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Removal of Ammoniacal Nitrogen from Effluent through Electrochemical Oxidation: A Review

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Abstract: ***Human society always tries to elaborate itself towards the progress. During this journey, human needs to mitigate the Industrialization problems as well as the Environmental issues. The handling and management of wastewater generated is the major problem in every Industry. The wastewater contains different types of pollutants and it is important to remove the same from the wastewater before disposing it. We are focusing on the removal of Ammonical nitrogen from wastewater through Electrochemical Oxidation Process. This Electrochemical Oxidation method consists of carrying out the oxidation reaction at the anode where pollutants are transferred into non-toxic substances, by decomposition into simpler compounds or transferring into oxidation form. In this paper, Electrochemical Oxidation which have been used for removal of Ammonical nitrogen are studied with their results. A comprehensive study of the methodology and the factors affecting the Oxidation process has been carried out. The electrochemical oxidation of ammonia was investigated on different electrodes like Ti/RuO2-Pt, Ti/IrO2, Ni/Ni (OH) 2, and Ti/SnO2. It was inspected that at different operating parameters like pH, temperature and current densities, the oxidation of ammonia is different. Ammonia is oxidized into Nitrates and gaseous Nitrogen.***

Keywords: Electrochemical Oxidation, Ammonical Nitrogen, Wastewater, Current Density, Electrode, Efficiency, Pseudo-kinetics, Temperature, Power

I. INTRODUCTION

Electrochemical oxidation process is not an uncommon word when it comes to reduction of different types of organic and non-organic polluting species from waste water. Being a tested method, it is used vastly for the foresaid purpose and has produces fairly good results worldwide. Electrochemical oxidation is a process, whose driving force for the reduction of pollutants from waste water is the Voltage applied through a number of electrodes placed closely to each other. The number of electrodes can vary depending upon the need and amount of the quantity of waste water to be treated. When the voltage is applied to the wastewater, certain Redox reactions take place in the water due to the impurities and pollutants present. Those redox reactions are the root cause of reduction of the pollutants

Electrochemical cell can be defined as a device haing the ability of generating electrical energy from chemical reactions, it can also be used for conducting chemical reactions by the introduction of electrical energy. A familiar type of an electrochemical cell is a conventional 1.5 – volt cell which is available on all departmental stores. An electrochemical cell possess of two half-cells. Each half-cell consists of an electrode and an electrolyte. Both of the two half-cells may use the similar electrolyte, or they may use different electrolytes. The chemical reactions in the cell may involve the electrolyte, the electrodes, or an external substance (as in fuel cells that may use hydrogen gas as a reactant). In a full electrochemical cell, species from one half-cell lose electrons (oxidation) to their electrode while species from the other half-cell gain electrons (reduction) from their electrode.

Ammonia (NH3) is a very commonly produced commercial chemical in the world. It is widely used in industry and commerce, this also remains present in the nature in different forms. Ammonia is vital for a lot of biological processes and used to initialize amino acid and nucleotide synthesis ammonia is a part of nitrogen cycle and lifeline for a lot of microbes, which tells about its role in environment. Ammonia is also generated as a byproduct of rotting organic matter, including plants, animals and wastes. Nearly, 80% of the ammonia generated by companies is used for the agriculture as fertilizer.

Ammonia has been used since ages in different industries like chemical manufacturing, metal industries, petroleum industries, pesticide industries, food and beverage units, refrigeration and cold storage units and many more. These industries represent only a fraction of the areas where ammonia is being used for varying purposes. Almost all of the above mentioned industries release wastewater, whose composition consists of certain amount of Ammonia in different forms and few may be toxic to the environment. There are a lot of processes that are currently being used and some were used formerly so as to remove the Ammonia concentration from wastewaters. Some of them are Air stripping, Activated sludge process, Sequential batch reactors, electrochemical oxidation,

Ion exchange through resins and zeolites etc. Electrochemical oxidation of Ammonia seems to be a promising method that can with certain process modification and improvisations, result in limiting the Ammonia quantity cathode industrial wastewaters. Electrochemical oxidation process provides a higher degree of control, as it may get started and terminated just by controlling a switch, it uses almost no chemicals, can be used to treat wide variety of pollutants along with ammonia.

II. LITERATURE SURVEY

Gerischer and Mauerer[3,7] have proposed a mechanism, where Platinum adsorbs the dissolved Ammonia and converts it into (N_2) gas by dehydrogenation. However, this process gets severely affected due to formation of atomic nitrogen which gets strongly adsorbed on the surface of the Platinum catalyst and blocks the reaction active sites. This mechanism consists of following six steps, in which sequential dehydrogenation of nitrogen species occur and various reaction intermediates are formed on the surface of the electrode in an adsorbed form.

$NH_{3\,(aq)} \rightarrow NH_{3,ads}$ (1)

$NH_{3,ads} + OH^- \rightarrow NH_{2,ads} + H_2O + e^-$ (2)

$NH_{2,ads} + OH^- \rightarrow NH_{,ads} + H_2O + e^-$ (3)

$NH_{x,ads} + NH_{y,ads} \rightarrow N_2H_{x+y,ads}$ (4)

$N_2H_{x+y,ads} + (x + y)OH^- \rightarrow N_2 + (x + y)H_2O + (x + y)e^-$ (5)

$NH_{,ads} + OH^- \rightarrow N_{,ads} + H_2O + e^-$ (6)

However, recent studies also point that instead of the adsorbed nitrogen, co-adsorbed OH^- may be the cause of inhibition that occurs during electrochemical oxidation of Ammonia.[8,9]

Yan Liu et al.[11] have investigated the effect of Ti/IrO_2 as the anode material for the electro oxidation of the Ammonia. The sample consisted raw municipal wastewater after aerobic or anaerobic treatment and the ammonia concentration of the sample was predetermined. The results of electro oxidation of Ammonia using Ti/IrO_2 were compared to those obtained by using Ti/RuO_2 as anode material. The parameters that varied were pH value, current intensity, chloride concentration. The results obtained were as follows:

Chloride Concentrations	30mgCl L^{-1}	120mgCl L^{-1}	225mgCl L^{-1}	300mgCl L^{-1}
Rates using Ti/IrO_2	1.1mgNL^{-1} h^{-1}	4.4mgNL^{-1} h^{-1}	8.3mgNL^{-1} h^{-1}	9.2mgNL^{-1} h^{-1}
Rates using Ti/RuO_2	1.0mgNL^{-1} h^{-1}	4.0mgNL^{-1} h^{-1}	8.3mgNL^{-1} h^{-1}	12.3mgNL^{-1} h^{-1}

A. Degradation Rate Of Ammonia At Different Initial Chloride Concentration For Both The Anodes[11]

Four different current densities were used in the experiment as 3.8, 7.6, 11.5 and 15.4mAcm^{-2}.The results made it clear that the concentration of ammonia went down with time and as a general observation, the degradation increased with increase in current density. Also, using Ti/RuO_2 as anode increased the degradation rates to a slight extent. The chloride present in the samples only acted as a catalyst and did not participated in the reaction itself and was evident from the chloride concentration at the end of the oxidation process, which came out to be the same as the initial concentration. The degradation rates of Ammonia were quite similar for both the electrodes at different chloride concentrations however; Ti/RuO_2 resulted in a slightly better performance at chloride concentrations of 300 mg/L. The degradation rates were not affected by the concentration of ammonia and followed pseudo zero order kinetics at low chlorine concentrations of about 300mgL^{-1}

Nigel J. Bunce, Dorin Bejan[12] has investigated the oxidation of ammonia on surfaces of different noble metals. A common observation is that the oxidation of ammonia is usually carried out in alkaline mediums due to more ease. They reported that in order to get good efficiencies for ammonia removal, the experiment has to be handled carefully and that the anodic potential should be negative with respect to SHE and the concentration of NH_3 should be high. They also reported that the metals used as anode were mainly 5d metals like Platinum and Iridium. Metals of 4d configuration caused very feeble to no production of N_2. The alloy formed from Platinum and Iridium exhibited voltammetric current peaks near +0.6 volts. In the ranges of water oxidation, the chances of formation of nitrogen products other than N_2 are possible due to over-oxidation. Such products includes hydroxylamines, nitrites and nitrates. The electro oxidation of ammonia carried out for the production of hydrogen for fuel cell with platinum combined with

different elements as anodes revealed that among Pt–Ir, Pt–Rh, Pt–Ru, and Pt–Rh–Ir, the starting of anodic current was lowest in Pt–Rh–Ir and equaled (−0.5 V vs. Hg/HgO; −0.4 V vs. SHE).

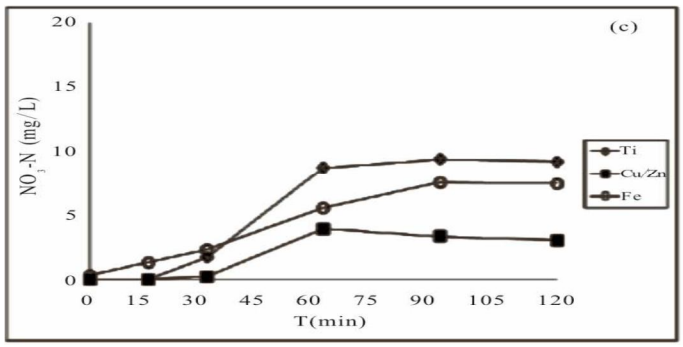
Electrochemical method are proven to give good efficiency, comparatively less space demanding and generate much lesser amounts of sludge but certain limitations affect their efficiency, like generation of nitrates. W.T. Mook et al. have mentioned in their study, the evolution and development of bio electrochemical reactors as a possible successor to the electrochemical method. The bio electrochemical reactors have the ability to oxidize total ammonia nitrogen from wastewaters and simultaneously generate electricity through microbial electrolysis cells. The parameters that affect this denitrification are pH, current density, cathode material. Simultaneous Removal of TOC can also be achieved through this method.

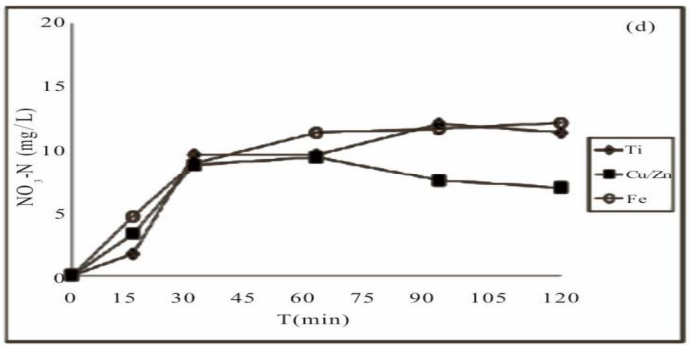
Thegy L. Lomocso, Elena A. Baranova[4] have studied the effect of electro catalysts in the form of nanoparticles Pt(y)M(y-1) (y=50) supported on conductive substances like carbon black, in alkaline mediums. Different catalysts like Pt, IrPd, Pt7Ir3, Pt7Pd3, Pt5Pd5, Pt7 (SnOx)3 were used for the study. Here, M represents any of the Ir, Pd, SnOx. Pt7Ir3 nanoparticles had a good tolerance with increase in quantity of Ammonia, whereas among all the catalysts studied, only carbon supported PtIr nanoparticles were reported to exhibit a fair combination of activity and stability for oxidation of Ammonia.

Wei-wu HU, Bin GONG, Chuan-ping FENG[13], has carried out an experiment on removal of Ammonical nitrogen from waste water by electrochemical oxidation method using Ti/RuO_2- Pt .This experiment include an electro bath, at an effective voltage of 0-50V and current of 0-5 A. Ti/RuO_2- Pt anode with dimensions of 15cm × 5cm × 1.5mm. Maximum removal rate is up to 88.3% of NH_3-N with 90% of COD removal rate [13]. Initially the concentration of NH_3-N was 40 mg/l in which NaCL is added in amounts of 0.3 g/l, 0.5 l, 1.0g/ml and 2.0g/ml at different current densities. The water is electrolyzed in 0-30min using Ti/RuO_2- Pt . Samples are collected at intervals of 5 min, to measure the rate of removal of NH_3-N. Almost 90% removal has been achieved by this method, hence it is considered to be a suitable method for water containing ammonia[13].

Yaning Wang, Xu Guo, Zhongfang Lie [14], has attend an experiment for removals of NH_3-N from waste water. The Batch experiment were performed at room temperature. Electrochemical cell was made up of acryl plates with 4 outerspots for the electrodes assembled. Three metal plates include Cu/Zn, Ti and Fe plates of 75 cm²,used as the cathode, and Ti/RuO_2-Pt used as anode with distance of 8.0mm centrally located. They had prepared synthetic ammonia solution using $(NH_4)_2So_4$ and distilled water to give concentration of 100.0 mg/l. NaCL dosage was added in this solution to inspect the important factors such as NaCL dosage, pH, current density, temperature. Na_2SO_4 is added to the solution. 1.5ml of sample has been taken out for analysis. Analysis has done according to standard methods (APHA,1998). It has been observed that, Cu/Zn cathode is more applicable for removal in absence of NaCL. All the cathode shows almost same results on removal of ammonia with dosage of NaCL. Overall 90% removal of ammonia is achieved[14]. Which was changed into N_2 gas with NaCL addition. In the present study, cathodic reduction of by-products, and anodic oxidation of ammonia were investigated in an undivided cell using Ti/RuO2-Pt plate as anode and three plates as cathode for treatment of the synthetic ammonia solution. Influencing factors like Chlorine presence, temperature, pH, current density are analyzed. The 400-mL electrolysis cell was made of acryl plates with four outer spots for the electrodes assembled. Three metal plates include Cu/Zn (Cu: 62.2 wt%; Zn: 37.8 wt%), Ti and Fe plate of 75.0 cm2 (15.0 cm × 5.0 cm) were used as the cathode more-over Ti/RuO2-Pt was used as the anode with the same area with a distance of 8.0 mm between the two electrodes respectively

B. Concentration Of Nitrate Versus Time Graph At Different Current Density And Nacl Concentration





Liang Li, Yan Liu [15], has investigated the mechanism and pseudo-kinetics for removal of ammonia by electrochemical oxidation with anode Ti/IrO_2 using batch test. Batch experiments were done keeping the same size of anode and cathode with distance of 10mm centrally located. They had used ammonia solution without any organic content. The solution was prepared with $(NH_4)_2So_4$ and An_2SO_4.NaCL was added into it. The evaluation was done under two conditions - ammonia solution with Cl addition and without Cl addition. The result shows that the removal rate of ammonia content in chlorine free solution was considerably low. The removal rate of ammonia in containing chloride is rapid with time. Results shows that with time the ammonical nitrogen almost reduce to zero. Oxidation of ammonia rate from direct oxidation at electrodes liquid interface of the anode by stepwise dehydrogenation and from indirect oxidation by hydrocyl radicals were too low.

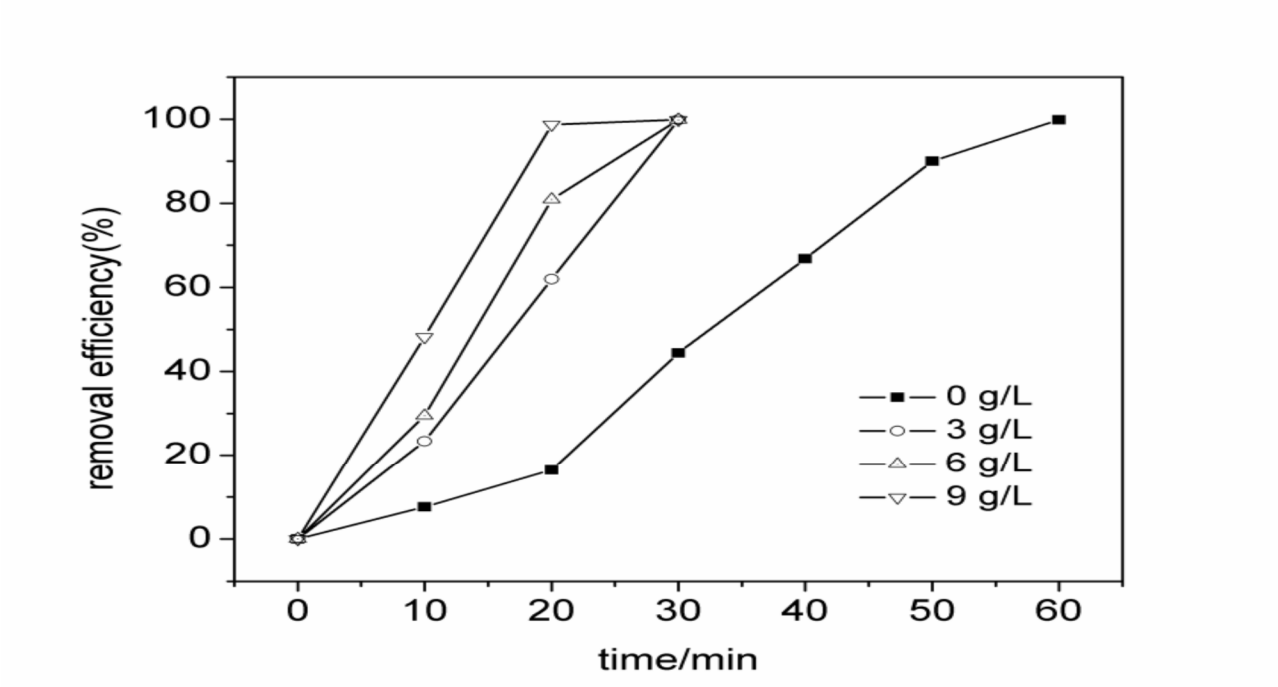
Wachter Agnieszka Kapalka, Michael Wachter[16], has investigated the electrochemical oxidation of ammonia on $Ni/Ni(OH)_2$ electrode. They found that oxidation of ammonia is pH dependent, and takes place at pH above 7. The oxidation of ammonia takes place at Ni electrode and this electrode is not deactivated even at high concentration of ammonia. In order to form nickel hydroxide the working electrode was prepared with potential cycling of nickel electrode. The concentration was checked using a Hach Lange spectrometer. They had used Pitzer approach to calculate the ion activities. At high pH, oxidation of ammonia switch to higher potentials . Nitrite was found to be below detection limit. The 55% of ammonia was decreased[16]. At the end the solution became grey due to corrosion of electrode.

Xuli Ma, Rongpeng Wang[17], had prepared $Ti/SnO_2+Sb/PbO_2$ by combining technologies of thermal decomposition and electrode position. Result conclude that the material of anode, current density, and concentration of chloride have influence on ammonia removal and 250 mg/l ammonia was removed in 60 minutes on Ti/SnO_2-Sb/PbO_2 anode at 0.05 A/cm² current density[17]. This anode is a promising material for electrochemical coking wastewater treatment. In the study, they had focused on the anodic oxidation for the removal of ammonia using Ti/SnO2+Sb/PbO2 anode. For treating 1 ton coking wastewater containing 250 mg/L ammonia consumes only 10.8 kWh energy.

Parameter of coking wastewater

Parameter	pH	Conductivity (mS/cm)	NH4+ (mg/L)	COD (mg/L)	TOC (mg/L)	Cl- (mg/L)
Raw wastewater	8	0.71	258.45	2000	196.9	1300

Efficiency Graph



The commercial application of Ti/SnO2-Sb2O5 is hampered by its short lifetime. PbO2 calls the attention as an electrode material due to its easy and rapid preparation, besides being of low cost and stable in high-applied potentials in different pH medias. The Ti plates (5 × 1 × 0.1 cm) were used as substrates and they are polished using 350 grit sandpaper and degreased with 40% NaOH sol at 80°C. A soln containing 10% SnCl4 and 1% SbCl3 dissolved in mixture n- Butanol + HCl. The PbO2 activated layer was prepared by electrochemical deposition method in 0.1 M HNO3 containing 1 M Pb (NO3)2 and 0.1 M surfactant (sodium dodecyl sulfate, SDS) at 60℃ for 1 h. The voltage was 1.5–2.5 V and the current was 8 mA/cm2.

Anodes Kinetic Parameters and stability table

ANODE	a/V	b/V	i0 /A cm2	Service life/h	Oxygen evolution potential /V
Ti/SnO2-Sb	0.532	0.489	8.17×10-2	20	2.15
Ti/PbO2	0.425	0.331	5.20×10-2	35	1.78
Ti/SnO2- Sb/PbO2	0.290	0.208	3.99×10-2	86	1.86

III. MATERIAL AND METHODS

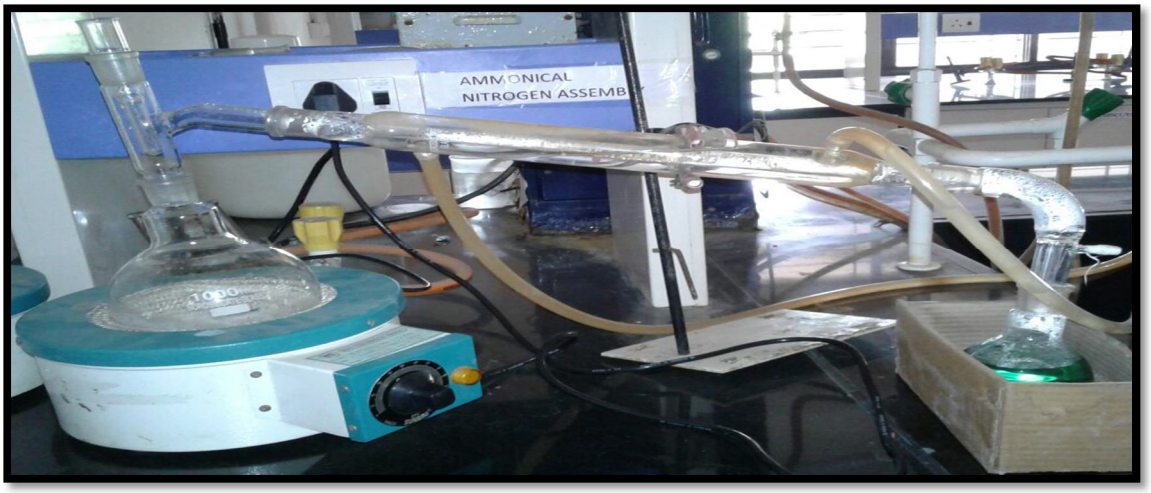
Electrochemical Oxidation process in terms of wastewater treatment can be defined as device having the ability of breaking down the pollutant present in the wastewater into simpler compounds with the help of electrical energy. This technology is applied to remove the Ammonical nitrogen from wastewater. For the process, basic laboratory equipments are needed, different types of electrodes, wires, nuts and bolts, etc. Batch experiments were conducted in an electrochemical oxidation apparatus. Here, the apparatus is equipped with pairs of anode and cathode. The electrodes were suspended in the effluent containing Ammonical nitrogen with the help of a support.

The anodes and cathodes are placed vertically and the electrodes are kept parallel to each other. A complete electrochemical oxidation cell is designed in our laboratory for testing the Ammonical nitrogen containing effluent. The parameters such as Ammonical nitrogen for the effluent are tested.

Direct current is supplied to the voltage of 0-10V at a constant current. The influencing factors of electrochemical oxidation of effluent containing Ammonical nitrogen are pH, sodium chloride dosage, current density, temperature respectively. Thus, all the factors are kept constant except one. Keeping one factor varying, note down the results.

A. Electrochemical Oxidation Setup

Ammonical Distillation Setup



IV.CONCLUSION

The literature reports electrochemical oxidation of Ammonia carried out during various researches. A wide variation has been covered with reference to the operating conditions like pH, use of electro catalysts, anodic and cathodic material, current densities etc. Though the process has greater energy demands compared to that of few biological methods for ammonia removal, still it has a lot of advantages over other conventional methods like usage of less space, high efficiency, less time consuming and no sludge generation. In most of the works, the electrochemical oxidation has been conducted in completely controlled small scale setups and has achieved good to excellent results, still very less number of studies have been conducted aiming specifically at oxidation of ammonia in industrial waters and its process optimization. This method provides a promising alternative compared to other biological denitrification methods and can be applied for facilities treating small volumes of wastewater containing ammonia.

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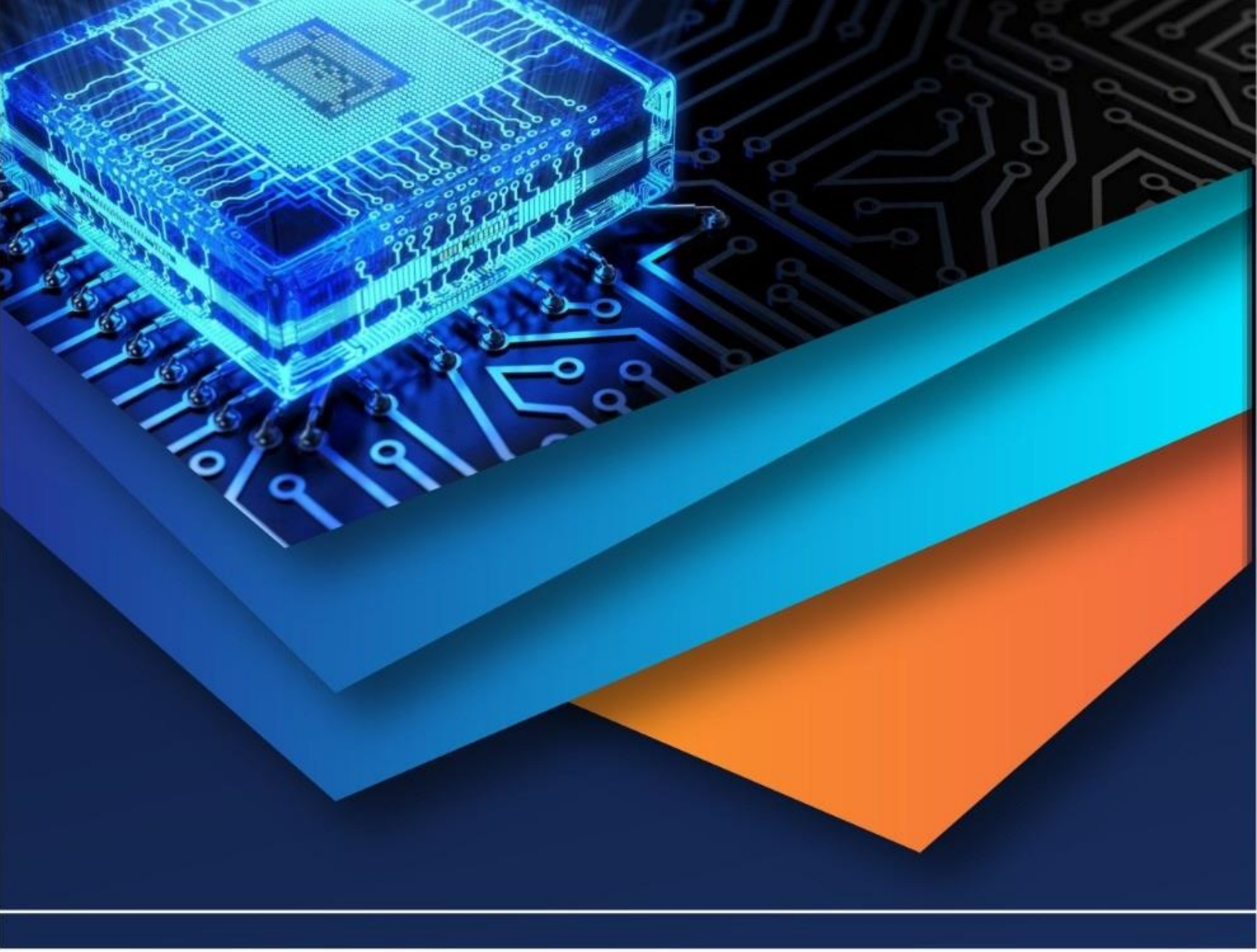

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