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Antibacterial mechanism of TiO_2 nanoparticles and optimize the parameters to maximize the antibacterial behavior of TiO_2 coated surface

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ABSTRACT

This paper gives a brief description of the antibacterial activity of TiO_2 nanoparticles along with the antibacterial mechanisms. The killing mechanism of bacteria and the reactions behind them have also been shown. An optimization was carried out to maximize the antibacterial activity using Central Composite Design (CCD) by employing response surface methodology. There are some dependent factors which are responsible for antibacterial activity of coated surface. Three different design factors i.e., the concentration of TiO_2 nanoparticles in the plating bath solution, water contact angle of the coated surface and the total surface energy of the substrate surface were selected as the process parameters.Among them the concentration of TiO_2 nanoparticles in coating bath solution plays an important role for the antibacterial behavior. By optimizing these three parameters, the surface energy of electron donor component (γ^-) was taken as a response factor. The greater value of (γ^-) shows the highest antibacterial behaviour. The main aim of this optimization is to enhance the surface energyof electron donor component (γ^-) of the coated surface in order to obtain the best protection from bacteria.

Key words: *Antibacterial activity, TiO_2 nanoparticles, Water contact angle, Hydrophilicity, Electron donor component.*

Introduction

Hygiene control of the surfaces is very important in food, cosmetics, pharmaceutical industries, catering and especially in medical appliances. Regular and thorough surface disinfection is necessary in microbiological laboratories and areas of intensive medical usage, to reduce the number of bacteria and prevent bacterial transmission. The TiO_2 nanoparticles play a very significant role in the case of antimicrobial activity. The TiO_2 nanoparticles show antimicrobial activity against some common pathogenic microorganisms such as *Escherichia coli*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* (Desai and Kowshik, 2009; Pazokifard, Esfandeh, and Mirabedini, 2014). Titanium dioxide (TiO_2) is a standard photochemically responsive and extremely photoactive non-toxic semiconductor that is exploited to develop biomaterial surfaces with self-cleaning and self-disinfecting properties (Cho *et al.*, 2005; Murugan *et al.*, 2013; Nguyen-Tri *et al.*, 2019). Matsunaga *et al.*, (Matsunaga *et al.*, 1985) first identified microbiocidal impact of TiO_2 in 1985. After that several other scientists studied the microbiocidal functions of TiO_2 photocatalysts in detail (Huang *et al.*, 2000; Wong *et al.*, 2006; Xiong, Zhang, and Pan, 2011). Since then, researchers emphasized more on TiO_2 photocatalytic killing mechanism in a wide spectrum of species including bacteria (Desai and Kowshik, 2009), viruses (Cho *et al.,* 2005), fungi (Mitoraj *et al.,* 2007), cancer cells (Zhang and Sun, 2004) and algal toxins (Srinivasan and Somasundaram, 2003). As ultraviolet (UV) irradiation from sunlight is sufficient to maintain the hydrophilic surface so that contaminants can be easily removed by rain, such highly hydrophilic surfaces have many practical applications, for example, self-cleaning and antifogging materials. This attracted the attention of many researchers on hydrophilic TiO_2 films.

It has been observed from previous research that the surface energy of electron donor component (γ^-) of the TiO_2 coated surface increases significantly with increasing TiO_2 content in the plating bath solution and the number of adhered bacteria decreases with increasing the surface energy of electron donor component (γ^-) (Zhao *et al.,* 2013). Thus, there is a correlation between the concentration of TiO_2 nanoparticles and the surface energy of electron donor component (γ^-). If the the surface energy of electron donor component (γ^-) increases, then the surface of the substrate will be more likely to exhibit antibacterial behaviour. The present study focuses on the three variables for increasing the antibacterial properties of the TiO_2coated surface and to find the optimum conditions for obtaining the best (γ^-) value for the substrate. Central Composite Design (CCD) helped determining the optimum processing conditions. In the CCD modelling 12 set data of process parameters including response were incorporated and optimized. Analysis of Variance (ANOVA) was conducted to find out the significant parameters and their interactions affecting the (γ^-) value for the substrate.

Antimicrobial activity and mechanisms

When sunlight strikes upon the TiO_2 nanoparticles' coated surface then UV ray is generated and electron–hole pairs are created in the conduction band through excitation of electrons from valence band (Sun *et al.*, 2019; Zhu *et al.*, 2017). TiO_2 photocatalysts are indicated to produce good oxidizing power when illuminated by UV light having less than 385 nm wavelengths (Zhao *et al.,* 2013). Actually, TiO_2 surfaces then attain photo-activation energy with illuminating suitable photon energies (Chouirfa *et al.,* 2019) and it causes death of bacteria (Maness *et al.,* 1999) because it possesses a super-hydrophilic surface which reportedly decomposes adsorbed organic impurities (Aita *et al.*, 2009; Suzuki *et al.*, 2009). The death phenomena of bacteria have been shown in (Fig. 1).

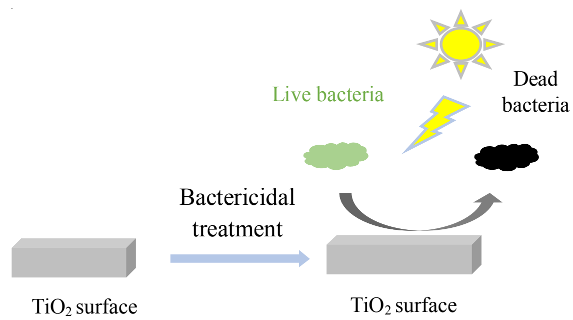

Fig. 1. Death phenomena of bacteria by UV light.

Fig. 2 exhibits the killing mechanism of bacteria through cell damage. TiO_2 nanoparticles' antibacterial behaviour relies mostly on the existence of reactive oxygen species (ROS) (Shibata *et al.*, 2010). The ROS activities basically enable a greater surface area of nanoparticles and enhance oxygen vacancies (Blake *et al.*, 1999). The growth in oxygen emptiness leads to more reactive oxygen species. ROS is largely based on two considerations (a) diffusion capability of the reactant and (b) the growth of oxygen vacancies (Rana and Singh, 2016). The photocatalytic operation of TiO_2 by acting as a bridge to move the photogenerated to e^- and h^+ another portion of the photocatalyst contributing to the inhibition of photogenerated e^- and h^+ recombination (Nijpanich *et al.,* 2019). The electron hole which emits from TiO_2 reacts with water molecules and produce hydroxyl radicals ($OH^\bullet$) and hydrogen ion (H^+). The free electron reacts with oxygen and produces oxide radicals ($O^{\bullet -}$). Dissolved oxygen molecules are converted into superoxide radical anions ($O_2{}^-$) and later it react with hydrogen ion (H^+) to produce (HO_2^-) radicals. The hydroxyl radicals is a powerful oxidation agent that can attack organic pollutants (Akpan and Hameed, 2010). The generated hydroperoxyl radical ($HO_2{}^{6\ -}$) reacts with H^+ ion to produce hydrogen peroxide (H_2O_2) molecule. The hydrogen peroxide (H_2O_2) molecules can penetrate into the cell membrane and can destroy DNA that leads to mineral, protein and genetic leakage and leads to death (Bahadur *et al.,* 2016; Monetta and Bellucci, 2014; Stan *et al.*, 2016). The Ti^{4+} ions can ensure the antibacterial activity of the surface. Gram negative bacteria includes thin peptidoglycan surrounded by lipopolysaccharides in their cell wall and it includes negatively charged particles, so titanium ions (Ti^{4+}) are easily able to connect enzymes of bacteria to the sulfhydryl group (SH), which contribute to rapid cell death (Kalaiarasi and Jose, 2017; Prashanth *et al.*, 2015). It is quite evident that hydroperoxyl radicals and superoxide radicalsalong the TiO_2 particle planes are appropriate locations for octahedral coordination of the incoming Ti^{4+} ions (Sasani Ghamsari *et al.*, 2017; Sugimoto and Zhou, 2002). The mechanism for generating free radicals with the assistance of TiO_2 and water when illuminated by light is described (Narayanan *et al.*, 2012) by following reactions.

$TiO_2 + h\upsilon \rightarrow TiO_2\,(e^- + h^+)$(1)

$H_2O + TiO_2(h^+) \rightarrow TiO_2 + OH^{\bullet} + H^+$(2)

$O_2 + TiO_2\,(e^-) \rightarrow TiO_2 + O^{\bullet -}$(3)

$O_2^{\cdot\cdot} + H^+ \rightarrow HO_2$(4)

$HO_2^{6-} + H^+ \rightarrow H_2O_2$(5)

Allion *et al.* (Allion *et al.* 2007) experimented the substrate of TiO_2 coated surface under UV irradiation and obtained a favourable outcome by observing the reduction of water contact angle to only 5°. Thus, TiO_2 films can decrease the bacterial attachment up to 80%. This result stipulates that UV luminescence on TiO_2 coated surface expose a super-hydrophilic surface (Li and Logan, 2005; Bastani *et al.*, 2014). It is really an outstanding feature for bacteria repellent. There is a correlation between water contact angle and antibacterial activity. It can be observed that the water contact angle decreases significantly with the increasing irradiation time in the first 60 min and then become stable (Matsunaga *et al.*, 1985; N. V. Motlagh and Taghipour-Gorjikolaie, 2018). The cells of bacteria in water are damaged

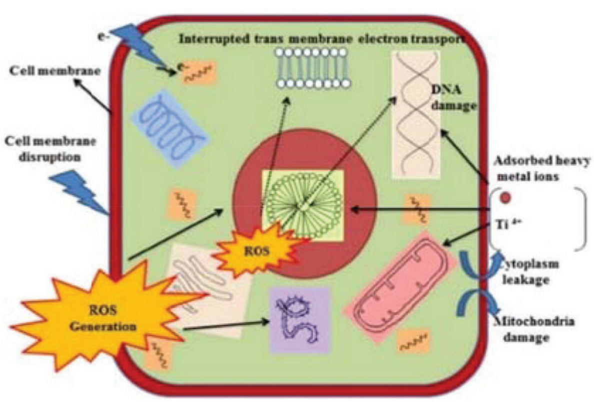

Fig. 2. Killing mechanism diagram of bacteria (Nithya *et al.*, 2018).

within 60 to 120 min by contact with a TiO_2 photocatalyst upon illumination of UV light (Matsunaga *et al.*, 1985). After a certain time of UV illumination, all films are converted to a hydrophilic state due to the decrement of water contact angle (Wang *et al.*, 2000).

The line graph (Fig. 3) shows data on the number of bacterial attachments on the basis of surface energy. As is observed from the graph, the highest number of bacterial attachments holds good for *Vibrio.* It is more than 800,000. With the increment of surface energy, the number of attached bacteria decreases sharply (Liu *et al.*, 2018; Zhao *et al.*, 2013). It is reported that when the electron donor (γ^-) component of a surface is higher, the surface is charged more negatively (Chibowski *et al.*, 1994; Liu and Zhao, 2011; Shao and Zhao, 2010). Thus, the larger the electron donor component γ^- of a surface, the more impervious to bacteria. When the surface energy exceeds 50 MJ/m^2, then the attached bacteria appear to be zero. Furthermore, an interesting fact is that among the three bacteria, *Cobetia* reveals less attachment to the surface compared to the other bacteria.

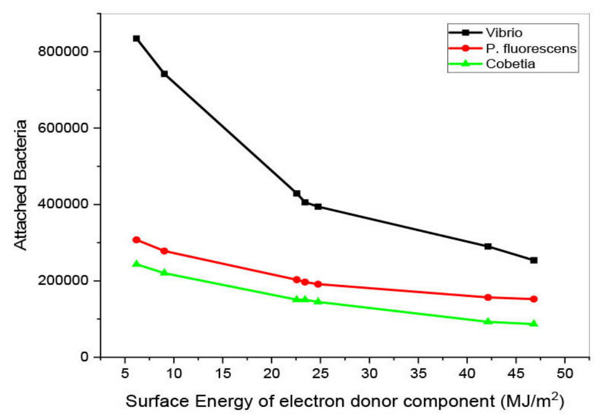

Fig. 3. Different bacterial adhesion based on surface energy of electron donor component (γ^-).

The wettability of any surface is measured through contact angle between water and the surface. When the contact angle is above 90° the wettability is bad, when it is below 90° the wettability is regarded as good. There can be categorized two types of forces which can specify the wettability of the surface, whether the surface is hydrophilic or hydrophobic based on the water contact angle. They are adhesive force and cohesive force. Adhesive forces can cause water droplet to scatter across the surface with keeping the water droplet height minimum and water can take supplemental place over the surface (Fig. 4a). This remains the water contact angle less than 90° and the surface acts as a hydrophilic nature with high wettability. Surface of substrate becomes more soaked when the water contact angle remains small. These hydrophilic molecules can attract water molecules more vigorously and can easily interact with water. However, cohesive forces tend to avoid the water droplet from spreading upon the surface through repulsion and cannot interact with water molecules readily. Here, water cannot take too many spaces of the surface. Because of this repulsion, the water droplet tends to squeeze with displaying the contact angle more than 90° and the surface can be termed as hydrophobic (Fig. 4b). The surface with hydrophobic nature possesses low wettability as it cannot soak more area on the surface.

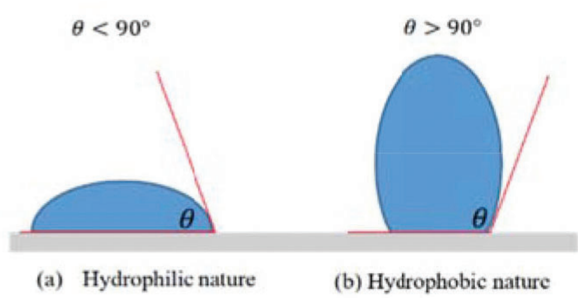

Fig. 4. Water contact angle in different surface nature.

According to pictorial chart (Fig. 5), there are five parameters which are directly responsible for antibacterial activity. Interestingly, these five sources of information are closely connected to each other and dependent on one another as well. As is presented in the diagram, the antibacterial action can be evaluated by using five different types of sources namely, surface wettability, hydrophilicity, contact angle, electron donor capability and surface energy. As per previous discussion, photo wettability of TiO_2 nanoparticles is extremely higher when sunlight strikes upon it. High photo wettability represents high hydrophilic nature. Low contact angle can be equalized as high surface energy and high interfacial tension. Surface free energy of a solid object provides a direct evaluation of intermolecular interactions at interfaces and has a significant influence on wetting, adsorption, and adhesion behavior. Depending on the context, adherence to solid surfaces may be acceptable or undesirable. When electron hole pairs are generated after UV illumination then more negatively charged electron attract and donate numerous amounts of electrons to the TiO_2 coated surface and then the TiO_2 can achieve photoactivation energies. The higher rate of electron contribution allows swift photoactivation energy which is really robust to terminate the bacterial action on the surface. Low contact angle provides high surface free energy and high interfacial tension. In the previous discussion, we have seen that higher TiO_2 content has lower contact angle and exhibits higher surface free energy. As we can see from the demonstration in (Fig. 5), these five parameters do not provide direct relationship among them and they are not directly proportional to each other. Only in case of water contact angle, the contact angle value must remain lower for making the surface antibacterial. If we move on to other parameters, then it is quite clear that the rest four parameters must be remain higher. So, we can conclude, the four parameters, surface wettability, hydrophilicity, electron donor capability and surface free energy should provide higher values to keep the surface active against bacteria.

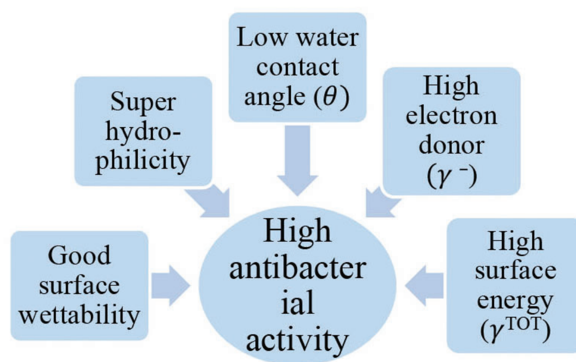

Fig. 5. Flow diagram of dependency of different parameters with antibacterial activity.

Results and Discussion

Statistical analysis was conducted to optimize the surface energy of electron donor component (“) of the substrate using Design Expert Software. The three process parameters and the response are indexed in Table 1.

ANOVA analysis

The analysis of results of ANOVA for response surface quadratic models representing the surface energy of electron donor component (γ^-) of coated surface is presented in Table 2.

The Model F-value of 44.96 implies the model is significant. There is only a 2.19% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. The F-value of TiO_2 concentration is 6.24 which is greater than the F-values of other two process parameters. This illustrates that the concentration of TiO_2 nanoparticles are having a significant influence on the response.

The Predicted R^2 of 0.6889 is in reasonable agreement with the Adjusted R^2 of 0.9729; i.e. the difference is less than 0.3. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 21.193 indicates an adequate signal. This model can be used to navigate the design space.

Mathematical Modelling

The results were completely analyzed via the analysis of variance (ANOVA) using Design Expert Software. The final equations in terms of coded factors and actual factors are represented by equation 6 and

Table 3. Statistical results of ANOVA analysis.

Specifications	Value
Std. Dev.	1.60
Mean	25.52
C.V. %	6.25
R^2	0.9951
Adjusted R^2	0.9729
Predicted R^2	0.6889
Adequate Precision	21.19

Table 1. 12 set of experimental variables for the Central Composite Design (CCD).

Run	Process parameters			Response
	TiO_2 concentration (g/l)	Water contact angle (degree)	Total surface energy (MJ/m^2) component (MJ/m^2)	Surface energy of electron donor
1	0.1	57.8	44.10	22.77
2	0.3	56.6	45.10	23.41
3	0.5	54.0	47.23	24.65
4	1.5	39.6	46.04	42.10
5	2.0	35.5	49.11	46.81
6	0.5	76.8	26.74	16.14
7	1.5	63.3	31.84	26.35
8	0.1	62.8	42.61	18.33
9	0.3	68.1	38.78	16.15
10	0.5	70.7	32.89	18.12
11	1.5	61.4	38.91	28.04
12	2.0	57.8	40.56	23.42

Table 2. ANOVA for Quadratic model.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	1029.53	9	114.39	44.96	0.0219
A-TiO_2 Concentration	15.88	1	15.88	6.24	0.1297
B-Water contact angle	6.40	1	6.40	2.52	0.2535
C-Total surface energy	11.95	1	11.95	4.69	0.1626
AB	11.20	1	11.20	4.40	0.1708
AC	14.87	1	14.87	5.85	0.1368
BC	17.33	1	17.33	6.81	0.1208
A^2	7.11	1	7.11	2.79	0.2366
B^2	7.22	1	7.22	2.84	0.2341
C^2	16.86	1	16.86	6.63	0.1236
Residual	5.09	2	2.54		
Cor Total	1034.62	11			

equation 7, respectively.

Final Equation in Terms of Coded Factors

Surface energy of Electron donor component = 16.86 + 20.32A + 35.70B + 43.17C 23.90AB 54.69AC 142.57BC 4.83$A^2$35.77B^2 69.01C^2. .. (6)

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Final Equation in Terms of Actual Factors

Surface energy of Electron donor component = 2904.24 + 296.24A + 35.83B + 85.76C 1.21 AB 5.14AC 0.617BC 5.35$A^2$0.083B^2 0.551C^2. .. (7)

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. Here, A, B and C denote TiO_2 concentration, Water contact angle and Total surface energy, respectively.

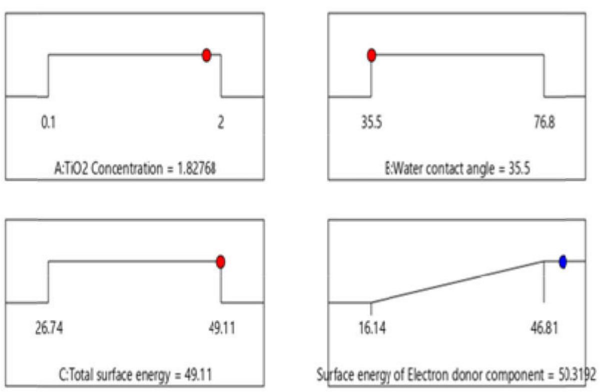

Fig. 6. The predicted parameters with outcome.

Predicted model analysis

The prognostication of the optimum process parameters with the response (outcome) has been shown in (Fig. 6). The red dots indicate the optimum values of process parameters. By using 1.83 g/l concentration of TiO_2 nanoparticles in plating bath solution, 35.5 ° water contact angle and 49.11 MJ/m^2 surface energy of the coated surface can provide the best value of surface energy of electron donor component (γ^-). The blue dot implies the γ^- value noting 50.31 MJ/m^2.

The red region of the contour plot shows the maximum height of the plot and hence represents the highest value of the surface energy of electron donor component (γ^-). The red colour covered area is the region where optimized values can be obtained and predict the best γ^- value with respect to TiO_2 Concentration, Water contact angle and Total surface energy. The blue covered region is regarded as the worst portion for the response due to having bent surface from upper to lower region. In order to get the best positive response, the surface energy of electron donor component must lie in the red zone.

Conclusions and future perspective

This contribution has aimed to provide a compre-

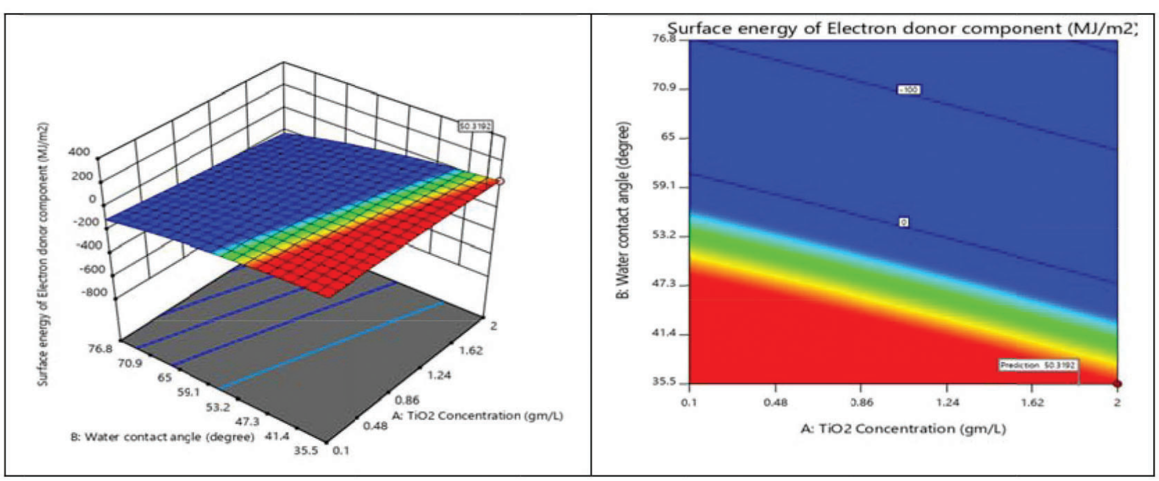

Fig. 7(a). Second-order 3D response surface plot and **(b)** contour plot to show the variation ofsurface energy of electron donor component with concentration of TiO_2 nanoparticles and water contact angle with indicating predicted optimum value.

hensive overview of antibacterial mechanism of TiO_2 nanoparticles. It can be inferred that higher TiO_2 contents exhibit higher antibacterial activity by reducing the contact angle value. The TiO_2 particles coated wall decreases the penetrability of oxygen and prevent the flow of electron. As it prevents the flow of electron and ion, then naturally it reduces the electron donor (γ^-) capability. ANOVA is performed to examine the significant effect of parameters and their interaction on the surface energy of electron donor component (γ^-) of coated substrate. It can be confirmed with higher F value from ANOVA analysis that the concentration of TiO_2 nanoparticles are having a significant influence on the antibacterial activity of the coated surface. The lower surface energy of electron donor component (γ^-) cannot enhance the antimicrobial activity for the substrates' surface. Therefore, it can be concluded that the optimized modelling value and the experimental value are almost identical, thus proving this modelling to be cost effective and time saving simultaneously. The developed model can be used to predict the antibacterial characteristics of the TiO_2 deposited coated surface in industrial applications without conducting extensive experimental trials.

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