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Impact of Meteorological Conditions on the Photocatalytic Efficiency and Stability of Titanium Dioxide-Based Paint

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Abstract: Photocatalytic paints have proven to be a promising solution for combating air pollution in urban environments by breaking down harmful pollutants into harmless by-products. These paints interact with meteorological parameters when exposed outdoors, and we have investigated the influence of these parameters on the degradation of the exposed paint. We conducted experiments in a controlled laboratory in which samples of the photocatalytic paint were exposed to different temperatures and humidity levels. Using a standardized test method, we determined the constant reaction rate and analyzed the data to understand the effects of temperature and humidity on photocatalytic efficiency. The results show a significant effect of temperature and humidity on the constant reaction rate. Temperatures from 10°C to 30°C and humidities from 10% to 50% were found to increase the reaction rate, leading to an improvement in photocatalytic efficiency. However, too wide a temperature range (30°C to 60°C) and too high a humidity (55% to 80%) had a negative effect on the thermal stability of the paint and its long-term durability. Over time, we observed an increasing loss of adhesion and fading of the paint as temperatures and humidity increased, leading to a deterioration of the photocatalytic paint. In summary, while moderate temperatures and humidity improve photocatalytic efficiency, extreme conditions can negatively affect the stability and long-term performance of the paint.

Keywords: Air pollution mitigation; Constant rate of reaction; Efficiency; Humidity; Photocatalytic paint; Temperature

Introduction

The escalating number of vehicles and population growth is propelling the world into a more pollution-intensive state, posing various health risks, and depleting natural resources (Kumar et al., 2021). Urgent action is imperative to identify and regulate pollution sources for a better future. Among the myriad forms of pollution, air pollution stands out as particularly perilous, claiming the lives of approximately 7 million people annually (Restrepo et al., 2004). Reactive secondary pollutants are major contributors to these issues and demand immediate attention (Gautam et al., n.d.; Chen et al., 2017; Bergstra et al., 2018; Semlali et al., 2021).

Despite notable reductions in harmful pollutant concentrations achieved through EU air quality policies, health risks persist, particularly from fine particulate matter (PM10 and PM2.5), nitrogen oxides (e.g., NO2), and ozone (O3)(Suarez, 2020). The World Health Organization's air quality guidelines indicated annual average threshold limits of 20 μg/m^3 for PM10 and 10 μg/m^3 for PM2.5, as the adverse health effects of PM are still significantly below the daily average limits set by the EU. These limits are frequently exceeded in Europe(Di et al., 2021; Semlali et al., 2021).

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In recent years, there has been a growing focus on developing innovative materials and coatings with enhanced functionalities to address environmental challenges (Him et al., 2019). Among these advancements, photocatalytic paints have emerged as a promising solution to combat air pollution and reduce the presence of harmful pollutants in urban areas (Li et al., n.d.). These paints leverage photocatalysts to initiate chemical reactions upon exposure to light, effectively breaking down volatile organic compounds (VOCs), nitrogen oxides (NOx), and other harmful substances into harmless byproducts (Salvadores et al., 2020). While extensive research has been conducted on the photocatalytic properties of these paints, a crucial knowledge gap remains regarding the impact of meteorological parameters on their performance and durability.

This study aims to explore how meteorological factors, such as temperature, humidity, wind speed, and solar radiation, influence the efficiency and durability of titanium dioxide based (TiO_2) photocatalytic paint.

Photo-degradation Mechanism

Photocatalysts decompose the contaminants generally using the light's energy (Dinh et al., 2021). When the light flows on the photocatalysts surface, it results the electron-hole pairs, which generate free radicals. Namely, these radicals attack the organic contaminant molecules (pollutant) as described in equation (1) and (2):

$$TiO_2 + h\nu \rightarrow h^{+}vb + e^{-cb} \quad (1)$$

$$TiO_2 + h\nu \rightarrow h^{+}dl + e^{-cb} \quad (2)$$

From the above equations $h^{+}vb$ is a hole in the valence band, $h^{+}dl$ is a hole in the donor level and e^{-cb} is an electron in the conductive band. The first reaction takes place when the energy of the photon ($h\nu$) is greater than the TiO_2 band gap and both the electron and the hole can diffuse to the catalyst's surface and to participate in further reactions. In the case of the second reaction, when the energy of the photon is lower than this of the TiO_2 band gap but is greater than the activation energy of the donors (TiO_2 is mostly n-type semiconductor) (Kozhukharov et al., 2022). In this case, the hole is trapped on the donor's level and cannot move towards the catalyst surface. However, another reaction is possible as reported by some authors (Guo et al., 2015) apart from equations 1 and 2.

$$TiO_2 + Ethermal \rightarrow h^{+}vb + e^{-cb} \quad (3)$$

$$TiO_2 + Ethermal \rightarrow h^{+}dl + e^{-cb} \quad (4)$$

In these cases, the excitation energy of the electrons is obtained from the thermal oscillations of the crystal lattice. Although, TiO_2 has the large width of the band gap and small value of the thermal oscillations at room temperature(Him et al., 2019).

Meteorological Parameter

Meteorology is the scientific study of weather and atmospheric conditions while meteorological parameter refers to the various variables and factors that are measured and used in meteorology. These parameters help meteorologists understand and predict weather patterns, climate trends and atmospheric phenomenon. Some common meteorological parameters include temperature, precipitation, humidity, wind (speed and direction), pressure, cloud cover, visibility, dew point, etc. However, these parameters constantly interact physically with the human environment and its activities. But the physical processes do not operate independently(He et al., 2013). Instead, they are woven together into a complex fabric of radiation, chemistry, and dynamics. Interactions among these can be just as important as the individual processes themselves, for instance radiative transfer controls the thermal structure of the atmosphere which determines the circulation, which in turn influences the distributions of radiatively active components like water vapor, ozone, and clouds. In view of their interdependence, understanding how one of these processes influences atmospheric behavior requires an understanding of how that process is linked to others.

However, regarding the outdoor interaction of meteorological parameter and structural building, outdoor paint is the most exposed part of building that interacts with. These parameters cause the exposed paint to fade and degrade over time(Li et al., n.d.). Therefore, there is need for practical concept that would evaluate the interaction between the meteorological parameter and photocatalytic paint in terms of pollutant degradation.

Due to the complex behavior of meteorological parameters, there were no single methods, or formulas that directly describe their interaction with other physical factors (Tian et al., n.d.). Thus, computer simulations have led to rapid advances in our understanding of the meteorological parameters and its interaction with other factors. This work employed the capacity of MATLAB software's environment to explore how meteorological factors, such as temperature, humidity, wind speed, and solar radiation, influence the efficiency and durability of titanium dioxide based (TiO_2) photocatalytic paint.

Temperature

Temperature is a key meteorological parameter that can significantly affect photocatalytic reactions(Sattler & Liljestrand, 2003). Different temperature ranges may lead to variations in reaction rates and overall efficiency of the photocatalysts. The thermal stability of the paint is also a crucial factor to consider, as temperature fluctuations can impact its ability to maintain photocatalytic activity over extended periods. Understanding the relationship between temperature and photocatalytic paint performance is essential for optimizing its effectiveness in diverse environmental conditions.

Humidity

Humidity levels play a critical role in the functionality of photocatalytic paint (Crain et al., 2017). The water vapor adsorption capacity of the paint is influenced by humidity, which, in turn, affects the availability of reactants on the surface of the photocatalysts. Higher humidity levels can enhance the efficiency of photocatalytic reactions by facilitating the adsorption of target pollutants. However, excessive humidity may lead to water condensation, potentially hindering the photocatalytic process and degrading the paint's performance. Investigating the impact of humidity on photocatalytic paint can provide valuable insights into its behavior under different moisture conditions.

Activation Energy

Activation energy is the minimum amount of extra energy required by a reacting molecule to be converted into product. It can also be described as the minimum amount of energy needed to activate or energize molecules or atoms so that they can undergo a chemical reaction or transformation. It is usually measured in joules (J) and or kilojoules per mole (kJ/mol) or kilocalories per mole $(kcal/mol)$.

In theory, activation of energy depends only on two parameters namely nature of the reactant and effect of catalyst(Heuser et al., 2022). In the case of ionic reaction, the value of (E_a) will be small because there is an attraction between reacting species, while in the case of covalent reactant the value of E_a will be large because energy is required to break the bond.

In addition, a catalyst is a chemical substance that either increases or decreases the rate of a chemical reaction. However, in case of the positive catalyst it provides such an alternate path in which the value of E_a will be small, while the negative catalyst provides such an alternate path in which the value of E_a will be large. Overall, energy activation does not depend upon the temperature, pressure, volume, concentration, or coefficients of reaction(Kempe et al., 2023).

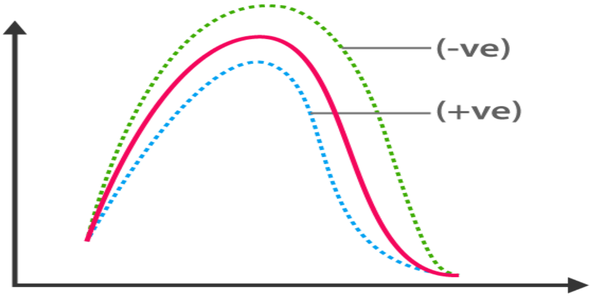


Figure 1. Graph of positive and negative activation energy

Arrhenius Equation

The equation was first proposed by Dutch chemist, J.H. Van't Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation. The Arrhenius equation is based on the Collision theory. It is not an equation that is born out of pure math that we can derive. It is an empirical equation that fits experimental data in most situations. The Arrhenius equation 5 express as:

$$k = k_o \exp\left(-{}^{E_a}/_{RT}\right) \tag{5}$$

where k_O is the Arrhenius factor or the frequency factor. It is also known as the pre-exponential factor. This constant is specific to a particular reaction. R is the gas constant and E_a is the activation energy which is measured in joules/mole. According to the Arrhenius equation, a reaction can only take place when a molecule of one substance collides with the molecule of another to form an unstable intermediate(Batiot et al., 2021). This intermediate exists for a very short time and then breaks up to form two molecules of the product. The energy required to form this intermediate is known as activation energy (Ea).

Arrhenius Model

Empirical formulations first emerged, and then they were followed by many authors attempting to use statistical physics theory to justify the form of the empirical laws previously found. These drew a parallel between gas phase and solid phase kinetics. Dating to the middle of the 20th-century, several authors questioned the form of the statistical distributions when applied to the reactions resulting in thermal degradation of solids (Batiot et al., 2021). Among the different approaches, the most common approach that establishes a non-oxidative degradation reaction, the production rate (r) is given by:

$$r = \left(\frac{\rho_s}{\rho_s(0)}\right)^{n_s} A^{pf} e^{-\frac{E_a}{RT}} \tag{6}$$

where n_s represents the reaction order, A^{pf} the pre-exponential factor, Ea is the activation energy, R is the perfect gas constant and T is the temperature. Then, $\left(\frac{\rho_s}{\rho_s(0)}\right)^{n_s}$ is the quantity of reactive mass, and $A^{pf}e^{-\frac{E_a}{RT}}$ is the reaction rate relation known as the Arrhenius relation, first established in 1889 by Arrhenius.

Although each author (Kohn & Sham, 1965)(Kim et al., 2009)prioritizes specific phenomena relevant to the processes they intend to model, they implement different simplifications and choose different expressions to model individual phenomena. In this paper, the same analogy was employed to remodel the effect of meteorological parameter on photocatalytic paint.

Arrhenius equation is a simple, but remarkably accurate formula for the temperature dependence of the reaction rate constant which can be used to model the temperature variance of diffusion coefficient, population of crystal vacancies, creep rates, and many other thermally induced processes or reactions. In general, for many common chemicals reaction at room temperature, for every 10℃ increase in temperature would double the rate of the reaction(Kozhukharov et al., 2022).

However, there is no general equation in the literature that directly relates the meteorological parameters with the rate of reaction or rate constant. Therefore, there is need to propose new approach that would inculcate the meteorological parameters into Arrhenius model as proposed in this work:

$$k = k_o \exp(-Ea/(RT)(1 + b(RH/100 - RH0/100) \quad (7)$$

where k_o is the pre-exponential factor, E_a is the activation energy, R is the gas constant ($8.314 JK^{-1}mol^{-1}$) , T is the temperature in Kelvin, RH is the relative humidity as a percentage, b is the humidity coefficient, and $RH0$ is a reference humidity.

Moreover, Arrhenius pointed out that the fraction of molecules colliding with sufficient energy to react is small, and according to Boltzmann principle, "the fraction of collisions in which the energy is more than a particular E is $e^{-E/RT}$ (Ibhadon & Fitzpatrick, 2013).

Usually, experimental data were used to determine the unknown parameters such as activation energy E_a, pre-exponential factor k_o, reference humidity $RH0$ and humidity coefficient from Arrhenius Model.

Method

To assess how temperature and humidity influence the constant rate of reaction in photocatalytic paint, we synthesized the paint composed titanium dioxide in the laboratory and applied it to a block substrate. The block was then positioned in a chamber equipped with LEDs to initiate the reaction as in (Crain et al., 2017)(Maria et al., 2022). Following established test procedures, we selected temperature and humidity ranges according to standard protocols (Arndt & Robert Puto, n.d.). Utilizing both theoretical and experimental data ranges, we optimized certain reference values using MATLAB computer software.

Conforming to standard test methods for measuring the rate of reaction of photocatalytic paint under various temperature and humidity conditions, we selected temperature ranges from 10°C to 70°C, with 10°C intervals, aligning with the destruction temperature of chemical reactions as in (Wolpert & Ampadu, 2012). Relative humidity (RH) levels ranging from 10% to 90% were employed, with 5% increments, to optimize reference humidity (RH0) at 0.6 and humidity coefficient (b) at 0.3 within the MATLAB environment as in the work of (Di et al., 2021). The concept of activation energy elucidates the exponential nature of the relation, where k_o is the pre-exponential factor ranging from 1 to 3 for the reaction as in the work of (Pal et al., 2016). We evaluated the rate of reaction and paint degradation by varying temperature ranges at constant humidity and vice versa. Simultaneously, we adjusted both parameters from lower to higher levels.

Result and Discussion

Due to human-generated pollution, particularly the environmental crisis stemming from air pollutants, addressing this crisis has led to a significant focus on developing photocatalysts for degrading air pollutants (Durante, 2021). The 3D figures presented below illustrate the complete photocatalytic activity across different temperature and humidity ranges (both high and low). The color spectrum, transitioning from blue to red, signifies the nature and magnitude of the reaction rate. The blue to red gradient represents the lower to higher ends of the reaction rate, while intermediate colors represent ranges in between.

Figures 2a to 2d depict the photocatalytic rate constant at a constant temperature of 45℃ and varied humidity ranges, incrementing by 5%. Examining the color flow in Figures 2a and 2b, it suggests a partial blue and red flow, indicating a normal and constant reaction rate without any signs of paint degradation. However, in Figure 2c, as humidity surpasses 50%, the color darkens, revealing paint degradation in Figure 2d when both temperature and humidity reach extremely high levels.

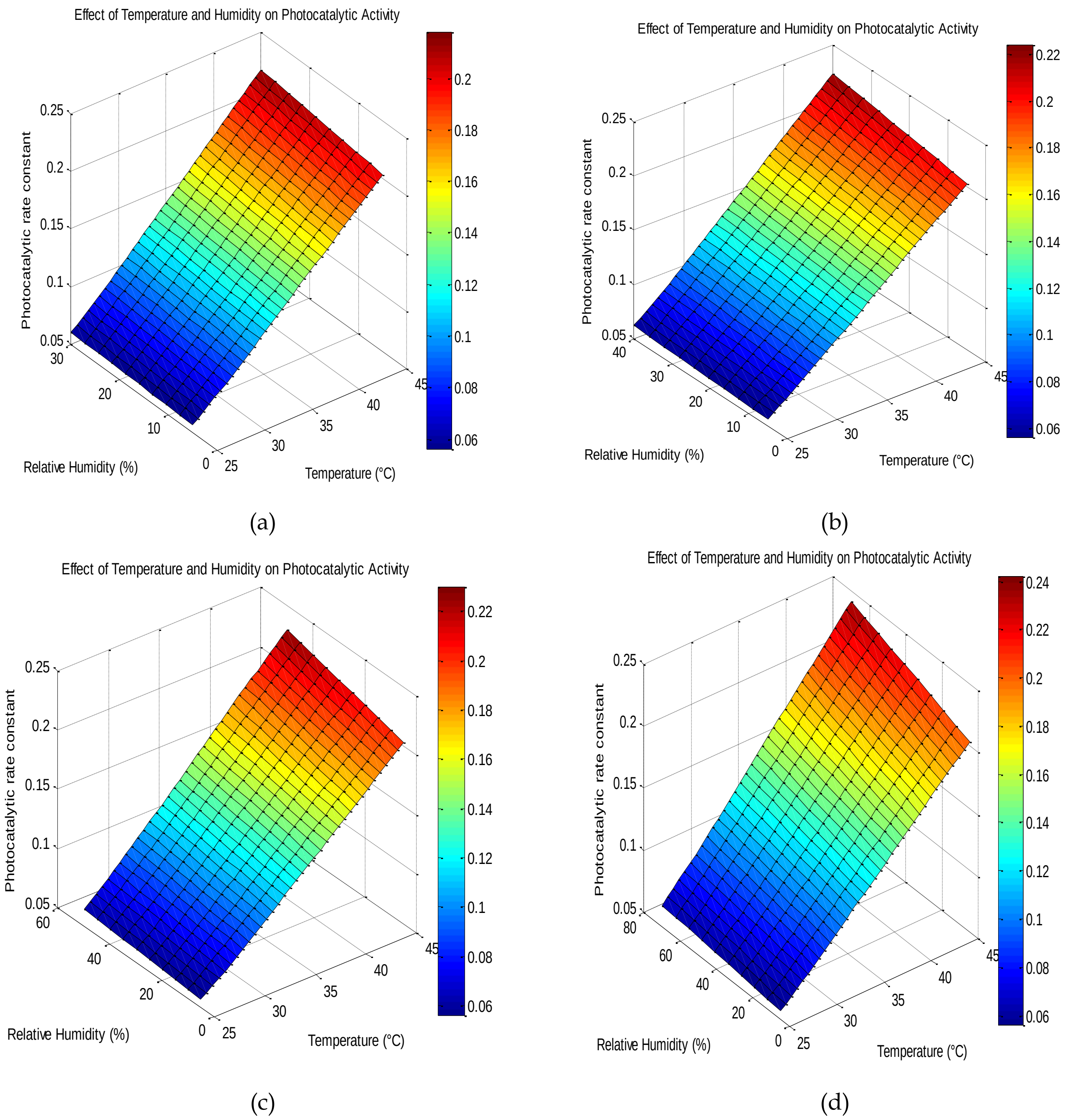
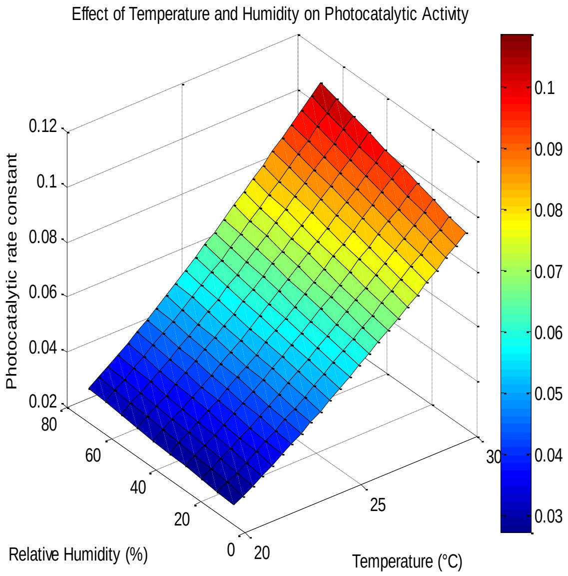


Figure 2. Effect of Temperature and Humidity on Photocatalytic paint

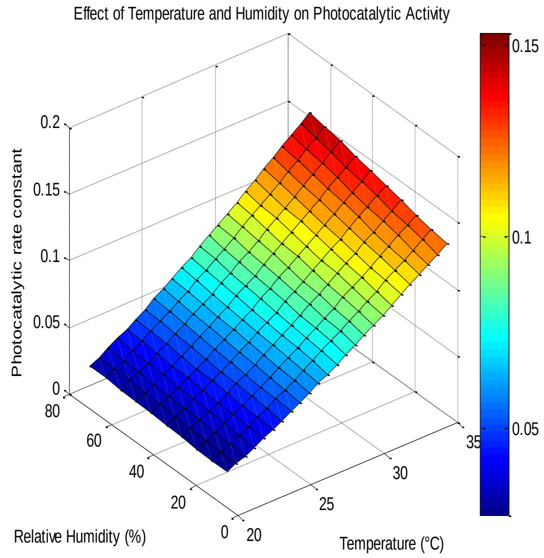
Maintaining a constant humidity level of 80%, we altered the temperature from 10℃ to 45℃ in increments of 10℃, as illustrated in figures 3a to 3d. The results demonstrate a steady increase in the reaction rate at 30℃/80%. However, at 35℃/80%, the reaction unexpectedly accelerates without the usual gradual increment, leading to significant degradation of the paint. Subsequently, as the temperature exceeds 35℃, the reaction rate returns to normal. However, at extreme conditions (60℃/80%), the constant rate reveals further degradation of the paint.

The temperature and humidity were adjusted to fluctuate within a 10℃/5% range, ranging from 10℃ to 60℃ for temperature and 10% to 80% for humidity, respectively. This variation was maintained for a duration of 15 hours to assess its impact on the adhesion and color stability of the photocatalytic paint as also suggested by (Laboratories & Lane, 1985)(Газеев et al., 2015). Figure 4 illustrates that both adhesion loss and color fading increased after the 13-hours mark. This suggests that with the passage of time and the rise in temperature and humidity, there is a corresponding increase in adhesion loss and color fading in the photocatalytic paint, leading to significant degradation of the coating.

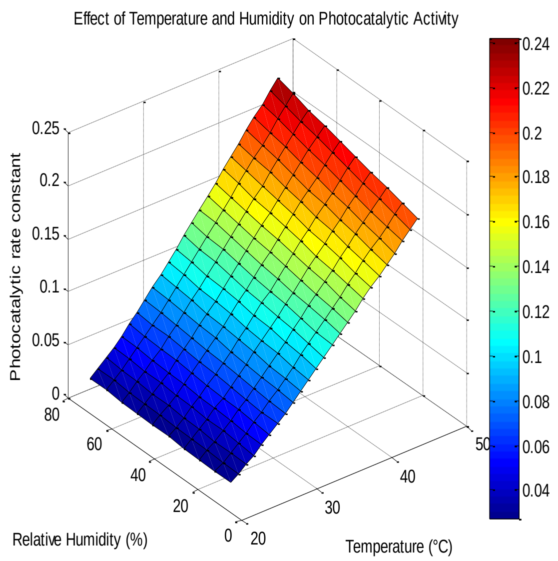
Having the ability to degrade the pollutant by photocatalytic paint, its durability to perform at outdoor conditions is recommended.



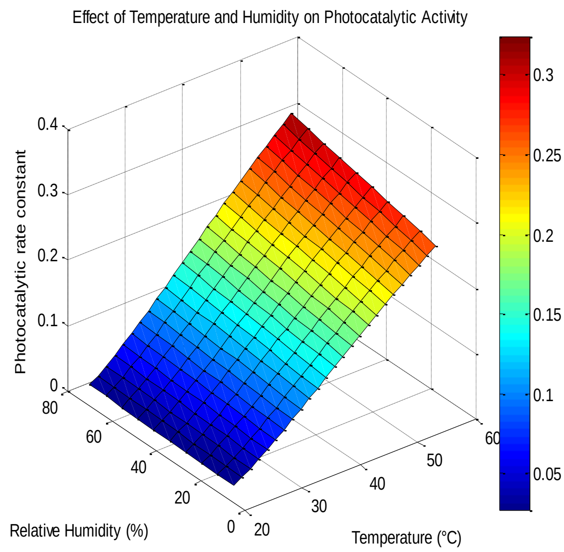
(a)



(b)



(c)



(d)

Figure 3. Effect of Temperature and Humidity on Photocatalytic paint

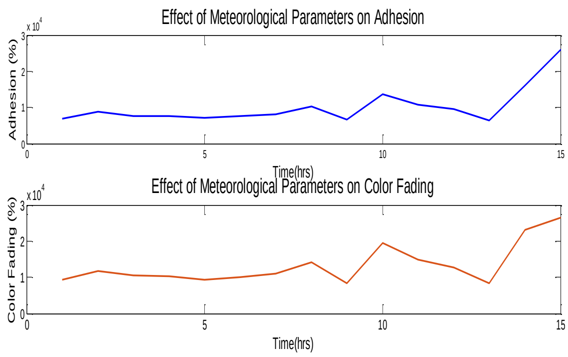


Figure 4. Effect of meteorological parameters on color fading and adhesion loss

Conclusion

In conclusion, the study underscores the potential of photocatalytic paints as an effective strategy for mitigating air pollution in urban settings. The interaction of these paints with meteorological parameters, particularly temperature and humidity, has been systematically investigated. Through controlled laboratory experiments, we observed a noteworthy influence of these environmental factors on the degradation of photocatalytic paint. Our findings reveal that moderate temperatures (ranging from 10℃ to 30℃) and humidity levels (10% to 50%) positively impact the constant rate of the reaction, leading to an enhancement in photocatalytic efficiency. This suggests the practical feasibility of utilizing such paints in regions characterized by these moderate environmental conditions. However, caution is advised, as our results indicate adverse effects on thermal stability and long-term durability when exposed to excessive temperatures (30℃ to 60℃) and high humidity levels (55% to 80%). These conditions contribute to adhesion loss and color fading over time, ultimately degrading the efficacy of the photocatalytic paint. In summary, while photocatalytic paints exhibit promises in addressing air pollution, the optimization of application conditions is crucial. Striking a balance between environmental parameters is essential to maximize the longevity and effectiveness of these coatings in real-world, dynamic urban environments. Our study provides valuable insights for the practical implementation of photocatalytic paints, emphasizing the importance of considering diverse meteorological conditions for sustainable and efficient air pollution control.

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Author Contributions
Conceptualization, Sunusi Dayyab Muhammad and Muhammad Mudassir Usman; methodology and software, Sunusi Dayyab Muhammad; validation, Sunusi Dayyab Muhammad and Muhammad Mudassir Usman; formal analysis, Sunusi Dayyab Muhammad; investigation, Sunusi Dayyab Muhammad, Muhammad Mudassir Usman and Abdullahi Muhammad; resources, Bayero University, Kano; data curation, Sunusi Dayyab Muhammad and Muhammad Mudassir Usman.; writing—original draft preparation, Sunusi Dayyab Muhammad.; writing—review and editing, Muhammad Mudassir Usman, Abdullahi Muhammad and Maimuna Aliyu Abubakar; visualization, Abdullahi Muhammad and Maimuna Aliyu Abubakar.

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Conflicts of Interest
The authors declare no conflict of interest.

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