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Prediction of Photocatalytic Decolorization Acid Red 14 Dye in Aqueous Solutions by UV/NanoTiO_2 using Artificial Neural Network Model

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***Abstract*— An artificial neural network model was developed to predict the photocatalytic decolorization of azo dye Acid Red 14 (AR14) in water by a combination of UV/NanoTiO_2 system. The initial concentrations of dye, catalyst dosage, pH of the solution and temperature were employed as input to the network; the output of the network was decolorization efficiency. The multilayer feed-forward network was trained by 100 sets of input-output patterns using a back propagation algorithm; a three-layered network with six neurons in the hidden layer gave optimal results. A first order reaction with k= 0.0341 min^{-1} was observed for the photocatalytic degradation reaction.**

***Keywords*—Titanium dioxide, Artificial neural network, Photocatalytic decolorization, Azo dye**

I. INTRODUCTION

More than 10,000 species of dyes and pigments are utilized every year, and over 50% of these dyes are azo dyes which contain one or more azo bonds (–N=N–) and aromatics [1]. The release of wastewater containing these dyes is a dramatic source of aesthetic pollution, eutrophication and perturbations to the environment and aquatic life. Due to the complex molecule structure of azo dyes, conventional methods for waste treatment [2-4] are having several drawbacks and not effective for complete degradation of azo dye. Most of these technologies including chemical or biological ways [5] can only break little part of the azo bonds and remove some degree of color, while the azo linkages are just reduced to aromatic amines that are colorless but can also be toxic and potentially carcinogenic. Therefore, it is urgent to develop novel technology of water purification leading to complete destruction of the dangerous azo dyes. Recently, advanced oxidation processes (AOP) have been widely investigated of which heterogeneous photocatalysis has become the most popular. Most studies related to photocatalytic degradation of organic pollutants have been carried out using suspensions of powdered TiO_2 in the treated solution [6].

TiO_2 is a cheap, readily available material, highly stable chemically and the photogenerated holes are highly oxidizing. In addition, TiO_2 is capable of oxidation of a wide range of organic compounds into harmless compounds such as CO_2 and H_2O [7]. Artificial neural network (ANN) are now commonly used in many areas of chemistry and they represent a set of methods that may be useful in solving such problems [8-10].The first results of neural network application were published half a century ago (1943) by McCulloch and Pitts [11]. In particular their flexibility and their ability to model highly nonlinear phenomena make them a candidate method in multivariate calibration. The present investigation discusses the use of a multilayer feed-forward neural network model to predict the colour removal efficiency of azo dye Acid Red 14 (AR14) solutions by UV/NanoTiO_2 process.

II. EXPERIMENTAL

A. Reagents

Degussa P-25 nano titanium dioxide with a crystallographic mode of 85% anatase and 15% rutile, a BET surface area of 40 m^2 g^{-1} and an average particle size of 30 nm (according to the manufacturer's specifications) and the azo dye, Acid Red 14 (AR14), was obtained from Alvan Sabet Company (Iran) and used without further purification. Fig.1. showed the structure of this dye. The pH values were adjusted at desired level using dilute NaOH and H_2SO_4. Other materials were all Merck products. Double distilled water was used for preparation of requisite solutions.

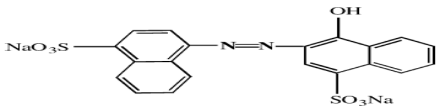

Fig.1 The chemical structure of Acid Red 14 (AR14)

B. Apparatus

For the UV/photocatalyst process, irradiation was performed in a photoreactor of 1 L in volume with a low mercury lamp 15W

(UV-C). A UV/VIS spectrophotometer (Jenway 6505) was employed for absorbance measurements using silica cells of path length 1 cm.

C. Procedures

For the photodegradation of AR14, a solution containing known concentration of dye and photocatalyst was prepared and was allowed to equilibrate for 30 min in the darkness. Subsequently 50 ml of the prepared suspension was transferred to a 1 L Pyrex reactor. The suspension pH values were adjusted at desired level using dilute NaOH 0.1N and H_2SO_4 0.1N (the pH values were measured with Horiba M12 pH meter). The degradation reaction took place under the radiation of a mercury lamp while agitation was maintained to keep the suspension homogeneous. The concentration of the samples was determined using a UV/VIS spectrophotometer (Jenway 6505) at λ_{max} = 514 nm. The efficiency of colour removal is defined by the following expression:

$$\text{Decolorization\%} = \text{X\%} = \left(\frac{C_0 - C}{C_0}\right) \times 100 \quad (1)$$

where C_0 and C are the concentration of dye at $t = 0$ and t, respectively.

D. Artificial neural network (ANN)

ANN are directly inspired from the biology of the human brain, where billions of neurons are interconnected to process a variety of complex information. Accordingly, a computational neural network consists of simple processing units called neuron. Each network consists of artificial neurons grouped into layers and put in relation to each other by parallel connections. The strength of these interconnections is determined by the weight associated with them. For every ANN, the first layer constitutes the input layer (independent variables) and the last one forms the output layer (dependent variables). Between them, one or more neurons layers called hidden layers can be located [12]. The hidden layers act as feature detectors and, in theory, there can be more than one hidden layer. The inputs to hidden and output layers are calculated by performing a weighted summation of all the inputs received from the preceding layer. The weighted sum of the inputs is transferred to the hidden neurons, where it is transformed using an activation function. The most widely used transfer function for the input and hidden layer is the sigmoid transfer function and is given by:

$$f(x) = \frac{1}{1 + e^{-x}} \quad (2)$$

The linear activation function (Eq. (3)) is used as the output layer activation function.

$$f(x) = x \quad (3)$$

The ANN was trained using the back propagation algorithm. All calculations were carried out with Matlab mathematical software with the ANN toolbox.

III. RESULTS AND DISCUSSION

A. UV- vis sp

Fig. 2 shows UV-vis spectrum of AR14, respectively during photoirradiation with Nano-TiO_2 catalyst. The spectrum of AR14 in the visible region exhibits a main band with a maximum at 514 nm. Based on these results, it was shown that the ultraviolet radiation are broken the structure of dye molecules and reduced absorption intensity.

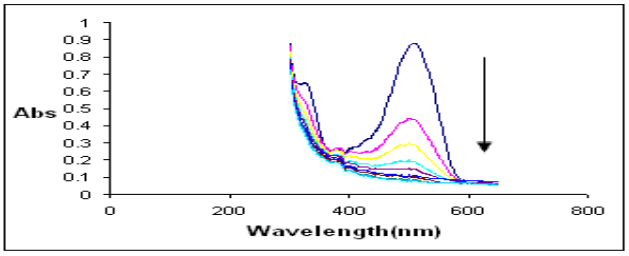

Fig.2 UV-vis spectra of AR14 (concentration of dye = 30 ppm, catalyst dosage= 75mg/lit, pH= 3, T=30 ^{O}C)

B. Effect of pH

pH is one of the main factors influencing the rate of degradation of some organic compounds in the photocatalytic process [13]. It is also an important operational variable in actual wastewater treatment. Fig. 3 shown the photodegradation of AR14 at different pH from 1 - 9, which clearly shown that the best results were obtained in acidic solution, (pH =3, X =82.1%). The charge of TiO_2, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. For the above reasons, dyes that have a sulfuric group in its structure, which is negatively charged, the acidic solution favors adsorption of dye onto the photocatalyst surface, thus the photodegradation efficiency increases. There is also the photocatalytic degradation of AR14 in acidic solutions, which is probably due to the formation of $^{\bullet}OH$ as it can be inferred from the reactions (4)–(7) [14].

$$e^{-}_{CB} + O_{2(ads)} \rightarrow {}^{\bullet}O^{-}_{2(ads)} \quad (4)$$

$${}^{\bullet}O^{-}_{2(ads)} + H^{+} \rightarrow HO^{\bullet}_{2} \quad (5)$$

$$2HO^{\bullet}_{2} \rightarrow O_2 + H_2O_2 \quad (6)$$

$$H_2O_2 + {}^{\bullet}O^{-}_{2(ads)} \rightarrow {}^{\bullet}OH + OH^{-} + O_2 \quad (7)$$

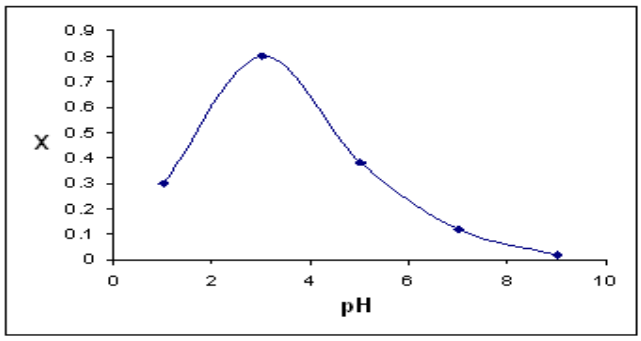

Fig. 3 Effect of pH on removal dye (concentration of dye = 30 ppm, catalyst dosage= 75mg/lit, T=30 ^{O}C).

C. Effect of initial AR14 concentration

The effect of initial concentration of AR14 on photodegradation efficiency is shown in Fig. 4. The photodegradation conversion of AR14 decreases with an increase in the initial concentration of AR14. The presumed reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of TiO_2. The large amount of adsorbed dye is thought to have an inhibitive effect on the reaction of dye molecules with photogenerated sites or hydroxyl radicals, which is due the lack of any direct contact between them. Once the concentration of dye is increased, it also causes the dye molecules to adsorb light and the photons never reach the photocatalyst surface, thus the photodegradation efficiency decreases.

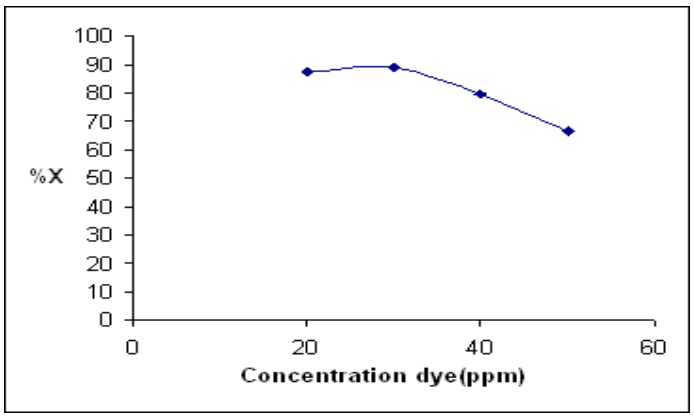

Fig. 4 Effect of initial AR14 concentration on photodegradation efficiency (catalyst dosage = 75mg/lit, pH= 3, T=30 ^{O}C)

D. Effect of catalyst dosage

At this stage, the effect of different amounts of catalyst between 25 to 100 mg/l was tested. The results in Fig. 5 shows that increasing the catalyst amount to 75 mg/l reaction rate increased and with increasing amount of catalyst concentration, reaction speed decreased. Because of reduced activity of photocatalytic in amount than 75 mg/l, which increases the photocatalytic phenomenon spread of light due to light rays with the catalyst dispersed in the solution occurred, and lost the number of photons of light energy and thus is reduced the amount photocatalytic reactions[15].

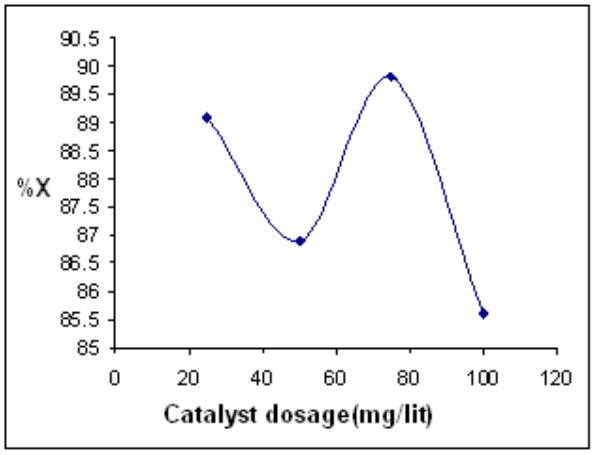

Fig. 5 Effect of catalyst dosage on removal dye (concentration of dye = 30 ppm, pH= 3, T=30 ^{O}C)

E. Effect of Temperature

Effect of temperature on the degradation process was tested in the range of 15- 40 °C are shown in Fig. 6. The positive influence of the temperature can be observed. Increasing temperature of 15- 40°C indicated that the percent conversion of dye decreases with increasing temperature. It is necessary to cause the temperature of 40°C was not selected was that at temperatures higher may vaporization of the dye solution increases and caused change the concentration of pollutant. However, an increase in temperature helps the degradation reaction to compete more effectively with valance band hole (h^{+}_{VB}) and conduction band electron (e^{-}_{CB}) recombination. On the other hand, the increase in temperature decreases the solubility of oxygen in water which is not desirable for photocatalytic processes. Therefore, the temperature of 30 °C can be applied as a mild temperature with significant conversion of substrate.

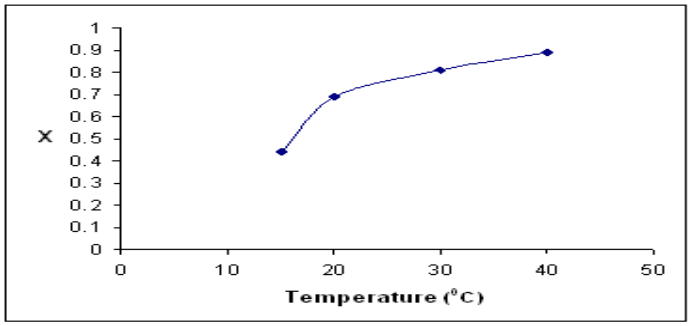

Fig. 6 Effect of temperature on removal dye (concentration of dye= 30 ppm, catalyst dosage= 75mg/lit, pH= 3)

F. Kinetics of photocatalytic degradation of AR 14

Photocatalytic decomposition reaction kinetics of AR14 completely corresponds to the kinetic of pseudo-first-order model reaction [16]. In the kinetic equation of pseudo-first-order, the relationship between concentration(C) and time (t) is as follows:

$$\frac{-dC}{dt} = k_{app} C \qquad (8)$$

The integral equation is as follows:

$$\ln(\frac{C_0}{C}) = k_{app} t \quad (9)$$

in which k_{app} is the apparent pseudo-first-order rate constant (that is affected by dye concentration), and t, is the reaction time.
A plot of ln (C_0/C) versus t, in optimal condition for photocatalytic degradation of AR14 is shown in Fig. 7. The linear plot suggests that the photodegradation reaction approximately follows the pseudo-first-order kinetics with rate coefficient k= 0.0341 min^{-1}.

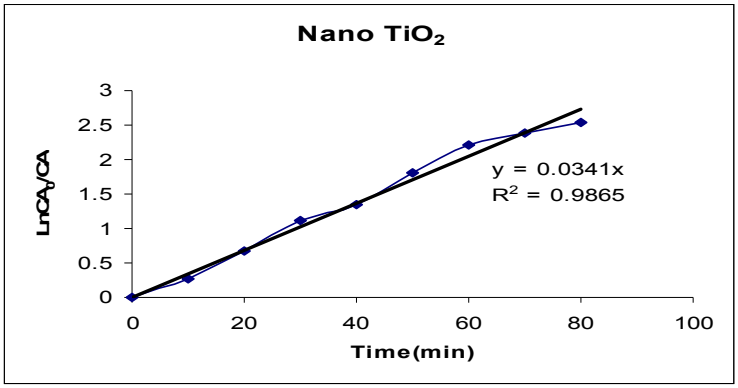

Fig.7 Kinetics of photocatalytic degradation on removal dye (concentration of dye = 30 ppm, catalyst dosage = 75mg/lit, pH= 3, T=30 ^{O}C).

G. ANN model development

In this study, one layer of hidden neurons was used. The net used was feed-forward neural network trained by back propagation algorithm. The input variables to feed-forward neural network were the initial concentrations of the dye, catalyst dosage, initial pH and temperature. The colour removal efficiency was the experimental response or output variable and was calculated by Eq.(1). The characteristics of input and output variables are shown in Table 1.

The topology of an artificial neural network (ANN) is determined by the number of layers, the number of nodes in each layer and the nature of the transfer functions. Optimization of ANN topology is probably the most important step in the development of a model [17]. In order to determine the optimum number of hidden nodes, a series of topologies was used, in which the number of nodes was varied from 2 to 10. The mean square error (MSE) was used as the error function. MSE measures the performance of the network according to the following equation:

$$MSE = \frac{\sum_{i=1}^{i=N} (y_{i,pred} - y_{i,\exp})^2}{N} \quad (10)$$

where N is the number of data points, $y_{i,pred}$ is the network prediction, $y_{i,exp}$ is the experimental response and i is an index of data.

Table I
Characteristics of input and output variables

Variable	Range
Input layer	
Initial dye concentration (ppm)	20- 50
Catalyst dosage (mg/lit)	25- 100
Initial pH	1- 9
Temperature (^{O}C)	15- 40
Output layer	
Decolorization (%)	0- 100

The primary goal of training is to minimize the error function (MSE) by searching for a set of connection weights and biases that causes the ANN to produce outputs that are equal or close to target values. In other words, the back propagation algorithm minimizes the MSE between the observed and the predicted output in the output layer, through two phases. In the forward

phase, the external input information signals at the input neurons which are propagated forward to compute the output information signal at the output neuron. In the backward phase, modifications to the connection strengths are made based on the basis of the difference in the predicted and observed information signals at the output neuron [18]. All samples were normalized in the 0-1 range. So, all of the data sets (X_i) (from the training, validation and test sets) were scaled to a new value x_i as follows:

$$x_i = \frac{X_i - X_{\min}}{X_{\max} - X_{\min}} \quad (11)$$

Each topology was repeated five times to avoid random correlation due to the random initialization of the weights. Fig.8 illustrates the network error versus the number of neurons in the hidden layer[19].

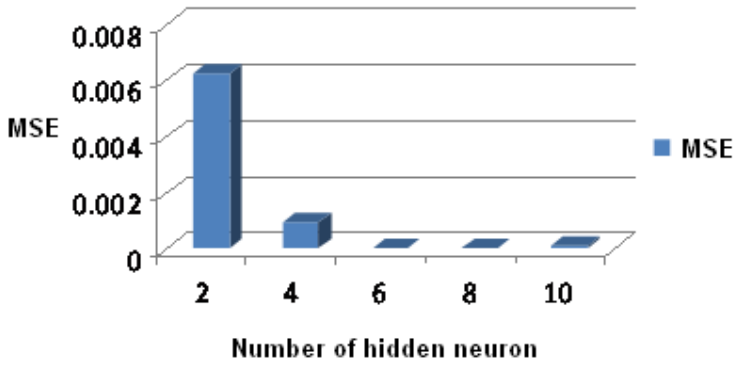

Fig. 8 Effect of the number of neurons in the hidden layer on the performance of the neural network

So, based on the approximation of MSE function, a number of hidden neurons equal to six was adopted and a three layered feed-forward back propagation neural network was used for the modeling of the process. (Fig. 9).

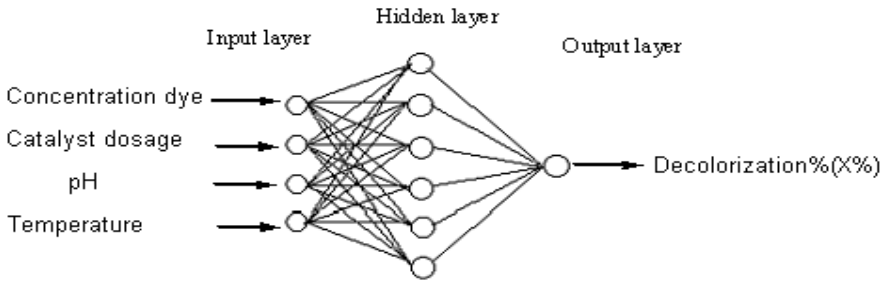

Fig. 9 ANN optimized structure

IV. CONCLUSIONS

The performance of photocatalytic decolorization of Acid Red 14 solution by UV/NanoTiO_2 process was successfully predicted by applying a three-layered neural network with six neurons in the hidden layer, and using a back propagation algorithm. Simulations based on the ANN model were performed in order to estimate the behavior of the system under different conditions. The optimal conditions such as, initial concentration of the dye=30 ppm, catalyst dosage=75 mg/lit, pH=3 and temperature=30 ^{O}C as analyzed and kinetics of photocatalytic decolorization reaction was determined. Pseudo-first-order model reaction corresponds to the experiment data of photocatalytic degradation of dye. The results of modeling confirmed that neural network modeling could effectively reproduce experimental data and predict the behavior of the process.

V. ACKNOWLEDGMENT

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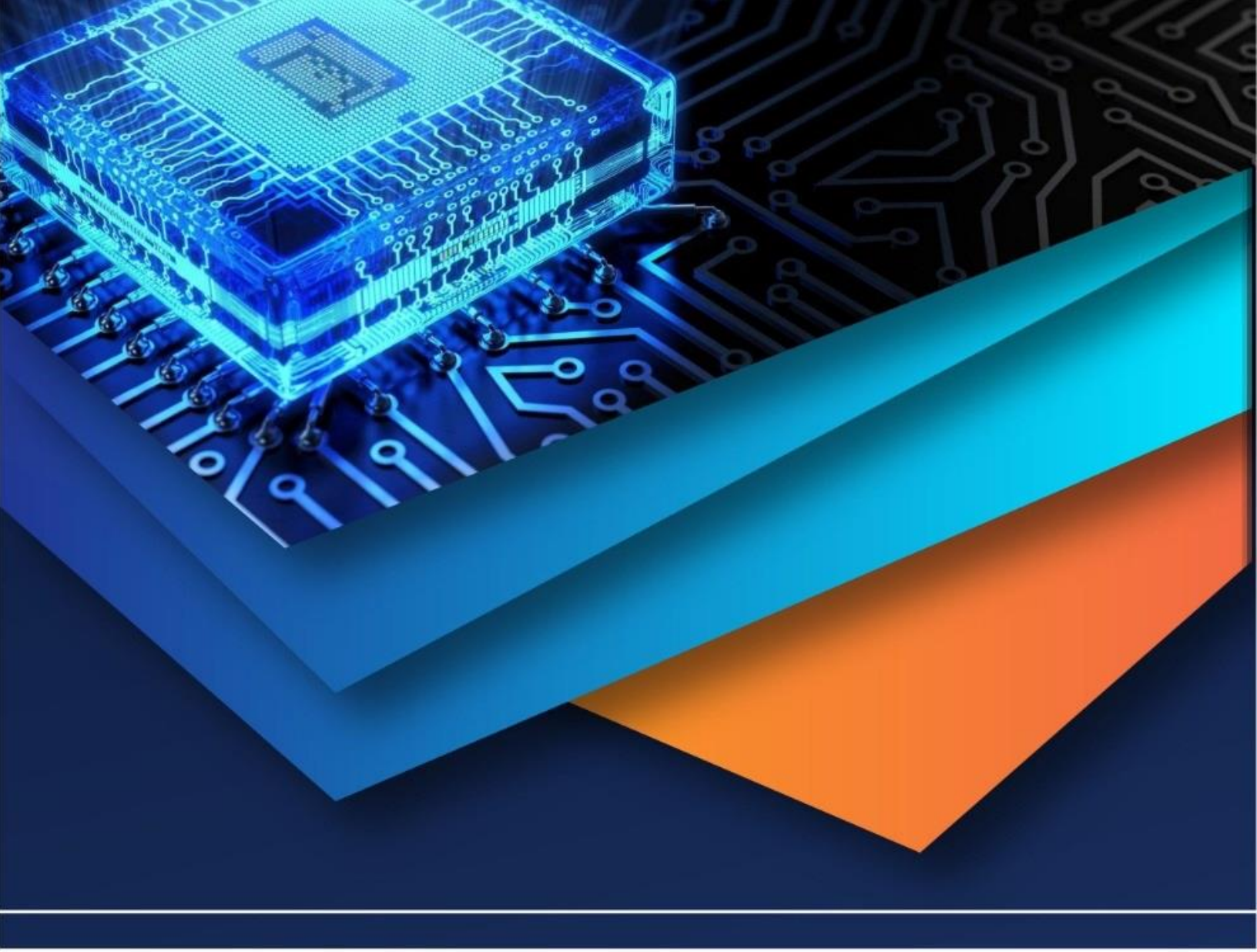

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