

The Effect of TiO₂ as a Photocatalytic Paint in The Indoor Air Purification Process

TiO₂'nin Fotokatalitik Boya Olarak İç Hava Arıtma Sürecindeki Etkisi

Ravan ALLABABIDI ¹



¹Yıldız Teknik Üniversitesi, Kimya
Mühendisliği Bölümü, İstanbul, Türkiye



ABSTRACT

Photocatalysis has applications in various fields, such as in air purification devices and even in coatings, where it can be incorporated into paint formulations to take advantage of its air purification and self-cleaning properties. This report looks not only at the process of photocatalysis, but also at studies that have been carried out on its incorporation into coatings using titanium dioxide (TiO₂). TiO₂ is commercially available and can be synthesized in the laboratory to improve its performance in air purification and decontamination of various pollutants. In addition, studies into enhancing TiO₂ semiconductor materials with a photocatalytic system, such as the inclusion of manganese, were emphasized. These studies presented findings on boosted decontamination performance, which is critical for enhancing indoor air quality through the elimination of harmful gases and organic compounds. Volatile organic compounds, such as formaldehyde, toluene, benzene, and NO_x, have extremely toxic health effects. Every year, indoor and outdoor air pollution causes a significant number of deaths. Considering that people spend more than 80% of their time indoors, the filtration of indoor air is even more important. Therefore, this article presents some studies on the further development of photocatalytic materials and technologies for the commercial application of photocatalytic paints. Commercial photocatalytic paints containing TiO₂ doped with magnesium (Mn), silicate paints and water-based styrene acrylic paints were investigated, focusing on their ability to reduce VOC emissions.

Keywords: Photocatalysis, TiO₂, indoor air quality, VOCs, photocatalytic paints

Öz

Fotokatalizin hava temizleme cihazları ve hatta boya formüllerine dahil edilerek hava temizleme ve kendi kendini temizleme özelliklerinden yararlanılabilen kaplamalar gibi çeşitli alanlarda uygulamaları vardır. Bu rapor yalnızca fotokataliz sürecine değil, aynı zamanda titanyum dioksit (TiO₂) kullanılarak kaplamalara dahil edilmesi üzerine yürütülen çalışmalara da bakmaktadır. TiO₂ ticari olarak mevcuttur ve hava temizleme ve çeşitli kirleticilerin dekontaminasyonundaki performansını artırmak için laboratuvarında sentezlenebilir. Buna ek olarak, manganez dahil edilmesi gibi fotokatalitik bir sistemle TiO₂ yarı iletken malzemelerini geliştirme çalışmaları vurgulanmıştır. Bu çalışmalar, zararlı gazların ve organik bileşiklerin ortadan kaldırılması yoluyla iç mekan hava kalitesini iyileştirmek için kritik olan artırılmış dekontaminasyon performansına ilişkin bulgular sunmuştur. Formaldehit, toluen, benzen ve NO_x gibi uçucu organik bileşiklerin son derece toksik sağlık etkileri vardır. Her yıl, iç ve dış hava kirliliği önemli sayıda ölüme neden olmaktadır. İnsanların zamanlarının %80'inden fazlasını iç mekanlarda geçirdiği düşünüldüğünde, iç mekan havasının filtrelenmesi daha da önemlidir. Bu nedenle, bu makale fotokatalitik boyaların ticari uygulaması için fotokatalitik malzemelerin ve teknolojilerin daha da geliştirilmesine ilişkin bazı çalışmalar sunmaktadır. Magnezyum (Mn) ile katılanmış TiO₂ içeren ticari fotokatalitik boyalar, silikat boyalar ve su bazlı stiren akrilik boyalar, VOC emisyonlarını azaltma yeteneklerine odaklanılarak araştırılmıştır.

Anahtar Kelimeler: Fotokataliz, TiO₂, iç mekan hava kalitesi, VOC'ler, fotokatalitik boyalar

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Sorumlu Yazar/Corresponding author:

Ravan ALLABABIDI,

E-mail:

ravan.allababidi@std.yildiz.edu.tr

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INTRODUCTION

The World Health Organization (WHO) and the Global Burden of Disease Study conducted by the IHME Institute have conducted studies confirming that between 6.7 million and 7 million die annually. The cause of these deaths is due to both internal and external pollution.¹

Volatile organic compounds (VOCs)²⁻⁴ are typical inorganic and organic indoor air pollutants, and their sources are varied such as cooking, furniture, building materials, combustion, tobacco smoke and even traffic pollutants from the outdoor air.

As a result, the air purifier industry has witnessed significant growth in terms of demand and sales in the recent period. Therefore, a lot of research has been focused on the various means of air purification⁵, including those that use HEPA filters⁶, electrostatic smoke precipitators^{7,8}, activated carbon⁹, and UV rays¹⁰ have been mentioned in air purifiers produced by manufacturers.

Additionally, brought up has been the subject of indoor air filtration for ventilation and air conditioning systems from viruses and bacteria. There are several methods for purifying air, including photo-oxidation¹¹, absorption¹², adsorption¹³, bio-filtration¹⁴, membrane filtration¹⁵, and combustion.^{16,17}

Adsorption techniques are regarded as an economically viable method, attracting significant attention due to their ability to recover and reuse adsorbent materials and volatile organic compounds. Enhancing the adsorption capacity of volatile organic compounds is achieved by increasing the specific surface area, pore volume, surface chemical functionality, and reducing the pore size.¹⁸ Membrane filters are commonly employed for the absorption and separation of VOCs such as chloroform. While they offer significant benefits in terms of high efficiency and seamless integration with complementary technologies, the predominant drawbacks include increased costs, potential membrane contamination, inadequate membrane stability, and restricted flow capacity¹⁹. Biofiltration methods have proven effective in removing VOCs, especially at low to moderate concentrations. Moreover, this approach typically requires backwashing the bed due to excess biomass accumulation on the filter surfaces²⁰. The absorption technique, while advantageous for recovering valuable compounds, often entails high costs²¹. The photocatalytic oxidation process has been proposed as an advanced oxidation technique that enables highly efficient and cost-effective removal of volatile organic compounds.

This method is recognized as an effective environmental treatment due to its moderate operating conditions, non-toxicity and resistance to photochemical degradation.^{22,23} The present review also provides an initial overview of one of the applications of photocatalysis as paints for air purification, using commercial paints with photocatalysis activity and synthesizing the photocatalyst on a laboratory scale.

Photocatalytic Processes

Most types of photocatalysts used in an air purification system are complex steel oxides, binary metal oxides, metal sulphides and metal-free substances. Photocatalytic materials and technologies for air purification utilize specific semiconductor properties to absorb radiation that generates reactive oxygen species (ROS) and effectively degrade a wide range of air pollutants into harmless end products while producing mild acids and organic intermediates.²² The bandgap is the distance between a valence band and a conduction band, which together determine the energy strength of the bandgap. When light falls on a semiconductor, it absorbs sufficient photon energy, causing electrons in the valence band to rise into the conduction band and leaving holes in the valence band.²³

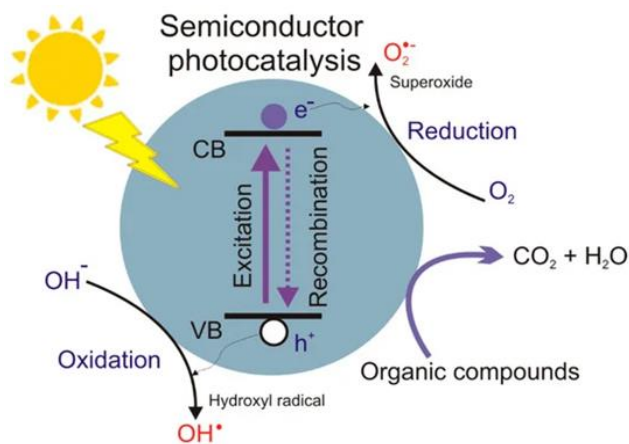
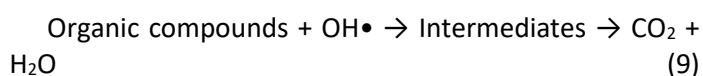
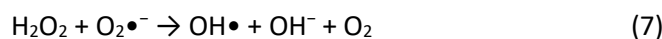
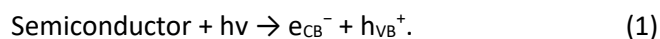


Figure 1. The Mechanism of Semiconductor Photocatalysis (used with permission)²⁴.

As shown in Fig.1 the presence of the active sites on the surface encourages the uptake of environmental species, then a redox reaction can take place in which the electron can interact with the electron acceptor and the holes with the electron donors. If these radicals are kept away from the surface and are mobile, they can form reactive oxygen

species that are susceptible due to their unsaturated state. The reactive oxygen species can move away from the photocatalytic surface. The reactive oxygen species, which are usually OH^\bullet and $\text{O}_2^{\bullet-}$, can break down organic and inorganic toxins into carbon dioxide, water and other inorganic substances such as nitrogen. The main reactions involved in the degradation of organic compounds in the presence of a metal oxide semiconductor can be summarized as follows.²⁵



All photocatalytic materials can be stimulated by ultraviolet (UV), visible (VIS) and a mixture of UV+VIS and solar radiation. Almost all commercial air purification systems use ultraviolet light sources with wavelengths between 351 and 400 nanometers. In addition, photocatalytic materials can be excited by sunlight and visible light.²⁴

There are two types of photocatalytic responses, homogeneous and heterogeneous photocatalysis. In homogeneous catalysis, the reactant and the catalyst are in the same stage, whereas in heterogeneous catalysis, both reaction participants are in particular stages.²⁵

Many studies have been conducted to prove that heterogeneous photocatalytic oxidation (PCO) is a successful technique for purifying water or air outdoors. So far, it has been confirmed to be effective in the photocatalytic oxidation of numerous materials or compounds such as ZnO ²⁶, CeO_2 ²⁷, ZrO_2 ²⁸, CdS ²⁹, WSe_2 ³⁰, Fe_2O_3 ³¹, SrTiO_3 ³², WO_3 ³³, the most commonly used heterogeneous photocatalyst is titanium dioxide, which is

used for photocatalysis (TiO_2)³⁴. Heterogeneous photocatalytic employment of semiconductor oxides illuminated with UV, near-UV or obvious light at comprehensive temperature and weight and in the presence of oxygen. The elemental instrument of Heterogeneous photocatalysis involves the era of electron-hole groups which, once isolated, decide the redox reactions of the species adsorbed on the dynamic surface. This strategy has been effectively used for wastewater treatment and is suitable for the complete degradation of organic and inorganic toxins, the degradation of volatile organic compounds in the air, etc.³⁵

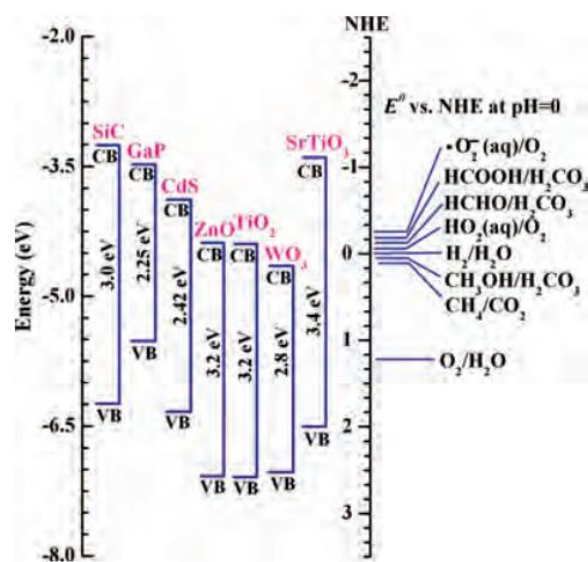


Figure 2. Band-side positions of a few normal semiconductor photocatalysts relative to the electricity stages of the redox couples worried inside the discount of CO_2 .³⁶

Based on Figure 2, depicts the relative positions of semiconductor bands and edges concerning the energy levels of various redox pairs. Titanium dioxide (TiO_2) is widely utilized as a photocatalyst because of its high chemical strength, low cost, good optical-electronic characteristics, and nontoxic nature. However, due to its slightly large band gap (3.2 eV), TiO_2 only utilized a small portion of the solar spectrum. The photocatalytic effect of TiO_2 in removing air pollution depends on various parameters. First and foremost, it is influenced by the interaction between the active surface and the chemical species, the efficiency of charge exchange recombination

and the nature of the reactive oxygen species, which are primarily formed by electron-hole groups. Since TiO_2 behaviour is greatly controlled by its surface characteristics, a variety of approaches have been used to investigate the surface properties that improve photocatalytic process performance.

However, there are obstacles due to the low harvesting capacity, the high energy band gap (almost 3.0 eV for rutile and 3.2 eV for anatase) and the high recombination rate of the electron-hole groups generated by light. To overcome these disadvantages and increase the performance of a photocatalytic system for TiO_2 , strongly oxidizing species (e.g. platinum (Pt)³⁷, zirconium (Zr)³⁸, nickel (Ni)³⁹, iron (Fe)⁴⁰, silver (Ag)^{41,42} etc. onto its surface. This leads to a contracted band hole of vitality for unmistakable light assimilation. The combination of TiO_2 with graphene oxide (GO) or reduced graphene oxide (rGO) can promote the exchange of light-generated electrons and in this way decrease the recombination of light-generated electron-hole groups ($e_{\text{CB}}^-/h_{\text{VB}}^+$) and increase the photocatalytic reaction range.¹⁵

Photocatalytic Paints as Air Purifiers

Nowadays, photocatalytic production eliminates indoor air pollution. Titanium dioxide catalysts are used in building products such as Bach wall paints.

According to current evaluations of photocatalytic paints as air purifiers, the investigation of photocatalytic paints and coatings demonstrates that they exhibit particularly high pollutant degradation and selectivity. This growing discrepancy is due to the commercial project of different photoreactor designs and sizes, operating conditions, experimental toxins, photocatalytic materials and coating formulations. In that regard, the evaluation is not always consistent, as the resulting materials sometimes vary depending on the main organic matter. One way to be reasonably independent of the operating conditions and experimental setups such as catalytic area, airflow, pollutant concentration and radiation flux is to calculate the amount of light and PE (separately) of the photocatalytic reactant framework.⁴³

Some of the photocatalytic internal paints with distinctive binder frameworks and one reference paint have been examined for their functionality to decontaminate indoors. Several of these photocatalytic paints are now commercially available.

Photocatalytic Performance of Various TiO_2 -Based Paints

In the study by (Joonas Auvinen et al)⁴⁴, different amounts of TiO_2 with and without added materials were used in the detailing of water-based paints and other paints. Water-based paints were preferred over other definitions as they release much less VOCs overall during drying and are thus particularly environmentally friendly. In this unused substance, photocatalytic paint coatings were tried for 2 everyday situations: (i) under Neath a seen mild supply to degrade an everyday indoor air pollutant (acetaldehyde) and (ii) under Neath UV radiation to degrade a not unusual outdoor air toxin (NO_x). The optical residences of the colors were measured, and the close-by floor photon retention rate (LSRPA) was calculated to attach them with the contaminant elimination ability and to assess the coating execution in phrases of photonic and quantum efficiencies. In expansion, the photocatalytic movement of the deliberate substances after a long period of reaction underneath UV radiation is evaluated. Testing was performed on six photocatalytic interior paints with special bonding structures and one reference paint for her cap potential to purify indoor air, the primary traits that had been used were included waterborne, poly becausei-siloxane), (Water-borne, silica sol-gel), (Waterborne, lime), (Waterborne, PVAc/ethene),(Waterborne, PVAc/ethene), (Waterborne, styrene acrylic, (Waterborne, PVAc/ethene), (Gypsum binder, water mixable) and (Polymeric binder, water mixable) from under research and commercial sources.

The paints that he conducted experiments on, which were 3 paints, were commercial. The commercial paints had a system of binders: siloxane, PVAc-ethene copolymer, styrene-acrylic copolymer, PVAc-ethene copolymer and silica gel, and lime was the self-product. The paint experiments were based on gypsum modified with polymer, gypsum, and glass. The tests were conducted in three different sections, firstly to get rid of formaldehyde, secondly to know the organic bond, and finally to purify indoor air from five volatile organic substances through photolysis for all experiments. Tests were conducted in environmental test chambers. The volume of chambers was 27 dm³ under the following conditions Temperature 21 °C Humidity 50% and discussion trade rate 0.5 h⁻¹. Chambers stacking was 2.28 m². Before each experiment, the experiment chambers and other surfaces were cleaned with water and ethanol. The visible values for ketones and aldehydes were 25 µg M⁻³ and for VOCs 10 µg M⁻³. The study showed that organic substances in paints and coatings, including binders and additives, can be degraded by photocatalysis. This self-

degrading effect might also additionally produce an excessive stage of herbal compounds, like aldehydes and ketones. These compounds are very solid indoor air pollution and may lower the pleasantness of the air. The cowl must be strong sufficient to face up to deeply energetic radicals. The antique photocatalytic surfaces had been as appropriate as the brand-new ones, regardless of the reality that the concentrations had been marginally better for some matured paints. One opportunity is that the paint's chemical composition has been modified because it has aged. Some materials have disappeared because of evaporation and photocatalysis, which causes a higher motion of the titanium dioxide (TiO_2). Hence, the TiO_2 could respond more effectively with airborne compounds and its dynamic surface vary has expanded. The varied substrates (glass, gypsum, or chemical compound mortar) didn't have a significant impact on the photocatalytic conduct of the paints. The materials used with light activity did a good degradation process for volatile organic materials and formaldehyde, and the reason is due to several factors, as mentioned in the research.⁴⁵

In the study Th Maggos et al. a test was carried out on the use of industrial paint containing titanium dioxide.⁴⁶ The observation was primarily based entirely on the impact of the extent of relative humidity to compare the feasibility of photocatalytic building materials (paint) for air purification, and it was additionally determined that the presence of nitric oxide (NO) promotes the photochemical degradation of the building materials (paint). Toluene was pointed out that the improvement of toluene conversion to the technology of OH. Roots during the photolysis of NO. The experiment was conducted with two types of titanium-containing paints, the first type being silicate mineral paints and the second type being styrene acrylic paints. The results of the purification of toluene using the UV light experiment were 8.46% and 32.5%, respectively. The photocatalytic rate was also calculated and the rate of toluene removal for both samples. One sample of the styrene acrylic paint yielded higher photocatalytic residences than the metal silicate paint. The rate at which the mineral silicate paint containing the pollutant decomposed was calculated to be $0.011 \mu\text{g}/\text{m}^2$, while the corresponding value for the styrene acrylic coating was $0.015 \mu\text{g}/\text{m}^2\text{s}$. It was found that humidity significantly affects the photolysis of toluene. Extending the humidity level from 20% to 50% limited the photooxidation of toluene at the bottom of the tests. In this case, the photocatalytic fee decreased from 0.1/2

$\mu\text{g}/\text{m}^2\text{s}$ to $0.003 \mu\text{g}/\text{m}^2\text{s}$ when the styrene-acrylic paint was tested, while the photocatalytic efficacy was abolished in the silicate mineral paint. On the other hand, the proximity of NOx promoted the photodegradation of toluene in each test. Simultaneous injection of NOx and toluene into the chamber prolonged the photocatalytic degradation of the plant toxin on silicate mineral paint from 8% to 14% paint and styrene acrylic paint and from 32% to 46.8% separately. The association of gracious radicals in the photocatalytic removal of NOx is the most important parameter for the effect of the further development of NOx.

Evaluation of Industrial Indoor Self-Cleansing Photocatalytic Paints

By the looking at another study,⁴⁷ the effect of 3 industrial indoor self-cleaning photocatalytic paints for interiors was evaluated in one-of-a-kind situations following their photocatalytic properties in numerous situations. In this study, the objects and emblems were not specified. The manufacturers state that these dynamic paints are intended for indoor applications and do not require UV radiation for their activation. The selected paints were fully characterized and their photocatalytic properties against NO_x were researched⁴⁸ (i.e., for extrude of indoor talk quality) and Methyl red (MR) and methylene blue (MB) expulsion (i.e., for self-cleansing action) in keeping with ISO guidelines 10678, and 22197-1, individually. ISO measures have been considered to ensure an unbiased evaluation of the execution of coatings so that a benchmark is established to assess what has been achieved. In addition, promotional tests were planned to test their impacts in dyeing methyl red and methylene blue stains beneath diverse lightens were able to degrade the more susceptible VOCs (1-hexanol and nonanal).

The Effectiveness of Doping- TiO_2 (Mn- TiO_2) as Industrial Paint

V. Tudose, et al. investigated the effect of pure and varying concentrations of manganese (Mn) doped titanium dioxide (TiO_2) under identical conditions of atmospheric pressure and room temperature, where the pollutants turn into gaseous acetaldehyde in the presence of mild O_2 and ultraviolet radiation.⁴⁹ Since manganese-doped titanium dioxide (TiO_2) is an effective material, it is added to paintballs with a photocatalytic property that performs the process of purifying indoor and outdoor air. The percentage of manganese added to titanium dioxide (TiO_2) was 0.1%, 1%, and 5% mole percent. After driving the gas photocatalysis the utilized catalyst

characterizations were also investigated using FTIR absorption spectroscopy. Herein, carbon dioxide (CO₂) was found to be the most photocatalytic element. It was found that 0.1% manganese and titanium dioxide (TiO₂) caused the most noteworthy photocatalytic misfortune of CH₃CHO under obvious illumination.

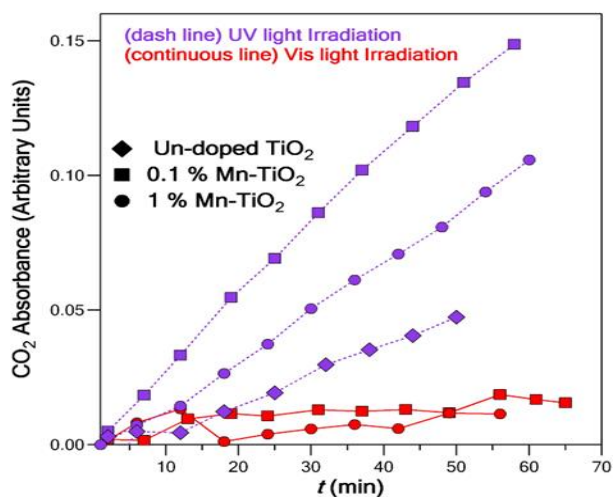


Figure 3. Comparing CO₂ formation Profiles in Photocatalytic Decomposition of CH₃CHO on Un-doped and Manganese-Doped Titanium Dioxide (TiO₂) under UV and Visible Light Irradiation (used with permission).⁴⁹

Referring to Fig 3. Typical CO₂ formation profiles in the course of photocatalytic decomposition of CH₃CHO on un-doped titanium dioxide (TiO₂) and doped with manganese samples below UV and seen mild irradiation. CO₂ yield became an awful lot better below UV mild than below seen mild irradiation, which suggests that the removing mechanism of CH₃CHO on manganese–titanium dioxide (TiO₂) is one of a kind than on TiO₂. This productivity was considerably lower with higher manganese doping (1–33%). CO₂ release was most remarkable in the 0.1% manganese –titanium dioxide (TiO₂) assays under UV illumination, consistent with the most remarkable CH₃CHO degradation rates observed. It was shown that low activity doping (0.1%) of titanium dioxide (TiO₂) with manganese leads to a remarkable increase in photocatalytic movement within the apparent progression compared to undoped TiO₂. This high effect is no longer present at high doping levels (1–33%). Finally, the instrument of photocatalytic decay of CH₃CHO on surfaces of 0.1% manganese titanium dioxide (Mn-TiO₂) under unmistakable illumination, which leads to low CO removal, differs from that under UV illumination, which leads to high CO removal.

Table 1. Comparative analysis of the referenced studies

No	Effective Material	Synthesis	Primary Objective	Experimental Parameters			Results	Reference
				Time of tests (hour)	Temp. (°C)	Light condition		
1	SCP-1, SCP-2 and SCP-3	commercial photocatalytic paints	VOCs(Nox) degradation and self-cleaning	10	25	visible light	(Nox) degradation SCP-1 (2.115 μmol), SCP-2 (1.303 μmol) and (SCP-3 0.205 μmol) self-cleaning SCP-1 (83%), SCP-2 (81%) and SCP-3 (34%)	47
2	M1 and M2	Two types of paint were examined: M1, which is a mineral silicate paint infused with 10% TiO ₂ , and M2, which is a water-based styrene acrylic paint also containing 10% TiO ₂ .	VOCs(Toluene) degradation	12	23	UV light	14% for M1 and 46.8% for M2	46
3	Mn-TiO ₂	The samples were fabricated using a modified sol-gel method. un-doping TiO ₂ , 0.1% Mn-TiO ₂ , 1% Mn-TiO ₂ , and 5% Mn-TiO ₂	VOCs(acetaldehyde) degradation	1	22.85	both UV and visible light	the best results for 0.1% Mn-TiO ₂ was 25%	49

CONCLUSION

It has been demonstrated that air purification of NO_x and VOCs in indoor air utilizing paints containing titanium dioxide (TiO₂) as a photocatalytic technique is successful. High humidity inhibits photocatalytic technology by preventing oxidation because water molecules and pollutant molecules compete for adsorption sites. Doping titanium with other metals could increase photocatalytic activity, such as manganese-doped TiO₂ coating, where air pollutants were degraded, and the increase in doping concentration increased the degradation efficiency.

The use of paints that provide photocatalytic ability is a promising application. Although it is a commercial product, more research is being done on this topic every day. The process of indoor air purification is currently one of the most important topics, as people spend up to 80% of their time indoors, especially after the last severe pandemic the world has experienced.

Hakem Değerlendirmesi: Dış bağımsız.

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