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Purification of Effluents from Small-Holder Textile Producers using Mango-Waste Activated Carbon-A Review

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Abstract: As a way of adding value to fabrics and second hand clothes, Small-Holder Textile (SHT) producers make printed, tie-dye and batik fabrics as well as garment articles. Producing and coloring these fabrics, articles require the use of different types of synthetic dyes and chemical auxiliaries to form the dye liquor which is toxic, corrosive, carcinogenic, allergic to humans and can cause environmental pollution when disposed off carelessly. Unfortunately, the dye liquor is discharged off by SHT producers without treatment in Uganda and Africa at large since the conventional Effluent Treatment Plant (ETP) is costly and hard to manage as they operate at small and medium scale. There is therefore a need for a cheap, affordable method and materials to be put in place and enforced to ensure the liquid wastes produced are treated before disposal to the environment so as to save the eco-system from depletion. This article studies the effectiveness and efficiency of using mango waste activated carbon (MWAC) as an adsorbent to purify dye wastes produced by SHT producers. MWAC has got moderate iodine number, low ash content, low moisture content and high fixed carbon which indicates its high adsorption capacity and potential. In addition, its surface morphology is characterized by well pronounced heterogeneous cavities and active functional groups and bonds which provide adsorption sites. This makes MWAC effective and efficient for purifying dye wastes. Therefore regulations should be put in place so that every SHT producer has this affordable (cheap), available, and effective method setup at their production centers and regulatory authorities must work hand in hand with SHT producers for enforcement.

Keywords: Small-Holder Textile (SHT) producers, dye liquor, Environmental pollution, adsorption, Mango Waste Activated Carbon (MWAC)

I. INTRODUCTION

The fast growing small-scale textile industries which are involved in the production of printed, batik and tie-dye fabrics by cottage textile dyers and printers contribute a lot of waste [1]. Wet processes such as dyeing, finishing and printing are main emitters of toxic substances [2]. Green-house emissions, water use, toxic chemicals and waste are the major environmental problems facing the textile industry [3]. Different types of synthetic dyes such as Vat dyes, reactive, sulphur, azoic and acetic dyes are mixed with auxiliary chemicals such as caustic soda, sodium hydrosulphite, sodium carbonate (soda ash), sodium sulphate (glauber' salt), common salt, etc. to form the dye liquor in a bath which has good fastness and solubility properties. It is this liquid waste that is an environmental concern since it is toxic and corrosive as it contains harmful chemicals like caustic soda and sodium hydrosulphite that are allergic and carcinogenic to humans. When uncontrolled and discharged, this liquid waste introduces heavy metals into water bodies thereby increasing Biological Oxygen Demand (B.O.D), Chemical Oxygen Demand (C.O.D), PH and turbidity. This interrupts with marine life, self-water purification process and leads to loss of soil productivity thereby resulting into the depletion of the ecosystem [4], [5], [6], [7].

Since they are small-scale units, the environmental protection agency (EPA) of most of the countries especially in Africa do not monitor and control how these release the waste dyes and chemicals after use. The dye liquor is discharged into domestic drains, gutters and nearby surroundings of the workshop or production unit. A number of suitable legislations and policies for controlling wastes were formulated and enacted in Ghana. These policies and guidelines however target large-scale production and industry players unintentionally excluding small-scale producers and this make small-scale producers rick havoc on the environment [5]. In order to transform Uganda towards a circular textile economy, small scale textile units around Owino market in Kampala add value to second hand clothes which are on a dramatic demand and supply rise by carrying out resist dyeing and printing processes (tie-dye, batik dyeing, screen and stencil printing, etc.) as a way of recycling and reuse so as to reduce the volume of solid textile wastes requiring management at landfills. However this rather produces textile effluents (dye wastes) which is an environmental hazard [8].

Adopting friendly practices such as reusing and recycling waste waters is a great start for protecting the environment. Going "green" is the trend [9]. The waste can be controlled and managed through innovative methods to avoid pollution of river streams, food contamination and fauna destruction by the dyes and chemicals [10]. [11] compared different techniques for the purification of textile effluents among which include adsorption, electrocoagulation, advanced oxidation method, solvent extraction, and biological methods. The study concluded that removing cationic dyes with adsorption method while utilizing low cost materials as adsorbents (activated carbon) such as naturally occurring agricultural waste biomaterials is more effective and has a better removal efficiency. The Environmental Protection Agency (EPA) in the US approved the use of activated carbon as the most effective way of removing dyes [12]. Activated carbon made from mango seed coat treated by H_3PO_4 has got completely clear open structures and bigger pore size when compared to commercially available activated carbon which is very costly [13].

Mango fruit is one of the main foods in any agricultural country whose production is very huge and small amounts are utilized by traditional food industries and as the raw materials for mango candy industries. The mango seeds produced contribute large amounts of solid wastes and their direct discharge cause environmental issues in the landfills [14]. This study therefore highlights and summarizes the valorization of the mango waste (peels, seed and seed-kernel) to activated carbon and summarizes its potential for use in the purification of dye effluents.

II. LITERATURE REVIEW

A. Activated Carbon

Activated carbon was at first known as any form of carbon capable of adsorption. It started with the use of charcoal as a sorbent in both the Roman and Chinese empire. The romans realized that charcoal has the ability to purify water; a property we still use. However, it took humans over 3000 years to optimize charcoal for the removal of specific contaminants [15]. Activated charcoal is non-graphitic and non graphitizable carbon with a disordered microstructure. It has high potential for adsorption due to its high surface area and porosity [16].

B. Utilization of biomass carbon as an adsorbent

Carbon is one of the most versatile but expensive water treatment technologies that has the ability to remove a variety of compounds to nearly undetectable levels. Activated carbon is a microcrystalline form of carbon with very high porosity and surface area. The major use of activated carbon is in solution purification and for the removal of taste, color, odors and other objectionable impurities from liquids, water supplies, vegetable and animal oils[17]

The challenge with activated carbon production is to produce very specific carbons which are suitable for a certain application. The adsorptive properties of activated carbon from biomass may be further improved by subjecting the material to a hydrothermal treatment to change the precursor's chemical characteristics and increase its oxygenated functional groups since there is ability to attain 340% increase of oxygenated functional groups on hydrothermally treated pinewood compared to pinewood char obtained from pyrolysis [18].

An adsorbent is a material of natural or synthetic origin sometimes used in environmental application. The most common adsorbent is activated carbon which is widely used for the adsorption of pollutants from gaseous and liquid phases[19]

The high cost of activated carbon has stimulated interest in examining the feasibility of using cheaper raw materials. Agricultural wastes / by products are considered important precursors for production of activated carbon not just because of their low cost but because they are renewable. Besides, it is a way of recycling agricultural wastes which could otherwise constitute environmental pollution, especially as it relates to solid waste management.

Using by-products of agricultural wastes to make adsorbents for utilizing in treatment of waste waters have been attempted on many occasions. [20] Used palm kernel shells for household water filtration. The study optimized the carbonizing and activating process to enhance their ability in removing undesirable elements from water such as taste and color. The most efficient method involved carbonizing the shells first, pulverization and finally activation. [21] Developed and characterized activated carbons from Rosa canina sp. Seeds and used it to remove basic dye from aqueous solutions. [22] Prepared corncob based biosorbents using H_3PO_4 and NaOH as chemical activating agents. H_3PO_4 was found to be the best activating agent for corncobs since its activated carbon has a higher surface area and good pore volume compared to that made using NaOH.

[23] Reviewed and discussed the preparation of activated carbon from different low cost materials such as camellia oleifera shell, bamboo waste, cherry stones, waste tea, sugarcane bagasse, pineapple waste, fox nut, and paulownia flower. The activated carbon produced from these sources is capable of removing hazardous compounds and dyes from industrial waste gases and waste water in addition to their use as electrode material in super capacitors.

[24] Used the activated charcoal filtering tank to remove contaminants from grey soap water using chemical adsorption active and the PH was found to be lowered from 8.53 to 7.53 which is close to acquiring the water at an acceptable PH range for watering the plants during irrigation (6.5-7.5). The water obtained from activated carbon filter was very pure and was free from impurities, odor, taste, dissolved solids and turbidity.

[25] Used granulated activated carbon (GAC) made from pecan and almond shells to remove some Volatile Organic Compounds (VOC's), Chemical Oxygen Demand (COD), Copper (II) ions (Cu2+) and Zinc (II) ions (Zn2+) from municipal waste water. Efficient adsorbability of benzene and other halogenated aliphatic compounds was achieved. [26] Removed toxic anions, heavy metals, organic compounds and dyes from water using activated carbon made from jatropha husk. [27] Used avocado seeds as biosorbent (in form of activated carbon) to enable its valorization and its use in textile effluent treatment. The avocado seeds activated carbon (ASAC) was found to be efficient and effective in removing orange 2 sodium salt (OSS) dye.

C. Utilization of Mango waste activated carbon

[28], [29] Demonstrated the potential of using mango peels waste as cheap and efficient raw materials to produce activated carbon for methyl Blue removal. Mango peels activated carbon is an effective adsorbent for MB adsorption for uptake in dye effluent wastewater streams. The investigation indicated that H_2SO_4 treatment could improve the adsorption capacity of MPAC in removing MB from aqueous solutions. [30] Investigated the potential of activated carbon derived from mahachanok mango seeds on delaying the ripening of Nam Dok Mai mangoes and found promising results where mango ripening was delayed and mango quality was maintained for up-to 14 days of storage mostly when used at 10g dosage. Mango seed husk optimized at 1100^{o}C for preparation of activated carbon develops sustainable porous carbon materials which can be utilized in super capacitor applications. This contributes a to the efforts of developing new carbon based electrodes [31]. The activated carbons prepared by chemical activation using the highest concentration of the activating agent yields better results with respect to the amount of oxygenated surface groups, the total acidity and the amount of fixed carbon [32]. [33] Shows the use of mango peels and seeds as renewable precursors to give high surface area Mango-Seed Mango-Peel Activated Carbon (MSMPAC) with the ability to be applied in the removal of cationic organic dyes. Powdered activated carbon made from the endocarp of a mango seed was used to remove organic compounds from the aqueous solutions and its effectiveness was determined through measuring the Chemical Oxygen Demand (C.O.D) before and after treatment. The results showed its potential to remediate wastewater [34]. Carbon samples prepared using mango seed coat treated by H_3PO_4 showed a clear porous structure along with a large pore size compared to commercially available activated carbon [13].

Pyrolysis of mango seeds impregnated with sodium and potassium hydroxides produces materials with well-developed pore structure and very high adsorption capacities, making it possible to attain surface areas as high as 1987m^2g^{-1} and pore volumes as large as 1.18cm^3g^{-1}. KOH produces activated carbons with narrower micro-pore distributions than those prepared by NaOH [35]. [36] Optimized the conditions (with respect to PH, carbon doze, initial adsorbate concentration, particle size and contact time) for the removal of color (methylene blue) from waste water using mango seed shell based activated carbon. [37] Made activated carbon from the endocarp of local mango seeds using $ZnCl_2$ as the chemical activating agent in different (I.R) impregnation ratios (1:2, 1:3, 1:4, 1:5 and 1:6) and each activated carbon was used for removing color from textile effluents to obtain the best I.R which was found to be 1:4 and the optimum conditions were carbon doze=0.8g, stirring rate =90rpm, temperature =30^{o}C, PH=7 and contact time =40 minutes.

D. Preparation of activated carbon

For the preparation of activated carbon, the raw materials used are biomass, forestry and agricultural residue. The precursor used must be rich in carbon content for the preparation of activated carbon [16], [38]. Activated carbon can be produced through two processes; Physical and chemical activation.

1) *Physical activation:* It involves two procedures. Firstly, the raw-materials are carbonized followed by activation of carbonized charcoal at high temperature in the presence of steam, carbon dioxide and air. Carbonization occur in the range of 400^{o}C-800^{o}C and activation temperatures ranges from 800^{o}C-1000^{o}C [16].
2) *Chemical activation:* It's a one step process whereby carbonization and activation take place in a single step. The precursor is mixed with the chemical activating agent and kept for activation at high temperatures. The chemical agent acts as an oxidant and dehydrating agent. The commonly used chemical agents for activation are KOH, K_2CO_3, $ZnCl_2$, H_3PO_4 [16]. Chemical activation process has more merits than physical. These include; Single activation step, lower activation temperatures that is less than 800^{o}C, shorter activation times, higher yields and good porous characteristics [16], [39].

E. Structure and properties of activated carbon

Adsorption capacity of activated carbon depends mainly on its structure.

1) *Porous structure activated carbon:* The porous characteristics of activated carbon such as pore volume, pore size distribution, and surface area affects its adsorption ability. Its porous structure forms during the carbonization process and further develops during activation. The pores are of different types and each may vary in size and shape. They include micro-pores (average width(w) < 2nm), meso-pores (2nm ≤ w ≤ 50nm) and macro-pores (w > 50nm [16].

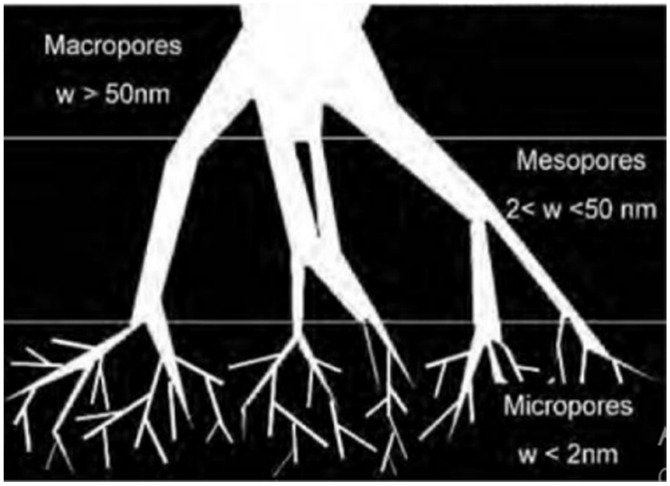

Figure.1 Pore structure of activated carbon [16].

2) *Crystalline structure:* The microcrystalline structure of activated carbon develops during carbonization. Activated carbons can be graphitizing and non-graphitizing. In graphitizing carbon, graphene layers are oriented parallel to each other. It's delicate due to the weak cross links between the adjacent micro-crystallites and therefore has less developed pores. Non-graphitizing carbons are hard due to strong cross linking between crystallites and have a well developed micro-pores structure. This is promoted due to availability of associated oxygen and (or) insufficiency of hydrogen in the precursor. The schematic representations of the structures of graphitizing and non-graphitizing carbons are shown in figure 2 and figure 3 below.

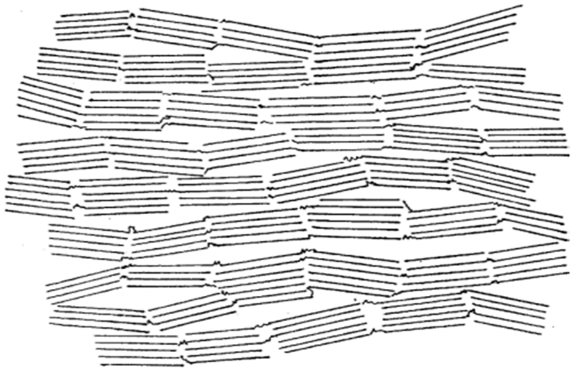

Fig.2 graphitized carbon [16]

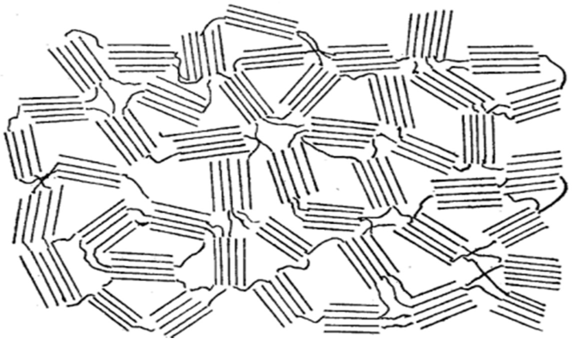

Fig.3 non graphitized carbon [16]

3) *Chemical structure:* It's got a relatively small amount of chemically bonded heteroatoms that is mainly oxygen and hydrogen. The difference in the arrangement of electron clouds in the carbon skeleton leads to creation of unpaired electrons and incompletely saturated valences which affects the adsorption properties of active carbons, mainly for polar compounds [16].
4) *Physicochemical characteristics of mango peel activated carbon (MPAC):* Mango peel activated carbon (MPAC) has a moderate iodine number, low bulky density, low ash content and low moisture content with a relatively high fixed carbon (yield). The external MPAC surface is acidic in nature and rich in functional groups, containing oxygen of carboxylic, carbonyl and phenolic species [28].

TABLE I
PHYSICOCHEMICAL CHARACTERISTICS OF MPAC [28].

TYPICAL PROPERTIES	
Bulky density (g/ml)	0.67
Iodine number (mg/g)	244.2
PHpzc	4.60
PROXIMATE ANALYSIS (wt. %)	
Ash content	5.84
Moisture content	12.23
Fixed carbon	67.35
Volatile matter	14.58
ULTIMATE ANALYSIS (wt, %)	
C	51.84
H	3.66
N	Not detected
S	0.85
O (by difference)	43.63

The surface features of MPAC are well-pronounced heterogeneous cavities which are well distributed across the surface. This surface morphology in addition to the availability of active functional groups and bonds on the activated carbon surface provides the adsorption sites for the potential to remove adsorbates [28].

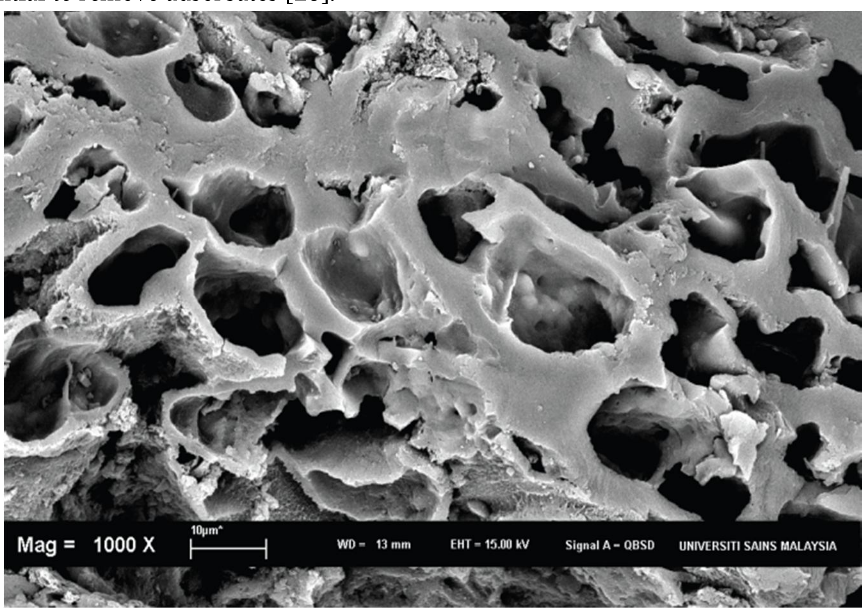

Fig.4 SEM micrograph of MPAC particle (1000x magnification) [28].

F. The filtration unit setup.

Materials required include; MWAC as the top layer, fine aggregate (sand) as the middle layer and coarse aggregate at the bottom

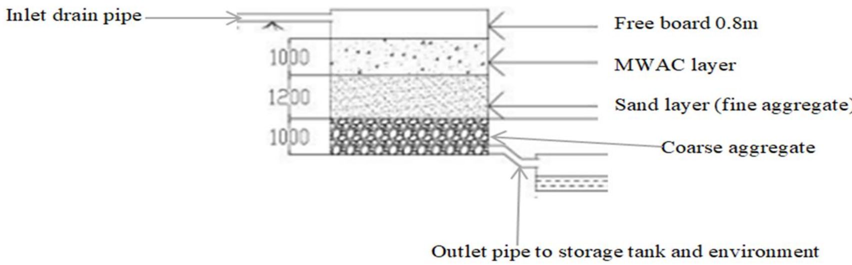

Fig.5 filtration unit, tank (5m*4.5m*4m) [24].

G. Adsorption studies of MPAC on methylene Blue, MB removal

1) *Effect of MPAC mass (Adsorbent dosage):* Increasing the mass of MPAC increases the removal percentage rapidly until a mass of 0.14g at a fixed volume of 100ml (optimum dosage) beyond which further addition has no significant effect on the MB removal efficiency [28], [40].
2) *Effect of MPAC PH:* Adsorption capacity of MB increase when PH is increased from 3 to 5 and there is no further change in the removal by increasing the PH to an alkaline environment. The optimum PH for the removal of MB by MPAC is 5.5 [28], [41], [42].
3) *Effect of initial dye concentration and contact time:* The amount of MB adsorbed by MPAC adsorbent at equilibrium increases rapidly as the initial dye concentration increases. For-example MB adsorbed increased from (9.6 to 265.50) mg/g as dye concentration increased from (25 to 400) mg/l. Also, more time is needed to reach equilibrium for higher dye concentrations [28], [40], [41].
4) *Effect of temperature on MB uptake:* As temperatures increase, the uptake of MB increases rapidly at first and then slows down gradually until it attains equilibrium beyond which there is no significant increase in the uptake. The adsorption process is favored at high temperatures and is endothermic. This is because the dye molecules are very mobile at high temperatures and their reaction is with surface functional groups of MPAC is enhanced [28], [41].

III. CONCLUSION

The valorization of the mango waste (peels, seed and the seed shell) into activated carbon is vital by reducing on the solid wastes discharged into landfills. The structure and properties of the MWAC which include well distributed heterogeneous cavities across the surface, the presence of active functional groups, clear porous structure and a large pore volume make it a potential adsorbent. The EPA should enforce the use of the filtration unit setup to all SHT producers since it is very feasible, affordable, efficient and effective in order to avoid the hostile environment from arising.

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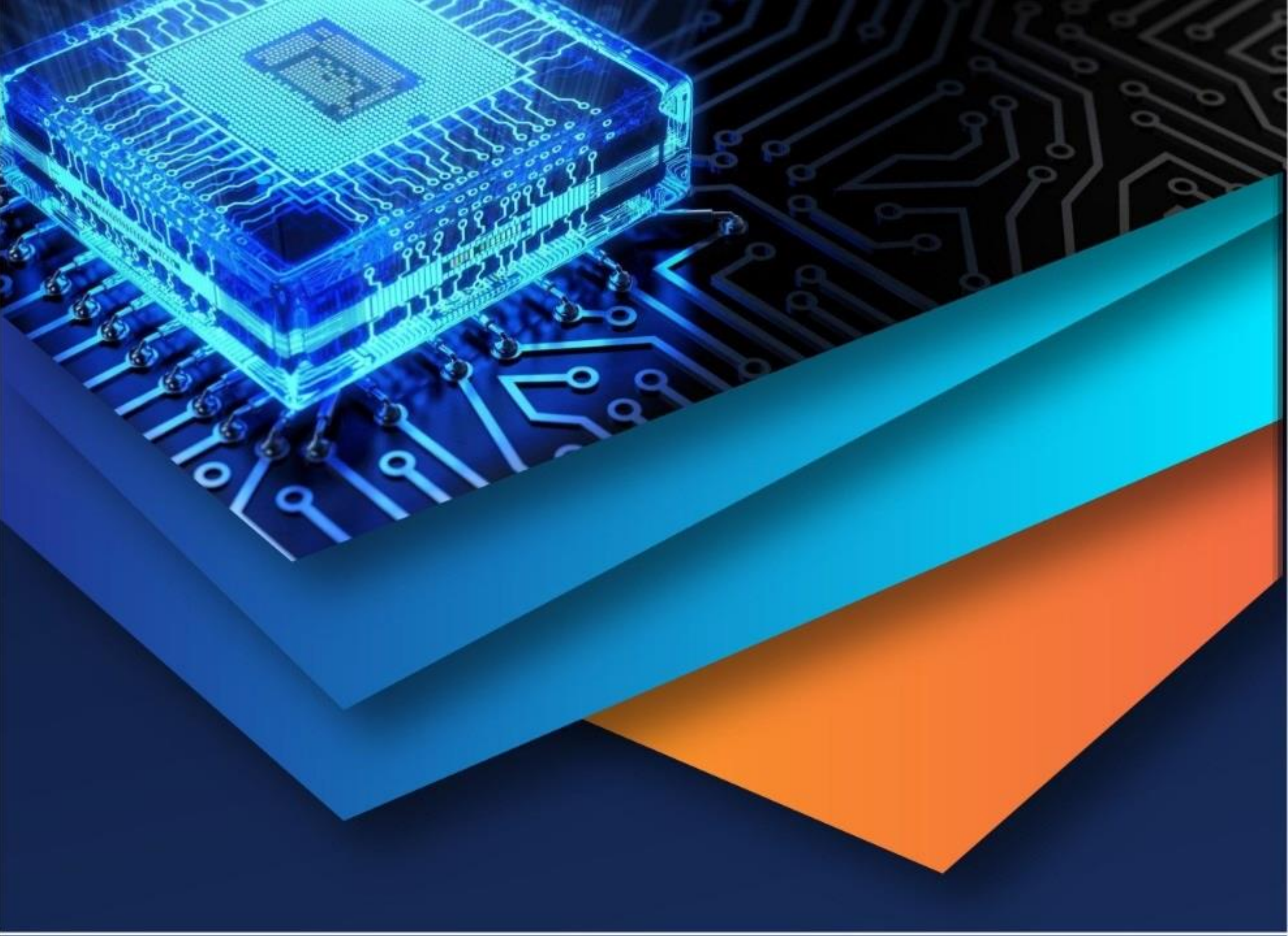

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