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Hydrogeochemical Modeling of Groundwater, Using WATEQ4F. A Case Study in Lower Varahanadhi Sub basin, Tamilnadu, India.

Ramamoorthy.P[1], Senthilkumar.S[2], Rammohan.V3
[1, 3] *Department of Geology, University of Madras. Chennai.*
[2] *Department of Geology, Wachemo University, Ethiopia .*

Abstract: Geochemical modelling attempts to understand and envisage the chemical reactions of minerals, gases and organic matter with aqueous solutions in real or hypothetical water-rock systems. A study was carried out in Lower Varahandhi sub basin to find out the relationship and behaviour of different Saturation Index (SI) of carbonate minerals .The Saturation Index of the carbonates helps us to recognize the thermodynamic stability of water and to find out the geochemical actions of water. A 59 groundwater samples were collected from open and bore wells during premonsoon season and postmonsoon season (2012). The physicochemical parameters such as pH, EC, TDS, Ca, Mg, Na, K, Cl, HCO3, SO4 NO3 etc were analyzed. Geochemical model, WATEQ4F has been used to calculate the SI of different minerals. SI of Carbonate minerals in the Pre monsoon and Post monsoon season of the study area indicate Under Saturation to Over Saturation state in both the seasons. The relationship between log pCO$_2$ and SIof carbonate minerals indicate has more atmospheric interactions during the post monsoon period.

Key words: Groundwater, Lower Varahanadhi sub basin, Saturation Index, WATEQ4F

I. INTRODUCTION

Hydrogeochemical composition of groundwater can also be suggestive of its origin and history of course through underground materials which water has been in contact with, in shallow and deep-seated conditions. Natural and anthropogenic sources along with chemical and biogeochemical constituents have been considerably changing groundwater quality in recent years. Modeling of chemical constituents is aqueous system encompasses the aqueous speciation of dissolved cationic elements, among organic and inorganic anionic lagans, of anion element. Chemical modeling is used to describe the chemical characteristic of an aqueous system whether lake or fluid in human digestive system (Senthil kumar et.al 2014).

The computerized geochemical models are reliable tools for understanding the chemical state of natural waters and for predicting the activities of such waters under variety of hypothetical conditions. The geochemical reaction simulation model WATQ4F (Truesdell and Jones 1973; Plummer et al. 1976) has been used to determine the solubility of equilibria for the groundwater of Gadilam river basin (Prasanna et al. 2006). During the reaction simulation, WATEQ4F calculates the total concentration of elements, log (ratio) for stability plots and distribution of aqueous species, the amount of minerals (or other phases) transferred in or out of the aqueous phase with respect to specified mineral phases. The data required for input to the model include the concentration of dissolved constituents, temperature and pH. The aqueous speciation is computed by an iterative process using equilibrium constant based on the free energy of reaction (Gibbs 1970). The present study was calculating the saturation index of the carbonate minerals for both the season. Many authors have used the saturation index of silicate, carbonate and weathering processes from aquifer matrix(Chidambaram et al 2007; Prasanna et al.2010). Hence, this present study focuses on the relationship and behavior of different SI of carbonate minerals in collected groundwater samples in both premonsoon and postmonson season.

A. Study Area

The study area(Fig.1) is located in the Tamilnadu and Puducherry state of union territory. It was surrounded by and Bay of Bengal in the east, Nallavur sub basin in the north and Ponnaiyar basin in the south and Varahanadhi sub basin in the west. The study area occupies an area of 539.45 sq.km. The study area mainly composed of Alluvium and then followed by charnockite, migmatite, sandstone, limestone is distributed in the northern part.

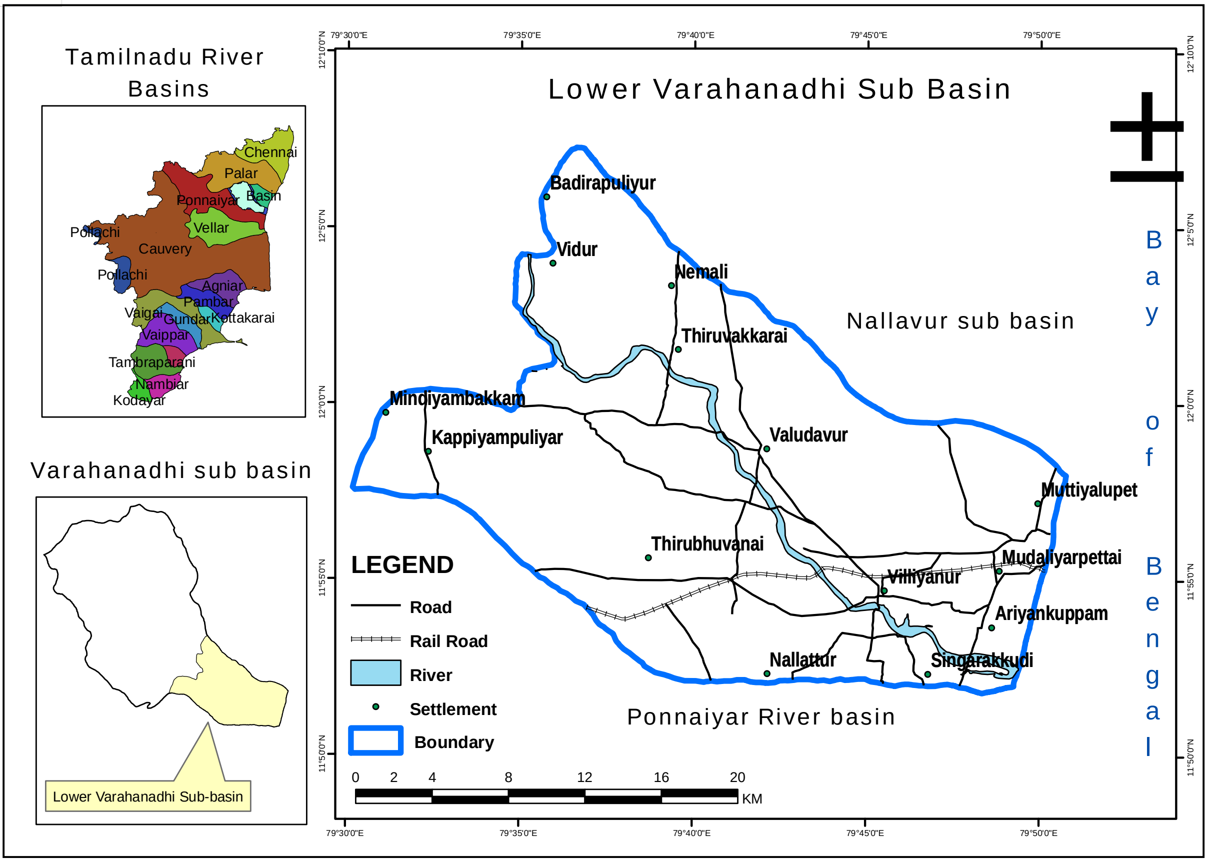

Fig: 1 Study area Map of Lower Varahanadhi Sub basin

II. MATERIALS AND METHODS

There are 59 groundwater samples from open and bore well of various locations of Lower Varahanadi sub basin area were collected during Pre-monsoon and post-monsoon season. The pH, electrical conductivity (EC), total dissolved solids (TDS) were measured at the sample site using handheld analyzing kits. Groundwater samples were collected, and the samples were kept in a polyethylene bottle at $10^{\circ}C$ for further laboratory analysis. Chemical characteristics were analysed following the procedure given in America Public Health Association (APHA, 1995). The geochemical reaction simulation model WATQ4F (Plummer et al., 1976) was used to determine the equilibrium solubility for carbonate and sulphate minerals.

III. RESULTS AND DISCUSSION

A. General Hydro Geochemistry

Minimum, Maximum, and Average values with reference to seasons in mg/l are given in (table.1). The groundwater in study area is generally alkaline with pH ranging from 6.96 to 8.53.The average value of pH for the Pre-Monsoon period is 7.67 for Post-Monsoon period. Is 7.47.The average EC values 1265.59 µS/cm during pre-monsoon and1187.79 µS/cm during post-monsoon. The Total dissolved solids (TDS) which is generally sum of dissolved ionic constituents various between 197 mg/l to 1953 mg/l. The average value of 711.13 mg/l for pre-monsoon and 690.35 mg/l for post-monsoon period.

Table 1: Maximum, minimum and average values of chemical constituents in groundwater during Pre-monsoon and Post-monsoon (all values in mg/1 except EC in µS/cm and pH)

	Pre-monsoon			Post-monsoon		
Parameter	Min	Max	Avg	Min	Max	Avg
TDS	205.08	1785.59	711.13	197	1953	690.35
pH	7.01	8.53	7.67	6.96	8.46	7.47

EC	310	3280	1265.59	330	3380	1187.79
Nitrate	0.23	143.84	31.61	0.62	170.5	38.78
Sodium	1.84	441.83	149.49	5.36	347.3	112.94
Potassium	2.34	35.97	12.091	1.56	148.58	16.66
Calcium	14	104.00	45.2	14	208	56.47
Magnesium	6.08	126.46	41.91	9.7	155.65	43.47
Fluoride	0.1	1.4	0.66	0.00	1.49	0.44
Bicarbonate	61	658.80	291.68	36.6	481.90	257.94
Sulphate	1.6	241.8	80.83	0.96	244.8	72.98
Carbonate	0	108	14.033	0	96	15.18
Chloride	28.36	694.82	175.506	5.5	765.72	157.359

B. *Major Cations*

The high concentration of Ca, Mg Na, in groundwater is due to clay minerals such as montmorillonite, illite and chlorite (Garrels1976).

Calcium and magnesium ions present in groundwater is particularly derived from leaching of limestone, dolomites, gypsum and anhydrites, whereas the calcium ions is also derived from cation exchange process (Garrels1976). The concentration of calcium ion ranges from 14 to 208 mg/l, with an average concentration of 45.2 mg/l and 56.47 during premonsoon and postmonsoon. The concentration of magnesium ranges from 6.08 to 155.65 mg/l, with an average value of 41.91 and 43.47 mg/l during premonsoon and postmonsoon.

The concentration of Ca^{2+} in groundwater sample is due to rock weathering minerals like feldspars, pyroxene, and amphiboles. The concentration of Mg^{2+} in the groundwater is due to the exchange of minerals in soil and rock by water .weathering of silicate minerals might be the major cause for the high concentrations of major cations in the groundwater. (Rajmohan et.al. 2000).

The sodium concentration in ground water is varied between 1.84 to 441.83 mg/l with an average 149.49 mg/l in pre-monsoon and with an average 112.94 mg/l. The high variation of Na+ and Ca+ in the groundwater is attributed to cation exchange among minerals as well as irrigation return-flow .The feldspar of igneous rock is the source of sodium when weathered. Also, the agricultural activities may have significant influences the concentration of sodium in groundwater. The concentration of potassium ranges from 1.56 to 148.5 mg/l with an average of 16.66 mg/l during the post monsoon and 2.34 to 35.97 mg/l with an average of 12.091 mg/l during premonsoon it could be due to the agricultural activities and minerals like biotite and orthoclase. The concentration of potassium in groundwater is low because of the high degree of stability of potassium bearing minerals

C. *Major Anions*

The concentration of Bi-Carbonate in study area ranges from 36 to 658.80 mg/l with average value of 291.68 and 257.94 mg/l for premonsoon and post monsoon period. Concentration of Chloride in groundwater ranges from5.5 mg/l to 765.72 mg/l with average value of 175.5 mg/l and 157.3 mg/l during pre and postmonsoon. Sulphate sample analyzed average values is 80.8 mg/l for premonsoon and 72.9 mg/l for the post monsoon season was usually derived from oxidative weathering of sulphide bearing minerals like marcasite. The Nitrate concentration of ground water samples range from values 0.23 mg/l to 143.84 for pre monsoon and 0.62 mg/lto 170.5 mg/l for the post monsoon period with the average value of 31.6 mg/l and 38.7 mg/l during pre and postmon soon period.

D. *Geochemical Models*

The geochemical reaction simulation model WATEQ4F(Truesdell and Jones 1973; Plummer et al. 1976) has been used to determine the solubility of equilibria for the groundwater of Gadilam river basin (Prassanna et al. 2006). During the reaction simulation, WATEQ4F calculates the total concentration of elements, log ratio for stability plots and distribution of aqueous species, the amount of minerals (or other phases) transferred in or out of the aqueous phase with respect to specified mineral phases.

Disequilibrium indices Log(IAP/KT) was calculated by WATEQ4F geochemical model for those minerals and other solids stored in the model data book for which the dissolved constituents are reported in the groundwater analysis. Solubility equilibrium hypothesis were tested by computing ion activity product(IAP) from the activities of un complexed ions based on the stoichiometries of minerals and other solids in the WATEQ4F data base. The activity product are then compared to the solubility product (KT) for the same solid phases to the assumption that certain dissolved constituents in groundwater are in equilibrium with particular minerals and amorphous solids (Deutsch et al. 1982). Disequilibrium indices log (IAP/KT) were calculated to determine, if the water is in thermodynamic equilibrium log (IAP/KT=0), oversaturated log (IAP/KT>0) or under saturated log (IAP/KT<0) with respect to certain solid phases.

Bicarbonate derived by the pressure of weathering or from other source remains in the aqueous medium trying to equilibrate with different ions like Ca, Mg, or both to attain Saturation with different minerals like Calcite (SI_C), Aragonite(SI_A), Dolomite(SI_D) and Magnesite (SI_M). SI of Carbonate minerals in the Pre monsoon and Post monsoon season of the study area indicate Under Saturation to Over Saturation state in both the seasons (Fig 2 & 3). The Saturation state of Carbonate minerals in this study area are in the following orders $SI_D > SI_C \geq SI_M > SI_A$. Saturation index of these minerals were plotted against the log concentration of HCO_3 in the study area no definite Trend of SI is noted with the increasing log HCO_3 in both the seasons. In the Carbonate minerals Calcite and Aragonite is most of the samples fall in the Over saturation state is common for both season. Otherwise most of the samples the saturation index of magnesite is equilibrium state for both the seasons. It is indicate among the carbonate minerals of the study area the effect of dilution of Calcite and Aragonite minerals is greater than the other carbonate minerals. Certain samples of both the depths show under saturation though with high HCO_3 due to non availability of cations (Ca^{2+} and Mg^{2+}) which might have removed from the aqueous system due to process of cations exchange (Gomez et al., 2006) or due to Precipitation and Removal of Ca^{2+} and Mg^{2+} as Calcite/ Dolomite due to super saturation.

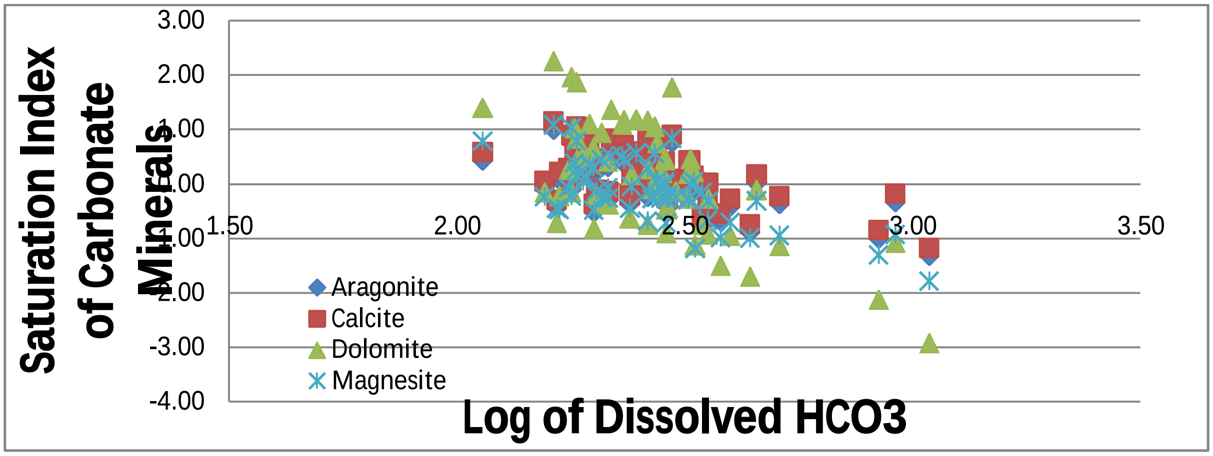

Fig.2 Variation of Saturation index of different Carbonate minerals with log dissolved HCO_3 – Pre Monsoon

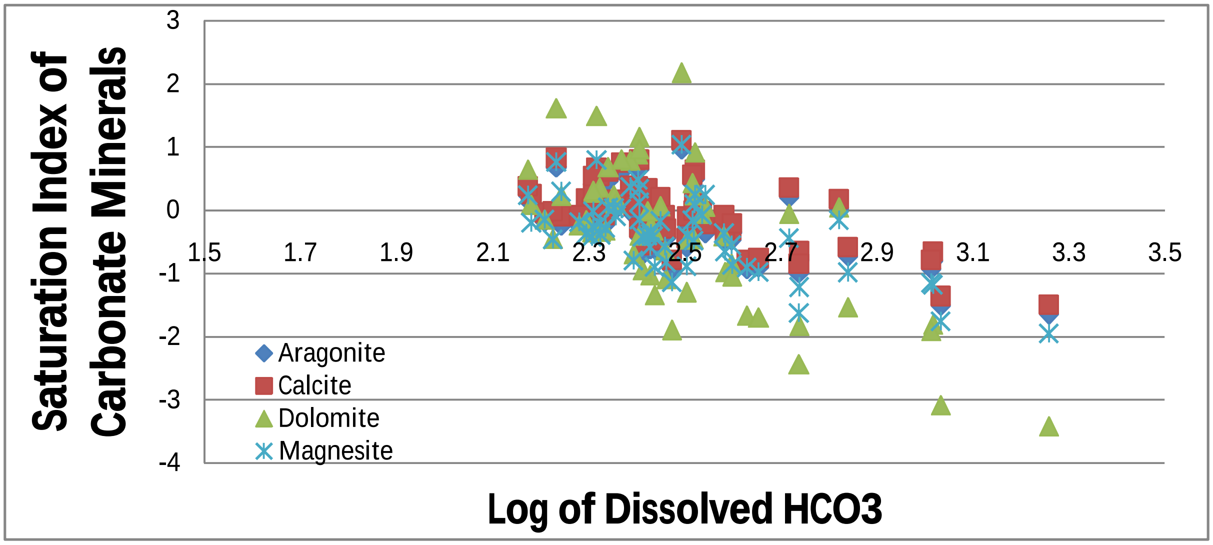

Fig.3 Variation of Saturation index of different Carbonate minerals with log dissolved HCO_3 – Post Monsoon

E. Variation of pCO_2

Partial presence of CO_2 plays a major role in the state of saturation of Carbonate minerals. The relationship between log pCO_2 and SIof carbonate minerals graph was plotted (Fig 4 & 5). The SI of Dolomite is higher in the supersaturated state and it is the least under saturated state i.e when pCO_2 increases. It is understood in the following figures that when the pCO_2 increases the SI of the carbonate minerals decreases. It is also observed that pCO_2 ranges from -3.2 to -1.5 in the Pre monsoon period and during the Post monsoon season the values various from -3.13 to -1.46 which is indicate has more atmospheric interactions during the post monsoon period.

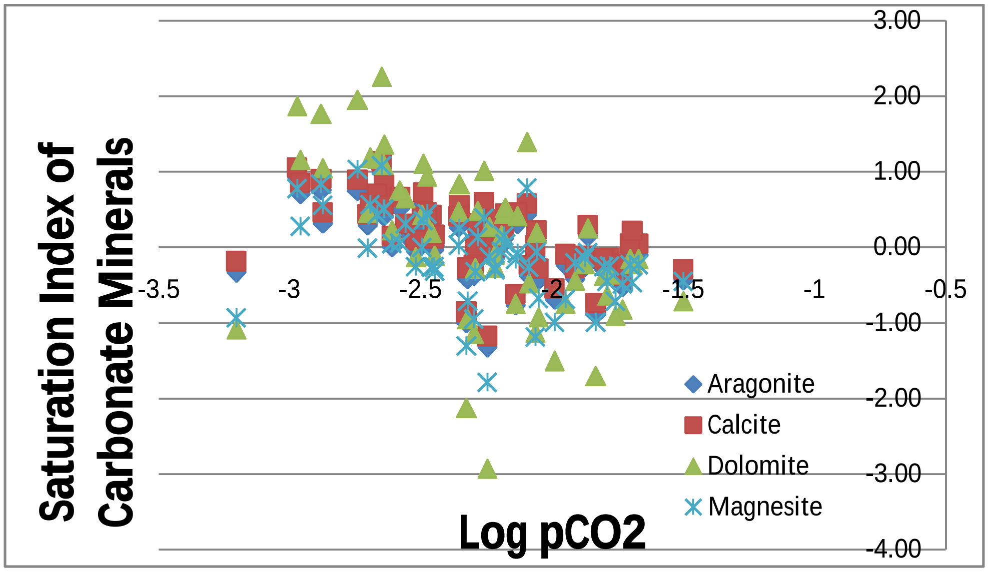

Fig:4.Variation of Saturation index of different carbonate minerals with log pCO_2 – Pre Monsoon

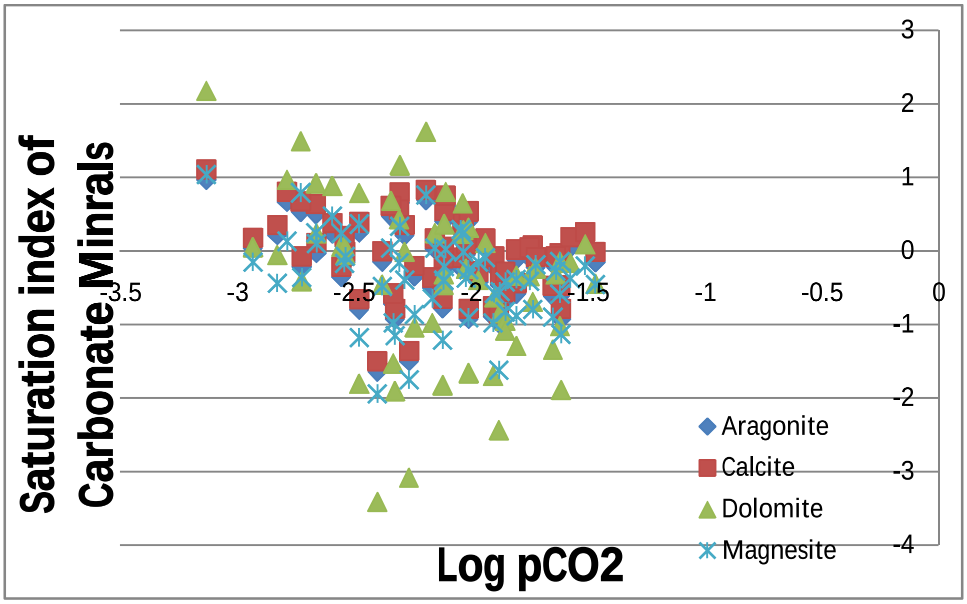

Fig.5. Variation of Saturation index of different carbonate minerals with log pCO_2 – Post Monsoon

IV. CONCLUSION

The study area Lower Varahanadhi sub basin, concentration of total dissolved solids was higher in Postmonsoonperiod.Ca ,Mg and Cl was higher in postmonsoon season, whereas sodium ,carbonate ,bicarbonate was higher in Premonsoon period. Hydrogeochemical modeling indicate the saturation index of carbonate minerals are following in the order: The Saturation state of Carbonate minerals in this study area are in the following orders $SI_D > SI_C \geq SI_M > SI_A$. Saturation index of these minerals were plotted against the log concentration of HCO_3 in the study area. Trend of SI is noted with the increasing log HCO_3 in both the seasons. The relationship between log pCO_2 and SIof carbonate minerals indicate has more atmospheric interactions during the post monsoon period.

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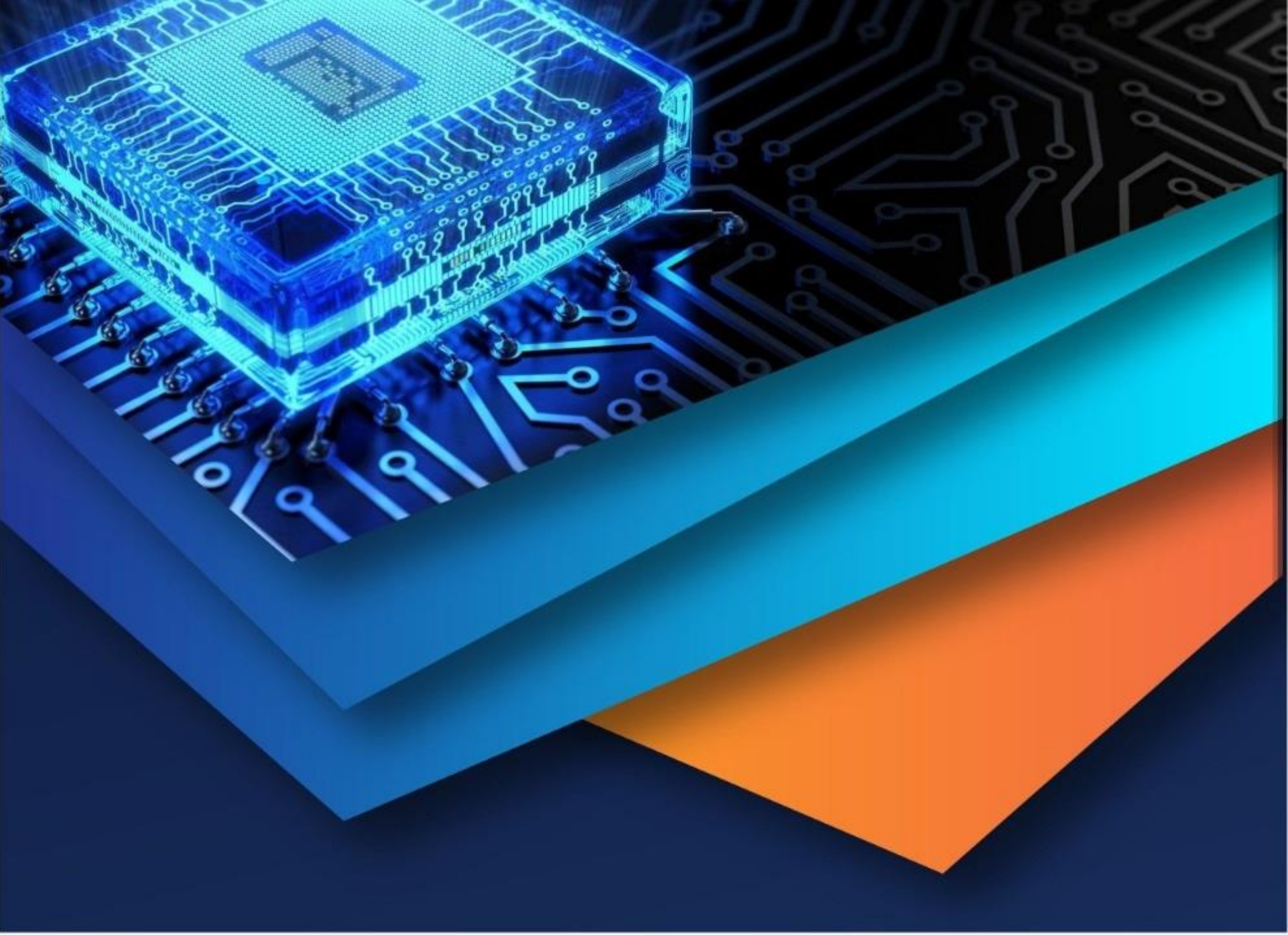

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