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Evaluation of Changes in Chemical Properties of different Cooking Oils sold in Local Market Before and After Frying

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Abstract: Vegetable oils are triglycerides extracted from plants. Edible vegetable oils are used in food, both in cooking and as supplements. Frying leads to oil decomposition. The nature, rate, and products of decomposition are influenced by the composition of the oil such as fatty acids pattern, physicochemical characteristics. In this study, There are eight different types of edible vegetable oils before and after frying were analysed using standard procedures. The physicochemical properties acid, peroxide, iodine, saponification and ester values were investigated. Acid value are found in the range of 0.33-4.48 mg KOH/g oil in fresh oil samples and 0.65-8.97 mg/KOH/g after frying while in case PV, it is in the rangs of 2.18-4.09in before frying and 4.12-14.4 meq/kg in after frying. Ester and Saponification values were ranged between 172.43-252.4and 172.78-256.88 in fresh oils and between 166.39-240.91and 167.24-249.88mg KOH/g oil in frying oils respectively. In case IV are 7.4-123.84in fresh oils and 5.88-115.74 in after frying oils. Furthermore, Acid and Peroxide values are found to exceed the permitted value of 6.0mg/KOH/g and 10 meq/Kg in after frying of edible oils.The standard mean error, it is in the range of 0.02-0.06 in fresh oils while it is 0.09-0.17 in after frying.

Keywords: Different cooking oil, frying ,Acid, Iodine, Peroxide, Saponification, Ester Values,

I. INTRODUCION

Since ancient times, plant, and animal products are cooked, baked, roasted, or fried, to make them more palatable and to improve their digestibility. The heat can be transferred from air, water, or oil to the product. Frying as a cooking method started probably around the 6th Century BC. It is the process of using oil as the cooking medium[1]. The range of temperatures used for frying is 150 – 200 °C. Heat transfer during frying can be by conduction, convection, or both [2].

Fried oil relies on changes in the stability of the taste or quality of the oil by hydrolysis, oxidation, and polymerization. Tocopherols, essential amino acids, and fatty acids in the diet degraded during frying. Changes frying oil depends on factors like the freshness of the oil, frying conditions, the original quality of cooking oil, fried foods, types of frying, antioxidants, oxygen concentration. Frying temperature is high, the amount of fried oil, free fatty acids, polyvalent metal, and unsaturated fatty acids decrease the stability of the oil due to oxidation and the taste quality of the oil. Frying oil with high temperatures can degrade the effectiveness of antioxidants.[3-4]

The peroxide value is used to determine the level of oil damage. The peroxide value standard for vegetable oils that do not undergo rancidity should be well below 10 meq/kg. The value of free fatty acid is often used as an indication of the general condition and the nature of the oil is safe to eat.[5]Saponification value is a rough index of the molecular weight of the fat or oil. The smaller the saponification value higher molecular weight. It also shows the magnitude of the amount of alkali required to convert the amount of fat or oil to be soap. It can be used for checking the purity of fats or oils.

II. RELATED WORK

Edible oils are derived from a wide variety of plants and plant seeds and are used in many aspects of domestic and world-wide food production. Once the oil has been extracted from a plant seed, it is refined as needed for use in foods such as salad dressings, margarine, shortenings, snack foods and frying oil. Edible oils are extracted and processed world-wide and hence are important domestic and international commodities. Edible oils are very important food for word. The human body uses oils and fats in the diet for three purposes, as an energy source, as a structural component and to make powerful biological regulators. Oils and fats also play an important role in metabolic reactions in the human body. Oils and fats contain fatty acids, which are susceptible to attack by a number of agents e.g. light, oxygen, metals, etc [6-8].

Edible oils from plant, animal, or synthetic origin, are used in frying, baking, and other forms of cooking, and in salad dressings and bread dips. Plant-derived edible oils consist of carboxylic acids with long hydrocarbon chains, in contrast to petroleum-based oils which lack the carboxyl group on the end. The carboxyl group makes the oils edible, providing a site for human enzymes to attack and break down the chain in a process called beta-oxidation. There are a wide variety of cooking oils from plant sources such as olive oil, palm oil, soybean oil, canola oil (rapeseed oil), corn oil, peanut oil and other vegetable oils, as well as animal-based oils like butter and lard. This paper incorporates a comparative study of different types of frying oils by their physicochemical properties and compositional qualities. There are numerous health benefits of frying oils which has been covered in the paper along with the future of edible oils in India[9].

Che et al (2000) stated and observed that deep frying is one of the most common methods used for the preparation of food. Repeated frying causes several oxidative and thermal reactions which results in change in the physicochemical, nutritional and sensory properties of the oil [10].During frying, due to hydrolysis, oxidation and polymerization processes the composition of oil changes which in turn changes the flavor and stability of its compounds [11]. During deep frying different reactions depend on some factors such as replenishment of fresh oil, frying condition, original quality of frying oil and decrease in their oxidative stability [12].

Fats and oils are parts of normal daily consumptions. As a major source of energy, fats and oils are considered as important nutrients in human diets. The edible oils are used in cooking as well as in traditional medicine for the treatment of colds, coughs, bronchitis, edema and burns, also play an important role in the body as carriers of essential fatty acids which are not synthesised in the body but are needed through the diet to maintain the integrity of cell membranes. They are also needed for the synthesis of prostaglandins which have many vital functions to perform in the body. Vegetable oils are beneficial and popular due to their cholesterol-lowering effect. In contrast to animal fats, which are predominantly saturated and hence do not react readily with other chemicals, especially oxygen, unsaturated vegetable oils are more reactive. Vegetable oils are essential in global nutrition depending on the regional conditions, a variety of oils are produced in different qualities [13-14].

The conventional standard analytical methods (SAM) used to determine both primary and secondary oxidation products. These have been used over the years as effective quality control and analytical tools to monitor frying fats and oils. While some are easy to determine by titration, others are laborious and involve large amounts of organic solvents and effluents[18].It includes iodometric titration procedures used to determine hydroperoxides (PV), degree of unsaturation (IV); ferrous oxidation method for peroxides; alkali based titration used for determination of free fatty acids (FFA); derivatization into methyl esters respectively before other analyses that follow [15-18].The analytical techniques requiring for direct determination such as ultraviolet-visible (UV-VIS) Spectroscopy and Chromatography. They are used to measure complex mixtures of lipid oxidation molecules of aldehydes, ketones, epoxides, hydroxyl compounds, oligomers, and polymers [19].

Several factors affect the edible oil quality such as agronomic techniques, seasonal conditions, sanitary state of drupes, ripening stage, harvesting and carriage systems, method and duration of storage, and processing technology. The major factors affecting edible oil quality are temperature, moisture, sunlight, soil fertility, and nutrients. It is possible to determine by different analytical techniques how to assess the quality of edible oil and to avoid possible adulterations [20].

The aim of present study was to evaluate the effect of frying on the chemical properties such as acid value (AV), iodine value (IV), peroxide value (PV), ester value (EV) and saponification value (SV) of some edible cooking oils were measured before and after frying and to assess whether these oils could be re-used or not.

III. MATERIALS AND METHODS

All the chemicals reagents and glassware used in this analytical work are analytical grade. Edible oil samples Olive(Ol),Groundnut oil(Gn), Sunflower(Sf) ,Corn(Cr), Soyabean(Sb), Canola(Cn), Coconut(Cc),Sesame(Ss) oils were purchased from some food super markets in Jalgaon city of Maharashtra, India and home kitchen uses. In this study, cooking oil samples of different types of oil were subjected to controlled heating and frying in the laboratory. The acid value, peroxide value, ester value and saponification value of edible oil before and after frying were measured according to the AOCS and AOAC [22-27]. All reagents are of analytical grade unless otherwise stated. Deionized water was used for preparation and dilutions of standard solutions. Nitric acid (HNO_3) and sulfuric acid (H_2SO_4) reagents were used for cleaning of glassware and for digestion of the samples. Representative edible oil samples were used for analysis. Chloroform, potassium iodide (KI), glacial acetic acid, and sodium thiosulphate were used for estimation of peroxide value. Hydrochloric acid (HCl), sodium hydroxide (NaOH), ethanol, and phenolphthalein indicators were used for estimation of acid value and saponification value, respectively; carbon tetra chloride, potassium iodide, and Wijs reagent were used for estimation of iodine value.

A. *Determination of Chemical Properties [22-27]*

1) *Method for Determination of Acid Value:* Five grams of each cooled oil sample was weighed in 250mL of conical flasks and 50 mL of freshly neutralized ethyl alcohol (ethanol) was added to the samples and then shaken well to dissolve sample. The sample solution was boiled for about five minutes and cooled and then 1mL of phenolphthalein indicator was added to the sample solution. The sample solution was titrated with 0.1N sodium hydroxide solution until permanent pink light color appeared. The acid value was estimated using the following equation:

$$\text{Acid value} = 56.1 \times V \times 100/W \qquad \text{---------------} (1)$$

Where W is weight of oil that equals 5 grams, V is titer value of 0.1N NaOH.

2) *Method for Determination of IV using Wijs Method:* An appropriate amount of sample was weighed of the dry oil/fat as per expected value (0.2-0.22mg) into a tarred Erlenmeyer flask with glass stopper, add 25ml of carbon tetrachloride and flask was swirled to dissolve the sample. To this was added 25 ml Wijs reagent. The sample was evaluated in three set of experiments. The flask was fitted with glass stopper wetted with KI solution, swirled for proper mixing and kept in a dark for about 30 minutes for reaction. Simultaneously a blank test was also performed. At the end of reaction, to the flask was added 15 ml KI solution followed by 100 ml freshly boiled and cooled water with rinsing of the stopper. Liberated iodine was titrated with standardised sodium thiosulphate solution (0.1N) using starch as indicator until the blue colour formed disappears after through shaking. The iodine value was determined as follows: Iodine value = 12.69* (B-S)* Normality of $Na_2S_2O_3$ /Weight of Sample taken----------(2)

3) *Method for Determination of Saponification Value:* Two grams of each oil sample was weighed in 250mL Erlenmeyer flasks; then 25mL of alcoholic potassium hydroxide solution was added into the flasks. The blank determination was conducted along with the sample. The samples flask and the blank flask were connected with air condensers and boiled gently in the water bath, steadily until the saponification was completed, indicated by absence of oily matter and the appearance of clear solution. Clarity was achieved in half hour boiling. After the flask and the condenser cooled, inside of the condensers was washed down with about 10mL of ethanol and then 1mL of phenolphthalein indicators was added to the solution. Excess potassium hydroxide was titrated with 0.5N hydrochloric acid until cloudy solution was formed. The saponification value was estimated using the following equation:

$$\text{Saponification value} = 56.1 \times (b - a) \times N/ W, \text{------------} (3)$$

Where W is weight of sample that equals 2 grams, b is blank titer value, a is sample titer value, and N is 0.5 normality of HCl.

4) *Method for Determination of Peroxide Value:* Five grams of each oil sample was weighed in 250mL of conical flask; then, 30mL of acetic acid and chloroform solvent mixture (3:2) was added to each oil sample and swirled to dissolve. Then, 1mL of potassium iodide solution was added to the solution. The solution was kept for 1min in dark room with occasional shaking and then 30mL of distilled water was added. Slowly, titrate liberated iodine in 0.01N sodium thiosulphate solution until vigorously shaking yellow color was gone and after that 1mL of starch solution indicator was added and we continued titration by vigorous shaking to release all I_2 from CH3Cl layer until blue color disappeared.

The peroxide value was estimated using the following equation:

$$\text{Peroxide value} = V \times N \times 100/W, \text{-------------} (4)$$

Where V is volume of sodium thiosulphate, N is normality used for titer and W is weight of the sample.

5) *Method for Determination of ester Value:* The ester value is the 'mg' of KOH required to react with glycerol/ glycerin after saponify 1 g of oil sample. Ester value is calculated by the following relation

$$\text{Ester Value} = \text{Saponification Value} - \text{Acid Value}$$

Table 1. Chemical characteristics of sun flower oil before and after frying.

Sr. no	Oil Code	Before frying					After frying				
		AV, mg KOH / g oil	PV, Meq/Kg	IV	SV, mg KOH / g oil	EV, mg KOH /g oil	AV, mg KOH / g oil	PV, Meq/Kg	IV	SV, mg KOH / g oil	EV, mg KOH /g oil
1	Ol	0.50	3.2	86.84	191.68	191.18	0.97	9.5	81.28	202.12	201.15
2	Gnt	3.23	4.09	91.28	192.48	189.25	7.61	4.12	84.68	201.48	193.87
3	Sf	0.44	3.72	121.58	190.56	190.12	0.86	9.65	114.84	199.46	198.6

4	Cr	0.22	2.4	104.24	193.12	192.9	0.65	10.0	99.48	203.14	202.49
5	Sb	0.33	2.96	123.84	192.24	191.91	0.74	13.6	115.74	201.82	201.08
6	Cn	0.35	2.18	108.86	172.78	172.43	0.85	12.7	102.36	167.24	166.39
7	Cc	4.48	2.42	7.4	256.88	252.4	8.97	14.4	5.88	249.88	240.91
8	Ss	2.69	3.78	102.12	190.36	187.67	6.84	9.85	96.58	199.84	193
9	Total	12.24	24.75	746.16	1580.1	1567.86	27.49	83.82	700.84	1624.98	1597.49
10	Mean	1.53	3.09	93.27	197.52	195.98	3.44	10.48	87.61	203.12	199.69
11	SD	0.098	0.1	0.2	0.32	0.12	0.24	0.2	0.31	0.14	0.3
12	CV	6.44	32.36	0.29	0.16	0.06	6.85	1.91	0.35	0.07	0.15
13	SEM	0.06	0.06	0.16	0.02	0.07	0.14	0.12	0.18	0.09	0.17

(*AV-acid value, IV-Iodine value, PV-peroxide value, SV-Saponification value, EV-Ester value, SD-standard deviation, CV-coefficient of variation, SEM standard error)

Table 2.Test results of frying oils and codex standardss

Sr.no	Test	Before frying	After frying	Codex Alimentarius commission standard	FSSAI
1	Acid value mg KOHg-1	0.33-4.48	0.65-8.97	0.6	0.5-6.0
2	IV $gI_2/100g$	7.4-123.84	5.88-115.74	--	--
3	Peroxide value meq O2/kg	2.18-4.09	4.12-14.4	10.00	1-10
4	Saponification value mg KOHg-1	172.78-256.88	167.24-249.88	---	--
5	Ester value mg KOHg-1	172.43-252.4	166.39-240.91	---	--

IV. STATISTICAL ANALYSIS

The data obtained from the experimental measurements and accuracy of different parameters for different varieties of oils have been analysed and the Statistical parameter like standard deviation, coefficient of variance and standard mean error were calculated for AV,IV,SV and EV for different brands of oils before and after frying. All the experiment was carried out in triplicate and the results are presented as the mean ± SD, CV, ± SEM. Accuracy and descriptive Statistics of different oils from different parts of India as shown in figure1to3.

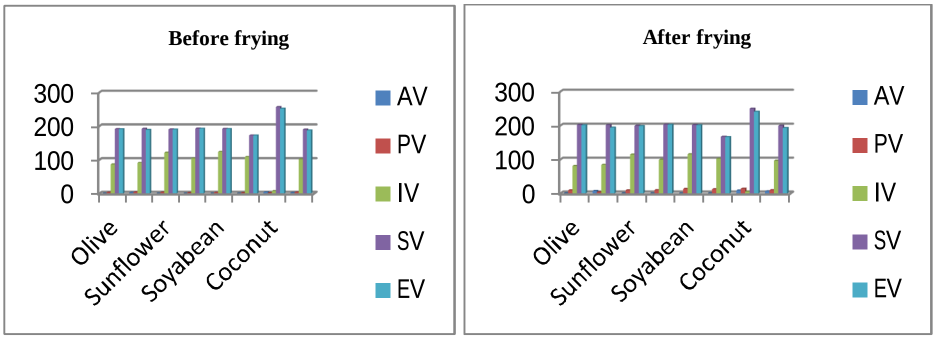

Fig 1-2 shows that plot of obtained results of different parameter of different edible vegetable oils before and frying.

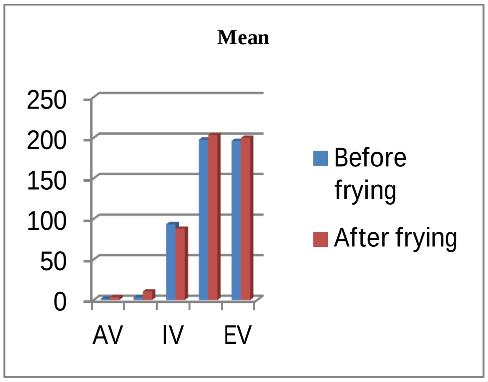

Fig.3 Accuracy and descriptive Statistics of different oils from different parts of India as shown in figure3.

V. RESULTS AND DISCUSSION

The chemical properties of eight edible oil samples such as Olive(Ol),Groundnut oil(Gn), Sunflower(Sf) ,Corn(Cr), Soyabean (Sb), Canola(Cn), Coconut(Cc),Sesame(Ss) oils before frying and after frying have been extensively investigated. The experimental obtained results saponification values, acid value, peroxide value, and ester values given oils are illustrated in Tables 1 with respective codex safety standard in Table-2 and statistical representation are shown in figures 1-3. It can be seen from the tables and figures that, AV and PV before and after frying of given oils were in the ranges of 0.33-4.48 in fresh oils ,0.65-8.97 in after frying oils and 2.18-4.09 in fresh oils,4.12-14.4meq/kg in after frying oils while in case of saponification and ester value were in the range of 172.78-256.88 in fresh oils,167.24-249.88 In after frying and 172.78-252.4 in fresh oils,166.39-240.91 in after frying oils. Iodine value are in the range of 7.4-123.84 in fresh oils and 5.88-115.74in after frying oils.

A.V. measures the content of free fatty acids formed upon the hydrolytic degradation of lipid molecules, thus contributing the reduction of shelf life of oil. According to Codex Alimentarius Commission standard acid value up to 5 mg KOH/gm of oil is safe for consumption. Here the acid value (table 1) are bellow 5 mg KOH/gm in fresh oils so it is safe for human consumption While it is above 5 mg/KOH/g of oil in after frying oils in sample no.2,7 and 8.These are deviates these codex standards. P.V. defines the content of lipid hydroxides in oil formed under conditions of auto and photo-oxidation. Here the oil shows the very low P.V. (table 1) which does not exceed the recommended limit of P.V. of oil (10 mequ O_2/Kg oil.) in fresh oils while in case of after frying oils, In sample nos.5 to 8 ,which are exceeding the codex limit of 10 meqO_2/kg. It is also clear from the obtained results of IV in frsh oils, It gradually decreases as compared to in after frying due to double bond destruction.

The SV and EV of sunflower oil, soyabean oil and groundnut oil before and after frying were almost the same range. Generally, the slight increase of the acid value of the investigated samples may attribute to the complete inhibition of enzymes activity (Tables 1). The obtained data indicated that the ester values of sunflower oil, soyabean oil and groundnut oil after frying had slightly higher value compared with that before frying as seen in table 1and Figure 1 to3.

Also, it is clear from the obtained results (Table 1and Figure 1to3) that, peroxide values of all the oils are increased after frying as to compare with that before frying, causing undesirable odor of oil sample after frying. These results might be due to the effect of high frying temperature causing destruction of some glycerides. The standard deviations are in the range of 0.1-0.32 in fresh oil while it is 0.14-0.32in after frying.

VI. CONCLUSION

The edible oils before and after frying collected from some markets in Jalgaon city of Maharashtra, India and home kitchen use as samples in this study. It is clear from the obtained results that, the acid and peroxide values of edible oil increased after frying compared with that before frying (might be due to the effect of high frying temperature causing destruction of some glycerides).Hence the value of peroxide value and acid value indicated that the oils are not fresh.The use of same oil for frying many times is a general practice mostly in commercial and sometimes in domestic cooking processes. This practice generates lipid per oxidation products that may be harmful to human health. In general feeding on these kinds of edible oils which have high values of acidity and peroxides is very dangerous because of the destructive effects of peroxide compounds and acidity on the components of the membranes of the living cell.

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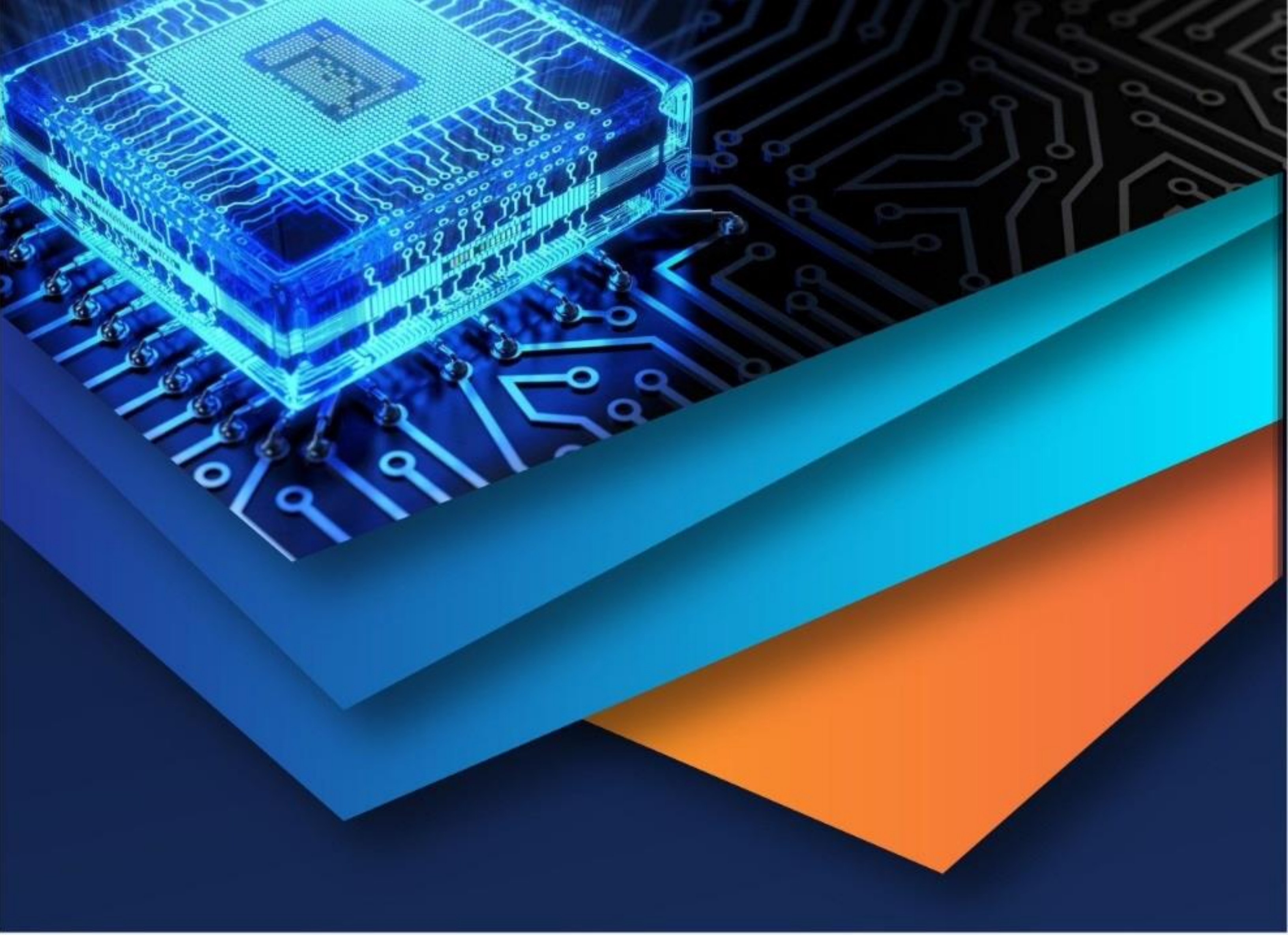

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