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A Review on Soil Contamination by Heavy Metals And Role of Analytical Technques in Quantitative Estimation of Envornmental Samples

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Abstract:*The contamination of soil is a source of danger to the health of people at different levels including villages and cities. Modern industrialization was the main causes to discharge various heavey metals and which reaches to the soil in the form of aerosols, particulate matter, dust, effluents and solidwaste. These heavy metals will transfer from soil to plants and ultimately endangers for human health. Therefore, the knowledge of the regional variability, the background values and anthropogenic versus natural origin of potentially harmful elements/metals in soils is of critical importance to assess on human impact. In view of its seriousness, quantification of heavy metals using analytical techniques in soils is significant. This review article is mainly focusing on extensive literature survey in respect of soil contamination through heavy metals, employing of various analytical techniques including AAS, ICP-AES, ICP-OES and ICP-MS in quantitative estimations of toxic metals and review of various research articles appeared in National and International Journals of repute.*
Keywords:*Soil contamination, Heavy metals, toxicity, anthropogenic, analytical techniques.*

I. INTRODUCTION

Soil contamination with anthropogenic heavy metals, mainly from industrial activities, agricultural practices and atmospheric deposition, has received increasing attention in recent years [1-2]. Continuous urbanization and industrialization, leads to increasing heavy metal pollution in urban soils [3]. The metals can be easily accumulated in the topsoil, resulting in bio-toxicity to plants & animals. Extremely high levels of contamination with heavy metals in urban soils had been found in many countries [4-5].

Soil is not only the key nutrient-bearing environment for plant life, but also a supplier of many pollutants to plants because plants can uptake toxic substances through their roots from soils [6-7]. The accumulation of heavy metals from soils to vegetables has been studied extensively due to the close relation of vegetables to human health [8]. There is increasing contamination of soil due to pollution effect on water and air from activities like urbanization, industrialization, application of chemical fertilizer and pesticide. Polluted soils transfer of heavy metals to plants is the major pathway of human exposure to soil contamination.

Heavy metals are harmful to humans, animals and tend to bio-accumulate in the food chain. Activities such as mining and smelting of metal ores, industrial emissions and applications of insecticides and fertilizers are contributed to elevated levels of heavy metals in the environment [9]. Some of the potentially toxic metal contamination in soil is widespread and contamination could be from geological sources or anthropogenic sources. The contamination of these toxic metals in agricultural land is a major concern. Once these potentially toxic metals are taken up by plants, they can enter the food chain and may be taken up by humans and animals leading to adverse health effect. The toxic metals are harmful to human's health for taken high concentration [10-11].

Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems [12,13,14]. Heavy metal pollution in soil is often mentioned by several countries. Scanty information is available on heavy metal transfer from soil to vegetable [15-16]. Few studies reported that the bioavailability of soil metal to vegetable was controlled by soil properties, soil metal speciation, and plant species [17-18]. In addition, foliar uptake of atmospheric heavy metal emissions has also been identified as an important pathway of heavy metal contamination in vegetable crops [19-20].oncentrations of metals in soil can pose a risk to agricultural production and to human health [21].The development of industries and modernization of agriculture; soil pollution has become increasingly serious. The heavy metal concentrations are so high in soils of many areas that they can poison the soil-plant system, degenerate the soil, and reduce the quality of products of

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crops [22]. Heavy metals from soil to plants enter primarily through the root system. In general, plant roots are the most important site for uptake of chemicals from soil [23].

Plants as essential components of natural ecosystems and agro systems represent the first compartment of the terrestrial food chain. Due to their capacity of toxic metals accumulating, when they grow on soils polluted with such metals, they represent a threat to the living beings which consume them. Also, their development and growth may be affected at high levels of metal concentration implying reduced cultures and economic loss [24].

A. Objectives of study

1) The possibilities and ways of soil contamination by different activities

2) The heavy metals transfer from soil to plants

3) To explore the need and demand of various analytical techniquies

II. LITERATURE SURVEY ON SOIL CONTAMINATION BY HEAVY METALS

Now a day's soil pollution is main problem to the agriculture. Soil pollution mainly from industrial wastes, sewage water, pesticides, fertilizers (chemical based), mining and smelting, fuel production, automobiles etc….. are discussed below.

Industrial activities are also caused for land pollution. Like chemical industries, paper and pulp mills, steel industries, pharmaceutical industries, mining industries, refieneries , pesticides and fertilizer industries, thermal and nuclear power plants, food processing industries, tanneries, textiles industries etc releases their effluents direct into lands.

N.srinivas et.al [25], reported the concentration of Pb, Zn, Ni, and Cu in air, soil and vegetables analysed by using ICP-ES. The work done mainly in industrial areas, sub urban, and rural areas of vishakapatnam. The Pb concentration is higher in industrial area reported as 1.46 µg/m^3. The Ni, Zn and Cu concentrations is higher in semi urban area than comparision with industrial area. The concentration of Pb in vegetables rural area 0.88 to 1.02 µg/g and sub urban area 3.55 µg/g. The Pb concentration is above the permissible levels (2.0-2.5 µg/g). The concentration of Zinc in vegetables, industrial and sub-urban areas is 19.93 to 41.46 µg/g and rural area in the range of 12.99 to 20.01 µg/g. So these concentrations are below the permisible levels (10-50 µg/g). According to WHO (1984) the Ni concentration in vegetables and fruits are reportd in the range of 0.02-2.7 µg/g. The nickel concentration in industrial and sub-urban areas is 1.29-2.62 µg/g and rural area in the range of 1.1-1.53 µg/g The Cu concentrations in three areas like 2.74 (rural), 3.60 (industrial) and 4.46 (urban) µg/g.

Opaluwa, O.D et.al, reported the level of metals present in selected dump sites in Lafia metropolis, Nasarawa state , Nigeria[26]. The author has evaluated the concentration of metals in soil at site-A was As(0.66), Cd(0.48), Co(0.58), Cu(0.91), Fe(0.63), Ni(0.31), Pb(0.49) and Zn(0.38), the site-B was As(0.55), Cd(0.84), Co(0.63), Cu(0.82), Fe(0.64), Ni(0.42), Pb(0.53) and Zn(0.40) mg/kg. The metal concentration in plant leaves and crops showed high level of Co(0.33) and Fe(0.32) in roselle leaves; Cu(0.71) and As(0.37) in groundnut; Cu(0.48) and As(0.28) in maize grains; As(0.36) and Co(0.32) in spinach leaves; and Cu(0.36) and Co(0.32) mg/kg in okro.In summary, the author concluded that allthough these metals were found in soils and plants around the dump sites analysis by using AAS VGB 210 system, the reported values were below WHO permissive levels.

Sumanta roy et.al, study was conducted in sub-urban region of Asansol,the work done both waste water and well water irrigated fields. In this fields cultivating vegetable samples and soil samples collected from selected fields. The heavy metals of Pb, Zn, Mn, Cr, Cd, and Cuwere analysed by AAS GBC avanta 932. The concentration of these metals in vegetables Pb(2.5-20 µg ml^{-1}), Mn(1-4 µg ml^{-1}), Cr(2-15 µg ml^{-1}), Cd(0.2-1.8 µg ml^{-1}), Zn(0.4-1.5 µg ml^{-1}), and Cu(1-5 µg ml^{-1}). The mean value of Pb, Mn, and Zn concentration in selecting fields (treated and untreated fields)showed the lower value comparision to FAO/WHO standards. But the Cr and Cu value in Wastewater and Cd valuein both type of water exceeded the FAO/WHO standards. This paper finally concluded that wastewater irrigation practice is not suitable for cultivating edible vegetables especially those are consumed regularly [27]

A.M.Basha et.al [28], work was conducted to investigate the quality of hen eggs due to the heavy metal contamination around mining site. The concentration of essential elements like Fe 34.4-98.3 mg/kg, Al 2.5-71.1 mg/kg, and Zn 3.9-63.0 mg/kg. The heavy metals like U and Cd in the range of 1.3-12.6 µg/kg and 2.3-15.4 µg/kg. The metal analysis by using ICP-MS. The authors reported these concentration levels in metals are found to be below the permissible limits in hen egg.

A.M.Basha et.al, work has been done in around new thummala palli uranium mining site. The trace metal analysis by using ICP-MS in chicken samples, the concentration of trace metals are found in the range of Al 23.5-309.0 mg/kg, Cr 1.9-2.9 mg/kg, Mn 0.8-2.3 mg/kg, Fe 56.8-87.3 mg/kg, Ni 0.2-0.6 mg/kg, Cu 0.6-2.3 mg/kg, Zn 16.8-31.6 mg/kg, Pb 0.3-0.7 mg/kg, V 88.2-160.6 µg/kg, Co 30.9-55.2 µg/kg, As 11.6-47.6 µg/kg, Cd 7.2-60.6 µg/kg and U 4.9-35.2 µg/kg. They are reported the average concentration of trace metals are below the permissible limits in chicken [29].

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Dubey et.al, reported that sewage sludge and effluents are frequently disposed off on agricultural lands for irrigation/manure purposes and both of them aggravate the problems, because sewage sludge and effluents may contain high amount of heavy metals.Soils normally contain low background levels of heavy metals. The effluent samples were analysed for EC, pH, DO, BOD, COD, TDS, micronutrients (Zn, Fe and Cu), heavy metals (Cd, Cr, B, Ni and Pb) [30].

Pawan.k.bharti et.al work has been conducted in heavy metal contamination of agricultural soil around textile industrial area at panipat city, india [31]. The contamination due to irrigation with contaminated ground water affected by industrial effluents. The metal transferred from ground water to agricultural soil and from soil to ground water were analyzed for heavy metals using Atomic Absorption Spectrophotometer (Model ECIL-4129). The authours found that the average concentration of heavy metals, i.e. Cd(1.927), Cu(26.633), Fe(44.078), Mn(9.90), Ni(7.96), Pb(42.358) and Zn(13.127) mg g-1 in the surface soil. The Fe, Pb, Cu were in high level due to their cumulative nad adsorptive nature in soil after continues irrigation by contaminated ground water. Cd and Zn were found minimum due to their weak adsorptive nature in soil. Transfer factors for heavy metals from effluent to ground water were observed to be 0.43, 1.180, 6.461, 2.401, 2.790, 3.178 and 0.634 for Cd, Cu, Fe, Mn, Ni, Pb and Zn respectively.

P.K.Chhonkar et.al observed the source of irrigation water from pulp and paper factory effluents contain appreciable amount of plant nutrients, like N, P, K, Ca, Mg and S etc. which can be utilized for crop production. The distillery waste water is charectarized by low pH, high BOD and COD values and contains a high percentage of organic and inorganic materials [32].

Noor-ul amin et.al focussed on heavy metal contamination of soils and green vegetables by industrial effluents at peshawar, Pakistan [33]. The authors intention of work is accumulation and bio-concentration of seven heavy metals in vegetables growing in a mixed industrial effluent irrigated agricultural fields. They reported the concentration of metals like Cu 0.044-0.504, Co 0.009-0.085, Fe 0.243-7.737, Pb 0.496-0.474, Cr 0.005-0.033, Mn 0.019-2.019, Zn 0.045-0.703 and Ni 0.017-0.108 ppm in edible parts of different vegetables in that area. The iron accumulated to the highest levels ($P < 0.05$) in all vegetables then compared with remaining metals.

Jerath and Sahai [34] observed the toxic effect of fertilizer factory effluent, containing high concentration of various forms of nitrogen, on seed germination and seedling growth of maize.

III. DETERMINATION OF HEAVY METALS IN CONTAMINATED SOILS BY VATRIOUS ANALYTICAL TECHNIQUES

This review considers the benfits and the drawbacks of some of the analytical tecniques used to identify and quantify different elements in a variety of matrices [35]. In olden days the metal determination in both liquid and solid samples by using titration process and electrode methods. Now a days its improving the technology advanced instruments are available in markets.

The electrode techniques such as voltammetry, stripping voltammetry, potentiometry and polarography are used sporadically.On the other hand, the flow-through coulometry may be useful in determination of trace metals and especially in aquatic environmental samples where low concentrations may be expected [36].

Stripping voltammetry is an alternative method for spectroscopy to determine trace metal content in various soil extracts [37]. Zn, Cd, Pb, Cu, Ni, Co and Cr metals were determined in $\mu g.L^{-1}$ levels with anodic, cathodic and adsorptive stripping voltammetry with glassy carbon working electrode [38]. Pb, Zn and Cd metals were analysed with mercury and bismuth modified pencil graphite working electrodes in anodic sripping voltammetry [39]. Now a days pencil graphite is commonly used as a working electrode for voltammetric measurements, due to simple use, low cost and commercial availability [40]. Adsorptive stripping voltammetry has been applied todetermination of trace organic species and metal complexes in various media either with mercury drop and solid electrodes [41].

Spectrophotometric method can be used for determination of boron in soil extracts after the addition of specific reagents. Azomethine-H method is perhaps the most commonly used spectrophotometric method on boron determination. However, Azomethine-H method suffers from some interference even if it is known as the most sensitive method [42]. A quantitative estimation of Mn in the digested samples was carried out using a UV Spectrophotometer (Sequoia-Tuner, Model-390) following permanganate oxidation method at 522 nm. Because of its distinctive color and stability, permanganate ion is preferably used as the determination form for manganese [43].

X-ray spectrometry (XRF) is characterized by good selectivity and low detectability limit of ppm-ppb [44, 45, and 46]. Additionally, it belongs to the non-destructive analytical techniques, i.e. techniques that do not damage the sample under study. This last feature is also characteristic for neutron activation analysis (NAA). It enables the simultaneous determination of up to 40 elements, which makes it one of the most universal analytical techniques [47]. Another technique, energy-dispersive XRF

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(EDXRF), is very useful in the in-situ analysis of trace elements at the measurement site, which enables shortening of the analytical process [48].

In later the advanced methods are improved for quantitative determination of heavy metals and metalloids include methods based on spectrophotometric techniques. They are based on the interaction of electromagnetic radiation with matter in all its macro and microscopic forms.

The most common technique in this group is atomic absorption spectrometry (AAS). It is an analytical technique based on the absorption of radiation by free atoms in the thermal plasma created in an atomizer, characteristic for a given element of spectral lines emitted by the source of radiation such as a hollow cathode lamp (HCD) or electrode less discharge lamp (EDL) [49,50 and 51].Increasing the popularity of AAS in quantitative analysis of elements is not surprising due to the high sensitivity and selectivity of the technique. Moreover, the technique is characterized by low detectability limit and high precision. The basis for more detailed classification of atomic absorption spectrometry is the type of atomizer used. The most common atomization technique was definitely flame atomization (F-AAS), where air or N_2O was used as the oxidizing gas and acetylene was usually flammable gas [52,53]. Another type of atomizer is electro thermal (ET-AAS), also readily used in determinations of metals [54]. Electrothermal atomization most often occurs in so-called graphite furnaces (GF-AAS) [55,56 and 57].

The furnaces are shaped like small tubes 4-6 cm in diameter with a hole placed in the upper part used for sample introduction. Hydride generation atomic absorption spectrometry is used in quantitative determination of metalloids (selenium, arsenic, antimonium) in the aquatic samples collected from surface and ground waters [58,59], or from ash landfill leachate. Cold vapor AAS technique (CV-AAS) was used in mercury determinations [60]. Special flow cells (quarz or glass with quarz windows) are used in the technique, and Hg must occur in ion form or in gases.Atomic Fluorescence Spectrometry is also worth mentioning here as it enables mercury determination when combined with the above atomization technique [61].

The papers raising the problem of heavy metals determinations also mention the use of spectrophotometric techniques that involve quantitative measurement of light absorption or emission by a sample. However, spectrophotometric techniques [62,63], including ultraviolet and visible light spectrophotometer [64,65], are rarely used in the analyses of environmental samples. The cause of such tendencies are the requirements concerning constant lowering of sample determination limits, as well as the large time expenditure necessary for the analysis [66]. That is the reason why spectrophotometric techniques are becoming less and less competitive in comparison to other methods.Classic atomic emission spectrometry (AES), combining it with a plasma spectrochemical source in the form of inductively coupled plasma (ICP-AES) was a breakthrough in the development of this method. As a result, a very sensitive and selective technique was created and used for the quantitative determination of metals in a variety of environmental samples [67,68].

Environmental applications utilizing ICP-AES for metal determination encompass a wide range of materials, such as natural waters, seawaters, soils, sediments, biological tissues, and air particulates. Waters, wastewaters, and solid samples should be prepared as described in U.S EPA method 200.2. U.S EPA method200.7 describes ICP-AES measurement of metals and some nonmetals. .Inductive Coupled Plasma (ICP) techniqueis widely used for trace boron analysis. ICP technique is applicable to the large number of elements with high reliability [69]. This method is applicable to the following analytes: Li, Be, B, Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Ce, Hg, and Pb. OSHA method ID-125G describes ICP-AES analysis procedure for metal and metalloids. It is applicable for the quantitative analysis of 13 elements found in welding fume: Be, V, Cr, Zn, Mn, Cu, Co, Ni, Sb, Fe, Cd, Pb and Bi [70].

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was developed as a commercial analytical technique in the early 1980's and has since been applied to the determination of trace, minor and major elements in almost every analytical field. Inductively coupled plasma-mass spectrometry (ICP-MS) is a powerful tool for analyzing trace metals in environmental samples. A large range of elements can be detected using an ICPMS [71]. The system of inductively coupled plasma mass spectrometry [ICP-MS] is a perfect instrument for the analysis of trace quantities of metallic elements. It is characterized by a low detectability limit and good selectivity. For that reason it is a common technique used for the determination of metal contents in different environmental samples (water, soil, tissues and ashes) [72, 73 and 74].

IV. CONCLUSION

The main object of this review article is i). The possibilities and ways of soil contamination by different activities results to emitted various metals beyond the threshold limits which are very harmful to the human health and interfering of different trophy's ii). The citation of various articles in respect of heavy metal[Zn, Mn, Mo, Cu, Cr, Fe, Ni, Cd, Co, As, Hg, B and Pb]. contamination of soils, leafy vegetables and planted roots appeared in various national and internal journals of repute andiii). To explore the need and

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demand of various analytical techniquies including ICP-MS/ICP-OES to address the different environmental issues particularly with toxic metals and their estimations at trace level.

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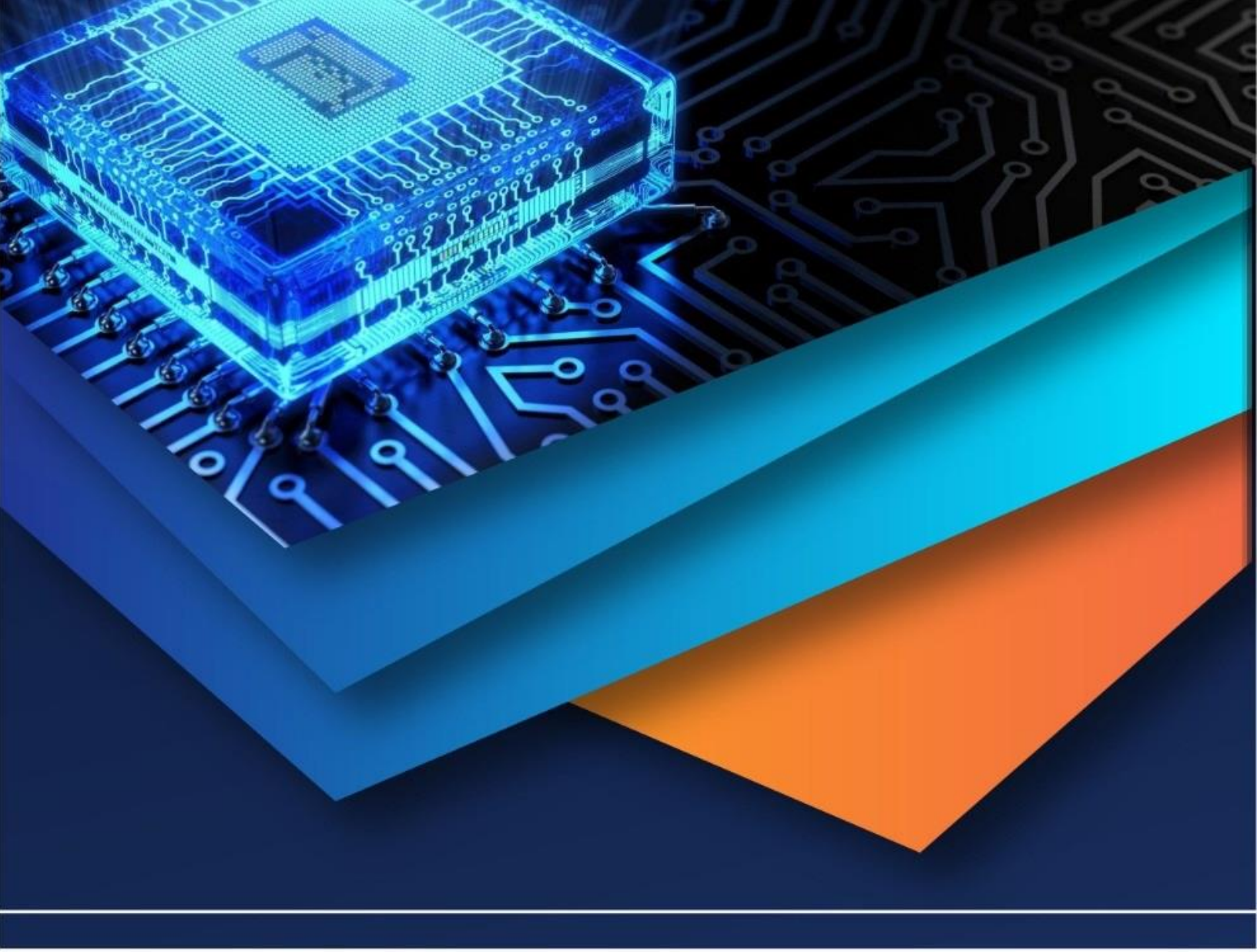

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