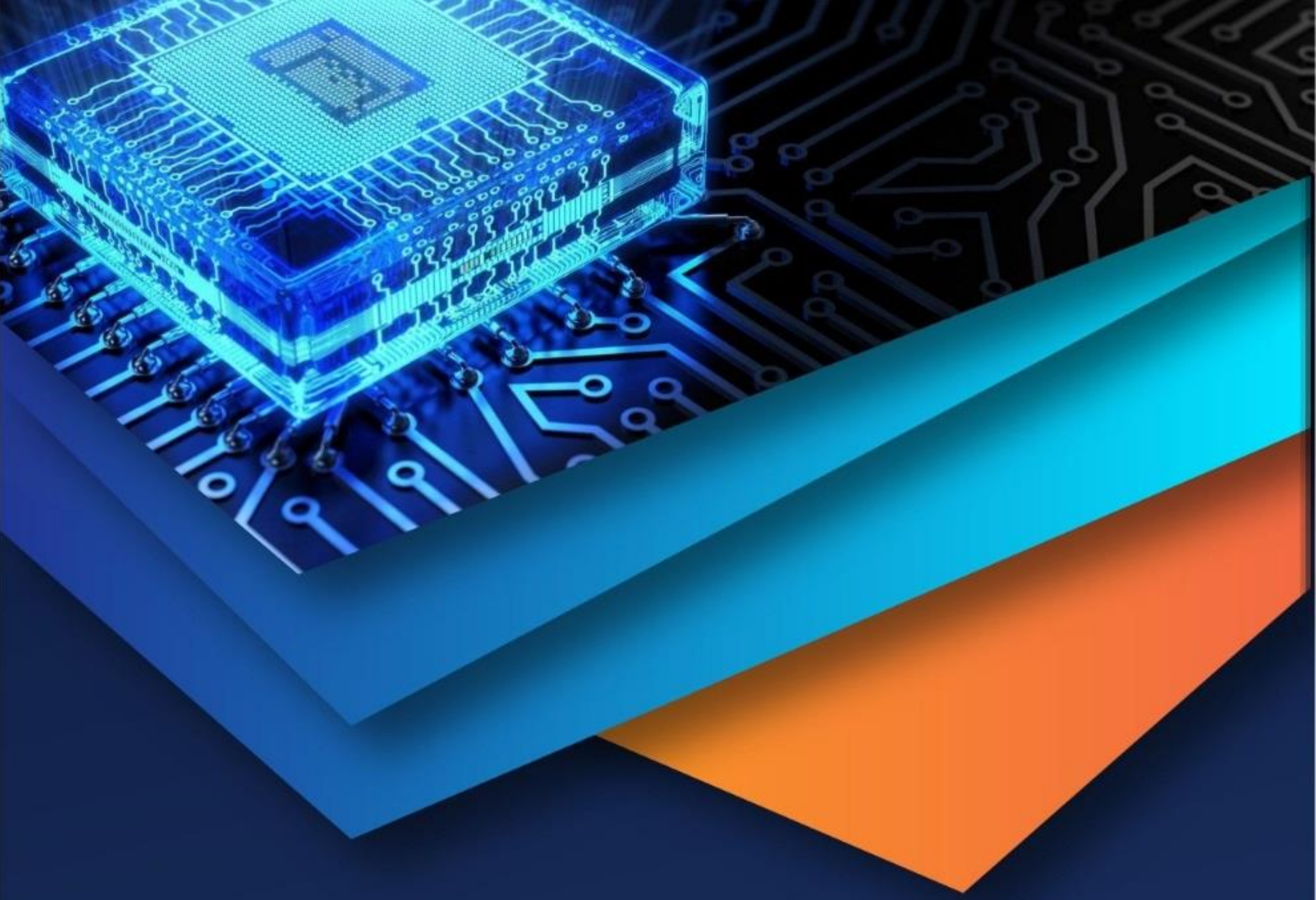

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