



A Comprehensive Review of Photochemical Degradation: An Advanced Oxidation Process for the Decomposition and Mineralization of BTEX Compounds in Gas Phase

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Abstract

Background: BTEX compounds are the most significant VOCs due to their carcinogenic potential and severe adverse effects on human health and the environment. Their removal from polluted air is therefore essential. The present study aimed to review and compare photocatalytic methods for removing BTEX compounds from air.

Methods: A comprehensive review was conducted by searching databases on Scopus, ScienceDirect, EBSCO, RSC, and PubMed from 2013 to 2024. A total of 245 articles were found, and 52 were finally reviewed, covering variables such as BTEX analysis methods, photocatalytic processes for their removal, their advantages and disadvantages, and the parameters affecting these processes.

Results: According to the findings, non-destructive methods are not suitable for air pollution control because they cannot eliminate pollutants and rely solely on transport to remove them. Destructive methods such as thermal oxidation offer higher degradation efficiency (up to 95%), but are associated with high energy consumption and formation of by-products. Photocatalytic degradation has emerged as a promising, environmentally friendly, and energy-efficient approach for VOC removal. The use of semiconductor nanoparticles such as TiO₂, ZnO, and V₂O₅, along with modifications to the visible light absorption range, reduction in energy demand and regeneration, enhancement of photocatalyst stability, and increased degradation efficiency (up to 99%).

Conclusion: Finally, the energy consumption and environmental compatibility evaluation confirmed that the doped photocatalysts not only offer superior performance but also comply well with the principles of green chemistry and sustainable environmental practices management.

Keywords: BTEXs, Nanocomposite, Catalyst, Photochemical, Degradation

Citation: Daraei H, Shirvani F, Hajghani L, Faghihi Zarandi A. A comprehensive review of photochemical degradation: an advanced oxidation process for the decomposition and mineralization of BTEX compounds in gas phase. Environmental Health Engineering and Management Journal 2026;13:1657. doi:10.34172/EHEM.1657

Article History:

Received: 25 June 2025

Revised: 4 November 2025

Accepted: 17 November 2025

Published: 5 April 2026

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Introduction

Although industrialization and the development of human societies are detrimental to a nation's economic growth, they have devastating effects on the health of living organisms and the environment due to the production of various hazardous pollutants (1). Air pollution remains a significant environmental issue that has gained widespread attention in recent years. Increasing levels of air pollutants, especially in urban and industrial areas, pose a substantial threat to human health and ecosystems (2,3). Air pollution can lead to respiratory problems, heart disease, reduced quality of life, and even premature death. In addition to its immediate health effects, it also

causes long-term changes in the global climate and has a detrimental impact on the environment (4-6).

Volatile organic compounds (VOCs)

VOCs are a group of major air pollutants that pose serious threats to human health and the environment. Due to their high volatility, these compounds are among the most critical environmental pollutants and are commonly found in densely populated urban and industrial areas (6). Household activities such as cleaning, smoking, cooking, painting, upholstery, and the use of building materials, furniture, carpets, furniture foam, glue, and cosmetics are important sources of these pollutants in



indoor environments. In addition, vehicle and industrial emissions from outdoor air can also lead to increased levels of these pollutants in indoor spaces (7,8). In outdoor air, VOCs are mainly released from fossil fuel combustion, vehicle emissions, petroleum product evaporation, and certain industrial and domestic source processes. Also, the extraction, exploitation, and refining of petroleum compounds are a serious problem in terms of increasing these pollutants into the environment (9).

BTEXs

BTEXs are a group of four volatile organic compounds, including benzene, toluene, ethylbenzene, and xylene, which are classified as light aromatic hydrocarbons due to their aromatic structure and are mainly emitted through industrial activities, fossil fuel combustion, and chemical processes (8). Due to their physical properties, such as high vapor pressure, these compounds readily enter the gas phase and contribute to air, water, and soil pollution. Long-term exposure to BTEXs can have severe health effects such as neurological disorders, liver and kidney damage, and the risk of developing various types of cancer. Therefore, these compounds have been identified by international organizations such as the EPA as priority pollutants for environmental control and monitoring. In general, BTEXs are among the most critical VOCs due to their simple aromatic structure, high volatility, and human and environmental toxicity. Additionally, due to their widespread distribution in the air and their role in the formation of secondary pollutants, they are considered one of the most important gaseous pollutants in both indoor and outdoor air (10).

BTEXs Classification

These compounds are studied based on their physicochemical properties, toxicity, and sources of release.

Chemical structure

BTEX compounds are a subgroup of monocyclic aromatic hydrocarbons (MAHs). The main characteristic of this group is the presence of a benzene ring with conjugated bonds. In this compound, benzene, as the simplest member of this group, is the purest aromatic form and has a hexagonal aromatic ring without side branches. While toluene has one methyl group (CH_3 -), ethylbenzene has one ethyl group (C_2H_5 -), and xylene, which has ortho, meta, and para isomers, contains two methyl groups at different positions on its aromatic ring. These compounds have higher molecular weights and tend to accumulate in aquatic or soil environments (11,12).

Environmental and toxicological characteristics

BTEXs have detrimental effects on human health and ecosystems due to their high toxicity, even at low

concentrations. Long-term exposure to these compounds can irritate the mucous membranes, cause headaches, nausea, lack of concentration, poor work efficiency, neurological disorders, respiratory problems, liver and kidney damage, and carcinogenicity and mutagenicity (8). Also, after absorption, these compounds are efficiently distributed throughout the body and excreted unchanged through urine (13).

In addition, BTEX, as a precursor of secondary organic aerosols (SOAs), plays a role in the formation of photochemical smog, increased ground-level ozone concentrations, the greenhouse effect, and climate change (14). The benzene ring is also classified as a Group 1 carcinogen. Toluene, ethylbenzene, and xylene are also of concern due to chronic non-cancerous effects, such as neurological, liver, and kidney damage (12). In addition to being dispersed in air and water, these compounds penetrate the soil through various pollutant sources, leading to the gradual loss of soil function. BTEXs also have limited solubility in water, although benzene is slightly more soluble than the other members (1.8 g/L in water at 25°C). Since the density of BTEX compounds is less than that of water (for example, the density of benzene is about 0.876 g/cm³), these pollutants typically float on the water's surface if leaked into aquatic environments. On the other hand, the stable aromatic structure of the benzene ring causes BTEX compounds to exhibit relatively high resistance to chemical and biological degradation, which contributes to their stability in the environment (15).

Sources of BTEXs Emissions

BTEXs are produced mainly from human and natural sources and can be dispersed in the gas, liquid, or soil phases. Natural sources of BTEX include natural forest fires, plant and soil releases, evaporation from water surfaces, and fermentation of organic matter in soil (16). Man-made sources of BTEXs also include chemical, petrochemical, and oil-refining processes, fossil-fuel combustion, oil spills from pipelines, ships, or oil facilities, and the manufacture of plastics, paints, and solvents (17). In particular, the relative solubility of these compounds in water allows BTEXs to dissolve in water readily and be transported to groundwater aquifers (18). Depending on the physicochemical properties of the soil (such as porosity, moisture, and organic matter), these compounds are adsorbed onto or infiltrate into the groundwater (16,17). In addition, due to their high vapor pressure, BTEXs can be converted into gases and transported from soil to the atmosphere. These pollutants react with hydroxyl radicals to produce secondary compounds such as ozone and organic aerosols (19,20). These reactions not only cause air pollution but also harm public health and ecosystems. Since BTEXs are compounds resistant to biological and chemical degradation, their long-term presence in aquatic, soil, and atmospheric environments

can cause severe environmental and health impacts (15).

Ecological and Health Effects of BTEX Compounds

BTEX exposure can have dangerous effects on human health. Benzene, the main component of BTEX, is known to be a carcinogen, and exposure to benzene can lead to blood disorders, damage to the brain and immune system, and an increased risk of blood cancers such as leukemia. Toluene and xylene can affect the nervous system and cause headaches, dizziness, drowsiness, and even mental disorders. Ethylbenzene also causes lung problems and asthma in people who are exposed to it. When BTEX levels in air or water are very high, it can lead to serious health problems such as shortness of breath, digestive disorders, and cardiovascular damage (21-25). In aquatic environments, BTEX compounds exert acute and chronic toxicity on different trophic levels. Fish and marine invertebrates are susceptible to benzene and toluene, which can impair respiratory and nervous system functions by disrupting membrane integrity and enzyme activities. Prolonged exposure reduces growth rates, reproduction, and survival of aquatic organisms. Benzene is known to cause hematological disorders in fish, whereas toluene and xylene affect gill and liver tissues, leading to oxidative stress and histopathological damage. In the soil environment, BTEX contamination interferes with microbial activity and nutrient cycling. High concentrations inhibit the growth of nitrifying and denitrifying bacteria, decreasing soil fertility and nitrogen availability. Some microbial species can degrade BTEX, but this process often results in the accumulation of toxic metabolites such as catechol and benzyl alcohol. These intermediates can further interfere with soil enzyme activity and microbial processes diversity. Plants growing in contaminated soil exhibit reduced germination rates, chlorosis, and impaired photosynthetic efficiency due to root uptake and oxidative damage induced by BTEX compounds. Airborne BTEX compounds also contribute indirectly to ecological degradation. As volatile organic compounds (VOCs), they participate in photochemical reactions with nitrogen oxides under sunlight, producing ground-level ozone and secondary organic aerosols. These atmospheric pollutants cause oxidative damage to plant tissues, reduce crop yields, and contribute to forest decline. Ozone and aerosol formation also influence global carbon cycling and climate regulation, connecting BTEX emissions to wider environmental impacts effects. The ecological risks are particularly high near petrochemical industries, refineries, and urban runoff zones, where continuous emissions sustain exposure levels that exceed the capacity of natural attenuation (10,26-29).

BTEX Removal from Gas Streams

Removing BTEX from the atmosphere remains a major challenge because of their volatility, toxicity, and

persistence. Conventional air-phase abatement methods include adsorption onto activated carbon or other porous materials, biofiltration/bio-trickling filters, thermal or catalytic oxidation, and advanced oxidation processes (AOPs) such as ozone or electron-beam treatment. For example, biofiltration of mixed BTEX streams achieved >99 % removal in lab-scale systems with mature microbial communities (30). Adsorption columns coated with activated carbon have also demonstrated high removal efficiencies for BTEX vapor streams, especially under moderate flow rates and residence times. (31). Yet each of these methods has limitations: adsorption merely transfers pollutants to another phase (requiring regeneration or disposal of spent media); biofilters can struggle with hydrophobic, low-concentration VOCs and require large residence times and microbial acclimation; thermal/catalytic oxidation requires elevated temperatures and may generate NO_x or other by-products; AOPs such as electron-beam or ClO₂ treatment offer high removal but often entail high energy consumption or complex apparatus (32). In contrast, heterogeneous photocatalytic oxidation (PCO)—typically employing a semiconductor such as TiO₂ irradiated by UV light to generate electron-hole pairs that produce highly reactive species ($\cdot\text{OH}$, $\cdot\text{O}_2^-$) for VOC degradation—emerges as an up-and-coming option for air-phase BTEX removal. In a recent indoor-environment simulation study, a TiO₂/volcanic-glass photocatalyst under UV-A (15 mW/cm²) and air flow of 55 m³/h was able to reduce low-ppmv BTEX levels to below detection limits; the sequence of degradation was o-xylene > ethylbenzene > toluene > benzene, although benzene's slower kinetics and regulatory priority were noted (33). The key advantages of photocatalysis in the air-phase context include:

- Potential for complete mineralization: Unlike adsorption, where the pollutant is captured, photocatalysis can convert BTEX to CO₂ and H₂O (and possibly CO, etc) under mild conditions.
- Low generation of secondary waste: The catalyst bed remains in situ, and pollutants are degraded rather than stored; thus, slight spent-media handling is required.
- Ambient-condition operation: Many PCO systems operate at ambient temperature and pressure, making them ideal for indoor air purification or duct-flow treatment.
- Continuous (rather than batch) application: Fixed-bed catalysts with light illumination can treat flowing air streams in real time.
- Non-selective oxidation capability: Photocatalysis can degrade a wide range of VOCs, including mixtures like BTEX, even at low concentrations.

Nevertheless, several challenges remain and should be highlighted in a review context. In gas-phase photocatalysis, the catalyst surface area, reactor residence

time, and light penetration are limiting factors – for instance, TiO₂ immobilised on activated carbon showed improved performance under humid conditions because the carbon enhanced adsorption and thereby boosted contact with the photocatalytic surface. Humidity and flow rate also strongly influence removal efficiency. Furthermore, the slower degradation kinetics of more stable compounds in the BTEX suite (e.g., benzene) mean that the design must consider residence time, catalyst loading, and exposure intensity to meet regulatory thresholds. Energy consumption of UV illumination and catalyst maintenance/regeneration are further practical considerations. In sum, while adsorption, biofiltration, and thermal/catalytic AOPs remain viable for air-phase BTEX mitigation, photocatalytic oxidation stands out as a sustainable, efficient, and versatile method — especially for indoor air, duct systems, and low-concentration streams. Future review discussions should therefore focus on: catalyst design for enhanced visible-light activation and surface area, reactor engineering for high air-throughput with short residence time, integrated systems (e.g., PCO + biofilter), and life-cycle/energy assessments to benchmark practical deployment (32-37).

This review provides a systematic, head-to-head comparison of various photochemical AOPs (e.g., UV/H₂O₂, UV/O₃, UV/Cl₂, photo-Fenton, photocatalysis like TiO₂/g-C₃N₄) specifically for BTEX. It also highlights their relative strengths and weaknesses in degradation kinetics for each BTEX compound, efficiency and cost of mineralization, susceptibility to matrix interference in contaminated air, and formation of hazardous by-products. It critically evaluates the gap between promising lab-scale results and the practical, large-scale implementation of these technologies, covering reactor design, energy consumption, and operating costs.

Materials and Methods

To conduct the above review, using the search method «P.R.I.S.M.A.», the keywords photocatalysis, photocatalytic removal of BTEX, BTEX compounds, gas phases, GC-MS analysis, analysis methods, catalyst, photolysis, BTEX photodegradation, photocatalytic removal of benzene, toluene, xylene, ethyl xylene photocatalysis were searched simultaneously in the abstract and title sections of the articles in the following databases: Google scholar, PubMed, Taylor and Francis, Wiley, American chemicals for sciences, Springer, Scopus, Web of Science (ScienceDirect), Royal society of chemistry. Considering the research objective, 245 articles were obtained between 2013 and 2024. After reviewing the title, abstract, and content of the articles, focusing on key parameters such as BTEX analysis and removal methods from the gas phase, AOP processes, photocatalytic removal of BTEX, types of photocatalysts, photocatalytic degradation mechanisms, effective factors

(light intensity, concentration, dose, temperature), and removal efficiency, 52 articles were finally selected for data extraction. The obtained data were then combined into several parameters based on the study objectives. By integrating the results of the articles, the performance of different photocatalysts was compared, research gaps were identified, and future directions were proposed. The results are presented in figures and tables, and the researchers provide relevant theories to support and strengthen the results and discussions. This approach helps to compile a comprehensive and practical review of the field of photocatalytic removal of volatile organic compounds.

Results

Chemical and physical properties

BTEX compounds have specific physicochemical properties that distinguish them from other volatile organic compounds due to their simple aromatic structure and small side groups (Table S1). All compounds in this group have relatively high vapor pressures, which causes them to rapidly transition from the liquid phase to the gas phase and become dominant in atmospheric environments (38).

Safety, health, and environmental regulations/legislation

BTEXs are subject to various regulatory and safety regulations in different countries due to their environmental and health risks. According to the USEPA guidelines, there are specific limits for BTEX concentrations in workplaces and the general public. The permissible concentration of benzene in the workplace should not exceed 1.0 ppm (39). In addition, according to industrial safety regulations, workers must wear personal protective equipment (PPE) such as special masks to prevent inhalation of BTEX (40). According to the WHO, the average annual concentration of benzene in outdoor air should not exceed 0.02 mg/m³ (29). In many EU countries, BTEX legislation also includes limits on the levels of these compounds in air and water. For example, in France, BTEXs must be controlled according to European regulations, and immediate action must be taken to reduce them if concentrations rise to dangerous levels (41). In the workplace, safety regulations include employee training, regular monitoring and measurement of BTEX concentrations, and the use of appropriate ventilation systems to reduce the risks of inhalation of these compounds (42).

Table S2 presents some data from the US Agency for Toxic Substances and Disease Registry (2000 and 2007), the International Program on Chemical Safety (1993 to 1997), the US Toxicology Program (2005), the World Health Organization (2008), and the Australian Drinking Water Regulations (2004).

BTEX Analysis Methods

To evaluate the efficiency of pollutant removal methods and determine the exact concentration of BTEX in air, it is essential to use accurate analytical techniques. One of the most common methods for analyzing BTEX compounds is gas chromatography-mass spectrometry (GC-MS), which serves as a reliable tool for identifying BTEX in various environments due to its high sensitivity, accurate resolution, and ability to detect very low levels of pollutants. (43,44). A summary of BTEX analysis methods is presented in Table 1.

GC-MS allows for the identification and quantitative analysis of these compounds in polluted air samples and provides accurate data for evaluating the effectiveness of removal methods (13,45).

Field Screening Methods (On-Site)

These are used for rapid, real-time assessment to determine if further action or lab analysis is needed (46).

Photoionization Detectors (PIDs)

The most common field tool. A UV lamp ionizes BTEX compounds, and the resulting current is measured. PIDs are highly sensitive, especially to benzene, and provide instant readings for airborne concentrations (47).

Flame Ionization Detectors (FIDs)

Similar to PIDs but use a hydrogen flame. They are robust and effective for measuring total volatile organic compounds (VOCs) but are less selective for BTEX specifically (46).

Colorimetric Tubes / Sorbent Tubes

Air is drawn through a glass tube containing a chemical reagent that changes color upon contact with a specific BTEX compound. The length of the color change indicates the concentration.

Gas Chromatography - Mass Spectrometry (GC-MS)

This is the definitive and most widely used method for BTEX analysis.

GC Component: Separates the individual BTEX compounds from each other and other VOCs.

MS Component: Acts as a detector that identifies each compound based on its unique mass-to-charge ratio, providing a “fingerprint” for confirmation. This is essential for regulatory compliance.

Gas Chromatography with Flame Ionization Detection (GC-FID)

Excellent for quantification as the FID's response is proportional to the mass of carbon. It is highly sensitive but cannot definitively identify compounds like an MS can. It is often used when the sample matrix is well-understood (43-45,48,49).

Compact Vacuum Outlet Gas Chromatograph

This system is designed to measure volatile organic compounds (VOCs) and their intermediate (IVOCs) up to 14 carbon atoms in a fully automated (no computer required), low-cost, and compact GC-based system for the quantitative analysis of complex mixtures without the need for high-purity compressed gases or expensive detectors. It is capable of measuring organic compounds at very low concentrations (at the picogram level) and separating challenging isomers with similar volatility, and can operate at higher optimal linear speeds than traditional GCs (48).

A compression gas chromatograph

This portable and small device can perform fast and accurate measurements on site. Given the very low detection limit achieved by this prototype, its use can be extended to other application areas such as the food industry, early cancer detection, or explosives detection by

Table 1. Summary Table of BTEX Analysis Methods (44-49)

Method	Principle	Key Advantages	Key Disadvantages
GC-MS(Lab-Based)	Separation by GC, identification by mass fingerprint.	Gold standard; unambiguous identification; high sensitivity and specificity; legally defensible.	Expensive, bulky, requires skilled operators, slow analysis time, not for field use.
GC-FID (Lab-Based)	Separation by GC, detection by carbon mass.	Robust, highly sensitive for quantification, wide linear range, and less expensive than MS.	Cannot definitively identify co-eluting compounds; requires confirmation with MS.
Purge & Trap / Headspace	Sample prep for GC: concentrates VOCs from water/soil.	High sensitivity (ppt-ppb levels); automated; handles complex matrices.	Adds complexity and time; extra instrumentation.
Photoionization Detector (PID)	UV light ionizes gases, measures current.	Real-time results; excellent sensitivity (esp. to benzene); portable; no flame.	Not compound-specific (measures TVOC); can be quenched by humidity; cannot separate BTEX.
Compact Gas Chromatograph with PID (GC-PID)	Miniaturized GC column with a PID detector.	Portable & on-site separation; identifies & quantifies individual BTEX compounds in the field; faster than lab GC.	Lower resolution than lab GC; limited to volatile compounds detectable by PID; requires field calibration.
Compact Vacuum Outlet GC (Lab/Field)	GC operated under vacuum at the outlet.	Very fast analysis (seconds to minutes); reduced power consumption; can be miniaturized.	Specialized design; potentially lower separation efficiency for complex mixtures; limited track record for BTEX.
Compression Gas Chromatograph	Uses pressure pulses (instead of continuous flow) for separation.		

measuring other VOC families or by changing the nature of the adsorbent. Several considerations can be made to improve this type of analysis. For example, reducing the mass yields faster heating, which transfers heat to the adsorbent more quickly and, consequently, accelerates desorption, ultimately yielding thinner chromatographic peaks. A shorter separation column based on microelectromechanical systems (MEMS) technology also has the potential to reduce the total analysis time. Furthermore, miniaturization of both components leads to a reduction in the energy consumption of the prototype, an increase in its autonomy, and an improvement in its portability(49).

Compact Gas Chromatograph with Optical Ionization Detector (GC-PID)

The GC-PID is a relatively inexpensive, field-deployable air toxics screening instrument that provides fast, accurate measurements and can be a good alternative to conventional benchtop GCs. The instrument uses ambient air as the carrier gas. It consists of a Tenax-GR-based preconcentrator, a gas sample valve, two capillary columns, and an optical ionization detector with a small footprint and low power requirements. The BTEX-GC instrument demonstrates the capability to detect BTEX at levels up to 500 ppb. With an analysis time of less than 15 min, the compact GC-PID is suitable for field deployment in polluted outdoor environments for real-time BTEX measurements. The compact design of GC-PID enables BTEX screening with higher spatial resolution, as well as the creation of dense networks of VOC measurements. Field-deployable GCs have the potential to aid in air quality emergency responses and provide near-real-time measurements of air pollution. On the other hand, these devices have limitations, such as reduced accuracy in polar acetone measurement at high humidity, and during use, it is necessary to pay attention to environmental conditions (50,51).

Conventional Methods for BTEX Removal

Given the health and environmental hazards posed by BTEXs, it is essential to accurately and sensitively detect these pollutants and to identify efficient, economical, and practical methods for their removal (44). Various techniques, such as surface adsorption, combustion, catalytic oxidation, ion exchange, membrane separation, photocatalytic technology, and advanced oxidation processes, have been investigated for the control and removal of BTEXs. However, all classes of adsorbents have problems, including high cost, safe transportation of adsorbent containing the pollutant, regeneration, and safe disposal. Among these methods, photocatalytic technology has been proposed as a promising solution due to its high efficiency, ability to effectively degrade pollutants at ambient temperature, photostability,

low cost, safety, flexibility of reaction conditions, and environmental compatibility (52-56). However, to increase the efficiency of this technology, it is necessary to improve the photocatalysts structurally. Improving photocatalyst performance can help, especially by increasing the rate of BTEX degradation under visible-light conditions and at ambient temperatures. Modifications such as loading active metals, doping with non-metallic elements, and using semiconductor compounds can help increase photocatalytic activity, reduce the electron-hole recombination rate, improve process efficiency, and reduce costs (57).

BTEX Removal Methods

In general, BTEX removal techniques are divided into two destructive and non-destructive categories.

Non-destructive Processes

In these processes, the pollutants are not destroyed; during operation, the desired pollutant is separated, absorbed, or concentrated from the environment for disposal or recycling at another stage. These methods are mostly used for low BTEX concentrations or pretreatment. The most critical non-destructive processes include adsorption, absorption, condensation, and membrane separation (58).

Destructive Process

Processes in which volatile organic compounds (such as BTEX) are converted to simpler, harmless compounds such as CO₂ and H₂O through the breaking of chemical bonds and oxidation. In these processes, complete removal of contaminants occurs rather than a phase-to-phase transition. These methods include thermal oxidation, catalytic oxidation, advanced oxidation, plasma, and photocatalytic oxidation, each of which has a specific mechanism for degrading the molecular structure of the pollutant and has different advantages and disadvantages depending on the operating conditions (8). Thermal oxidation is divided into two main types: Complete Thermal Oxidation and Incomplete Thermal Oxidation (59).

Catalytic oxidation

Catalytic oxidation is a chemical process in which organic compounds, including BTEXs, are converted to inorganic compounds such as CO₂ and H₂O in the presence of a catalyst and oxygen. In this process, catalysts such as platinum (Pt) and palladium (Pd) are commonly used, which accelerate the oxidation reactions and help reduce the temperature required to carry out the reaction (1,52,54). The reaction mechanism in catalytic oxidation processes includes the following steps:

- Adsorption: The organic compound is adsorbed on the catalyst surface.

- Oxidation reaction: The adsorbed organic compound reacts with oxygen in the presence of the catalyst and is converted to carbon dioxide and water.
- Catalyst regeneration: After the reaction, the catalyst is naturally recovered and can be reused (60).

Advanced Oxidation Processes (AOPs)

AOPs are a set of chemical methods that convert persistent organic pollutants into harmless products such as CO_2 , H_2O , and inorganic ions by producing active radicals such as hydroxyl radicals ($\bullet\text{OH}$) (54,61). These methods are used to treat contaminated water, wastewater, air, and soil. In this process, highly reactive, non-selective radicals produced can destroy the BTEX (benzene, toluene, ethylbenzene, xylene) structure by breaking C–C, C–H, and C–O bonds, attacking aromatic rings, and accelerating the complete oxidation of the pollutant. The main advantages of this method include the destruction of linear pollutants as well as the breaking down of cyclic and complex pollutants into simpler compounds, the absence of the need for a separating or absorbing phase, and the production of less residue (Figure 1). Previous studies that investigated the degradation process of BTEX components in photocatalytic processes have reported that benzene and xylene had the highest and lowest degradation rates, respectively (Figure 2) (62,63).

Major types of Advanced Oxidation Processes

Advanced ozonation ($\text{O}_3/\text{H}_2\text{O}_2$ or O_3/UV)

In this method, a combination of ozone and UV light, or H_2O_2 , produces hydroxyl radicals ($\bullet\text{OH}$), thereby effectively destroying resistant VOCs. However, the high cost and the need for precise control of operating conditions are disadvantages of this method (6).

Fenton peroxidation

This method uses the reaction between H_2O_2 and iron ions (Fe^{2+}) to produce hydroxyl radicals. It is a simple and relatively inexpensive method, but it has limitations due to the management of the iron sludge produced, and limited performance at high pH. This method is highly efficient in acidic conditions (64).

UV- H_2O_2

In this method, UV light decomposes H_2O_2 into hydroxyl radicals. This method can be used to destroy VOCs in the gas or aqueous phase. Since this method can be performed without a metal catalyst, it somewhat reduces operating costs. However, dependence on a strong UV source can be one of its limitations (61).

Photocatalytic Oxidation (PCO)

Photocatalytic oxidation has been described as an

Advanced Oxidation Processes for BTEX Degradation

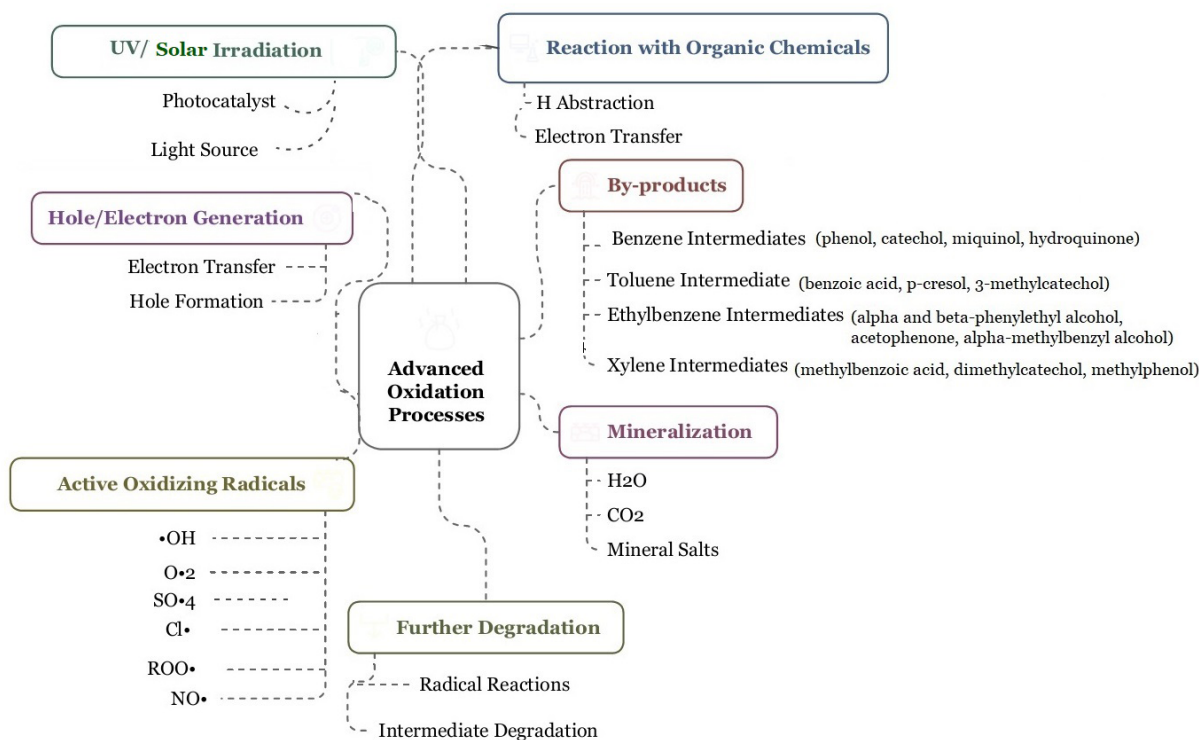


Figure 1. Advanced oxidation processes for BTEX degradation

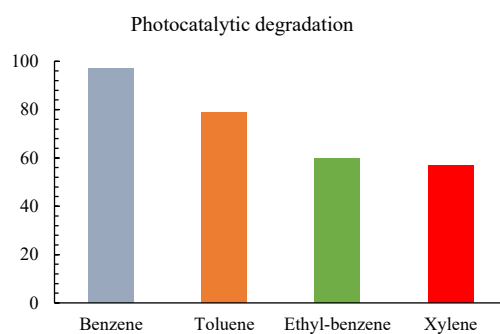


Figure 2. Degradation rate of BTEX compounds in AOPs

advanced, economical, sustainable, and safe technology for removing toxic volatile organic compounds (VOCs) from indoor air. This process can remove a wide range of organic pollutants and is based on the use of a semiconductor catalyst (usually TiO_2) and an activator (ultraviolet or visible light) to generate active oxidizing radicals. Factors such as the intensity and wavelength of the radiation, reaction conditions (temperature, pH, and the presence of other chemicals), and the properties of the photocatalyst affect the efficiency of this process. These factors affect the light absorption, charge separation, charge transfer, and surface reactions in the catalyst. Therefore, it is necessary to understand the types of photocatalysts and their characteristics to improve process efficiency. Various types of catalysts can be employed in photocatalytic processes such as AOPs based on TiO_2/UV ; Photocatalysis with Metal-doped TiO_2 ; Ag/TiO_2 filters; AOPs based on TiO_2 doped with non-metallic elements (S, C, N); Plasmonic Photocatalysis; $\text{TiO}_2/\text{graphene}$ oxide nanocomposite; TiO_2 loaded on ACF modified by $\text{Zn}(\text{CH}_3\text{COO})_2$; Zn-Ti-LDH photocatalyst; Micrometric TiO_2 Sample Powders; Mn- TiO_2 photocatalysts in fiber-optic honeycomb reactors; Acidic F- $\text{TiO}_2/\text{SiO}_2$ Catalyst; CuO- TiO_2 nanoparticles synthesized with blackening route Cobalt-Iodine-Doped TiO_2 ; Arrayed Dielectric Double Barrier Discharge (DDBD) Reactor with $\text{TiO}_2/\text{Al}_2\text{O}_3$ Catalyst; Use of Zn-Mn (S-AZMB) used alkaline batteries in TiO_2 compound; Cu_2O nanowire catalysts; $\text{TiO}_2/\text{UV}/\text{O}_3$ Photocatalyst (61,64,65). In nanoparticle-based photocatalytic processes, in addition to scavenging processes, adsorption also plays a key role in pollutant removal (Figure 3).

Generally, AOPs are the preferred technology for treating BTEX in aqueous matrices (groundwater, industrial wastewater) where the high reactivity of radicals is necessary to overcome the limitations of the water medium, despite the higher energy costs and complex byproduct profiles. On the other hand, catalytic Oxidation is the superior technology for treating high-volume gas streams (air emissions, soil vapor extraction off-gases) where its thermal efficiency and high mineralization capability lead to more economical and reliable operation, provided the catalyst is protected from poisons (1,63). A

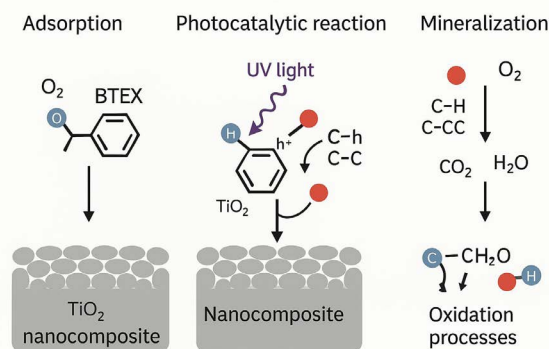


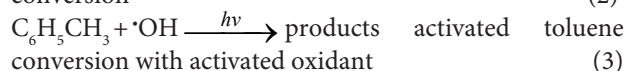
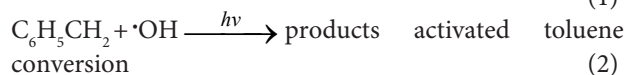
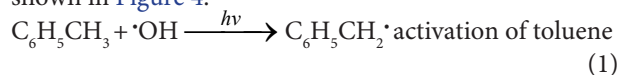
Figure 3. Mechanism of BTEX adsorption and degradation in photocatalytic processes

comparative analysis of advanced oxidation processes and catalytic oxidation for BTEX degradation is presented in Table 2.

TiO_2 photocatalytic reactor

Previous studies have shown that the TiO_2 photocatalytic coating agent can degrade toluene. The efficiency of this process can be increased as a primary function of changes in UV-A irradiation and reactor volume. However, since toluene is decomposed in this process, additional organic pollutants such as benzene and butadiene can be produced. TiO_2 photocatalysts decompose these pollutants, so the overall reduction performance may vary. However, TiO_2 photocatalysts can be used to investigate the effect of reducing indoor pollutants in indoor ventilation systems and building materials. In general, in a study conducted in this field, the appropriate titanium content for reducing toluene concentration in the coating was 29.51%, and increasing UVA light intensity and reactor volume led to higher toluene removal. The toluene concentration was decreased by 55.22% (0.23 ppm) to 32% (0.32 ppm) under varying UV-A radiation intensities and reactor volumes (UV-A: 15 and 20 W/m^2 , reactor volume: 20 and 15 cm^3). In addition to these advantages, the use of this method also faced limitations, such as the difficulty of providing sufficient UV-A light in indoor environments and the production of possible byproducts resulting from the photocatalytic reaction (66,67).

Mechanism of photocatalytic degradation of BTEX is shown in Figure 4.

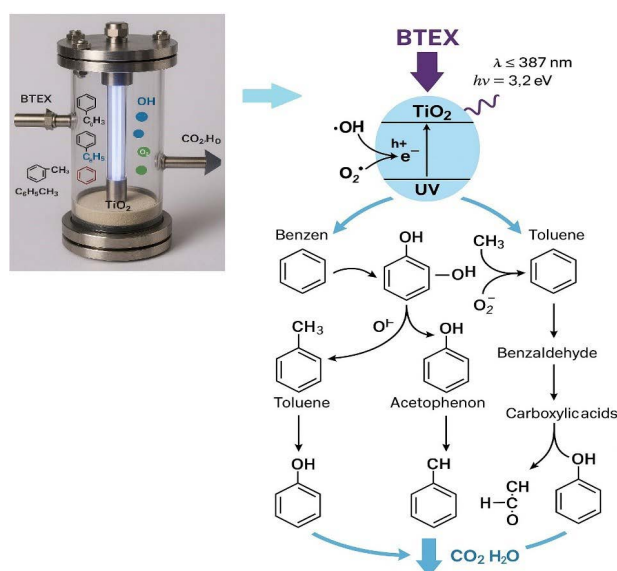


Metal-Based vs. Non-Metal-Based TiO_2 Photocatalysts

Metal-based and non-metal-based TiO_2 photocatalysts exhibit distinct advantages and limitations in photocatalytic applications. Metal-doped TiO_2 , such as

Table 2. Comparative analysis: advanced oxidation processes vs. catalytic oxidation for BTEX degradation (6,52,54,61-65)

Parameter	Advanced Oxidation Processes (AOPs)	Catalytic Oxidation	Remarks & Key Differentiators
Degradation Rate & Mechanism			
Kinetics	Very high initial degradation rates (pseudo-first-order). Rate constants (k) for $\cdot\text{OH}$ with BTEX are typically 10^9 – $10^{10} \text{ M}^{-1}\text{s}^{-1}$.	Slower surface-mediated kinetics (Langmuir-Hinshelwood model). The rate is highly dependent on temperature and catalyst activity.	AOPs are diffusion-controlled radical reactions. Catalytic Oxidation is limited by adsorption and surface reaction rates.
Oxidizing Agent	Non-selective hydroxyl radicals ($\cdot\text{OH}$), sulfate radicals ($\text{SO}_4^{\cdot-}$).	Molecular oxygen (O_2) activated on a catalytic surface (e.g., Pt, Pd, MnO_x).	$\cdot\text{OH}$ has a higher redox potential (2.8 V) than activated O_2 , leading to faster, less selective attack.
Energy Consumption			
Primary Energy Input	Electrical energy for UV lamps, ozone generators, or ultrasonication. Energy consumption is quantified by the Electrical Energy per Order (E_{EO}).	Thermal energy to heat the contaminated gas stream to the catalyst's ignition temperature (250–500 °C).	AOPs are often energy-intensive for mineralization. Catalytic Oxidation reduces energy vs. thermal incineration but still requires significant heating.
Relative Efficiency	Moderate to Low. Efficiency drops due to light scattering, radical scavengers, and mass transfer limitations. E_{EO} values can be high for complex matrices.	High. The catalyst lowers the activation energy, significantly reducing the required temperature (and thus energy) compared to non-catalytic thermal oxidation.	Catalytic oxidation is more thermodynamically efficient for concentrated gas streams.
Cost Analysis			
Capital Cost (CAPEX)	Moderate. Costs for reactors, UV lamps, ozone generators, and ancillary systems.	High. Costs for catalyst (precious metals), heat-resistant alloys, and heat exchangers for energy recovery.	Catalyst cost is a major CAPEX driver.
Operational Cost (OPEX)	High. Dominated by continuous electricity consumption for radical generation and chemical reagents (H_2O_2 , O_3).	Moderate. Dominated by fuel/energy for gas pre-heating. Lower once auto-thermal operation is achieved for high concentrations.	AOPs have high recurring OPEX. Catalytic Oxidation OPEX is highly concentration-dependent.
Byproduct Formation			
Primary Intermediates	Complex mixture of aromatic intermediates (phenols, benzaldehyde), followed by aliphatic acids (formic, acetic, oxalic).	Partial oxidation products like carbon monoxide (CO) and formaldehyde, especially at low temperatures or poor contact time.	AOPs produce a wider range of soluble, often refractory, oxidation byproducts.
Mineralization Efficiency	Can be incomplete, leading to accumulation of organic acids that act as radical scavengers. Requires optimized hydraulic retention time.	Typically high (>99%) when operated above the designed temperature with a healthy catalyst. Directly converts organics to CO_2 and H_2O .	Catalytic Oxidation generally offers a more direct and reliable path to complete mineralization for gas-phase treatment.
Other Risks	Formation of halogenated byproducts (e.g., bromate) in the presence of halides. Catalyst leaching (in photo-Fenton).	Catalyst deactivation via poisoning (S, Cl, Si), sintering, or coking (carbon deposition).	Byproduct management in AOPs is a chemical challenge, while in Catalytic Oxidation it is an operational/catalyst management challenge.

**Figure 4.** Mechanism of photocatalytic degradation of BTEX

Ag-TiO_2 or Fe-TiO_2 , enhances visible-light absorption and charge separation due to the introduction of

intermediate energy states. However, metal dopants may act as recombination centers, reducing efficiency, and can be prone to leaching or instability under harsh conditions. In contrast, non-metal doping (e.g., N- TiO_2 , C- TiO_2) improves visible-light activity without significant recombination losses, offering better chemical stability and environmental compatibility. Nevertheless, non-metal-modified TiO_2 often shows a lower redox potential than some metal-doped counterparts. The choice between these modifications depends on the specific application, considering factors like light spectrum, stability requirements, and cost-effectiveness (61,68-71). Comparisons of activation wavelengths and energies of metal-based photocatalysts, as well as the absorption spectra of TiO_2 and metal-doped variants (Fe, Ni, Co, Cu, Mn) with respect to wavelength, are presented in Figure 5.

Discussion

BTEX Non-destructive Methods

Adsorption

This is one of the most widely used non-destructive methods for separating pollutants from contaminated

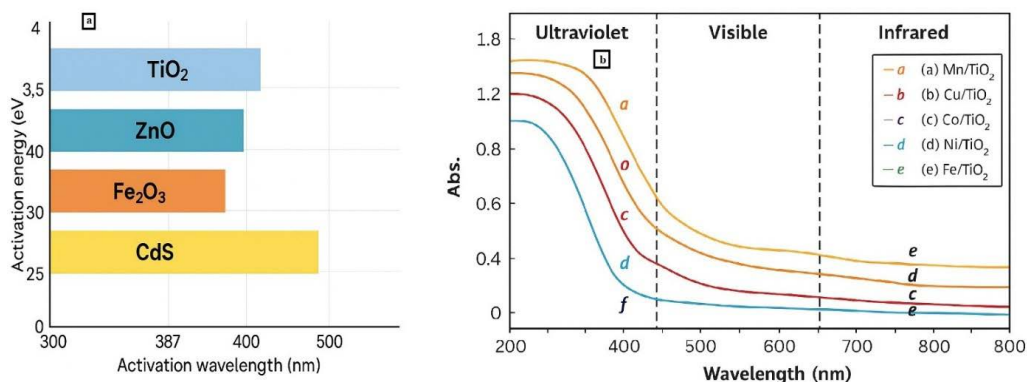


Figure 5. Comparison of activation wavelengths and energies of metal-based photocatalysts (a); Comparison of absorption spectra of different photocatalysts (TiO₂ and doped metals such as Fe, Ni, Co, Cu, Mn) in terms of wavelength (b)

environments. In this method, pollutants such as BTEX are adsorbed onto the surfaces of adsorbents such as activated carbon, zeolite, or resins. Depending on the adsorbent type and functional groups, a weak physical or chemical bond forms between the pollutant and the adsorbent. The advantages of this method include high efficiency for the separation of volatile organic compounds, simple design, low energy consumption, and the recyclability of some adsorbents. However, this method has disadvantages such as saturation of the adsorbent in a limited time, the need for regeneration and disposal of the adsorbent, and the possibility of re-release of the pollutant under certain conditions (7,55,56).

Absorption

In this method, gaseous pollutants are dissolved in a liquid (usually water or a chemical solution). This process is usually carried out in scrubber towers, and its advantages include its suitability for high-volume air flows and its ability to be integrated with chemical oxidation processes in the liquid phase. The disadvantages include periodic solvent replacement or purification, and low efficiency for poorly soluble compounds such as BTEX (72).

Condensation

This refers to the recovery of organic compounds from the air stream as a liquid and involves cooling the gas stream to a temperature at which BTEX is converted into the liquid phase. Its advantages include direct recovery of high-purity BTEXs and suitability for high concentrations and low-volume flows. However, the dependence on high cooling, high energy consumption, and low efficiency at very low concentrations are some of the disadvantages of this method.(21,58)

Membrane Separation

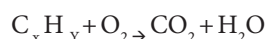
Refers to the selective passage of organic pollutants through a polymeric or organic-inorganic membrane and their separation from the air stream based on size or solubility. Selective separation, continuous system, and no need for chemicals are some of the advantages, while

high initial cost, clogging, and reduced membrane life are some of the disadvantages of this technology in removing pollutants (73).

BTEX Destructive Methods

Thermal oxidation

It is a chemical process used to remove organic pollutants, especially VOCs and BTEXs, from industrial and polluted environments. This process involves combustion reactions in which pollutants are decomposed at very high temperatures (700 - 1200 °C) in the presence of oxygen, converting them into simpler, non-harmful products such as CO₂ and H₂O. This process is widely used in the treatment of exhaust gases from chemical, petrochemical, and oil refinery industries (59). During thermal oxidation, the organic compounds in the exhaust gases are completely decomposed in the presence of oxygen. These reactions usually occur as follows:



In this reaction, the organic compound (C_xH_y) is converted into CO₂ and H₂O. One advantage of this method is that, with the appropriate temperature, almost all organic molecules are decomposed, leaving no contaminants.

Thermal oxidation is divided into two main types:

Complete Thermal Oxidation

In this process, all organic compounds in the gas are converted to carbon dioxide and water, leaving no pollutants. This process is generally very effective for organic pollutants with complex structures or toxic compounds (59).

Incomplete Thermal Oxidation

In this method, some organic compounds are not completely oxidized and may be converted to gases such as carbon monoxide (CO) and other semi-soluble pollutants. This type of oxidation usually occurs under suboptimal conditions or at temperatures below the

optimum (28). Thermal oxidation has advantages such as complete removal of pollutants, high efficiency of 99% in removing VOCs, the ability to remove various types of complex organic compounds, and the ability to operate on an industrial scale (6,28). However, this method can have disadvantages such as high energy consumption, high operating costs, the need for expensive equipment, greenhouse gas emissions, and the creation of secondary air pollution (6).

Catalytic oxidation

Catalytic oxidation is a chemical process in which organic compounds, including BTEXs, are converted to inorganic compounds such as CO₂ and H₂O in the presence of a catalyst and oxygen. Since this process is carried out at lower temperatures, it makes it a more efficient and economical method compared to thermal methods. In this process, catalysts such as platinum (Pt) and palladium (Pd) are commonly used to accelerate oxidation reactions and reduce the temperature required to carry out the reaction (1,52,54).

Catalytic oxidation process has advantages such as operation at low temperatures compared to thermal oxidation, reduced energy consumption, reduced operating costs, selectivity, high efficiency in the destruction of various pollutants (52,74).

However, these processes also have disadvantages, which are mentioned below.

Catalyst degradation

One of the significant problems with catalysts is the gradual decrease in their efficiency due to degradation.

During the process and after several test stages, catalysts may become blocked or lose their properties, which increases the need for their replacement (75).

Temperature limitations

While catalytic oxidation can be carried out at lower temperatures, some compounds require higher temperatures to be effectively oxidized, which can impose limitations on pollutant degradation.

Need for additional gases

In some cases, to ensure that catalytic reactions are carried out effectively, it may be necessary to provide additional gases such as pure oxygen, which may be costly (54,76).

Photocatalytic Oxidation (PCO)

Photocatalysts based on metal oxides (such as TiO₂, ZnO, Fe₂O₃) can efficiently degrade organic pollutants, such as BTEX compounds, when activated by UV/visible light. These processes have attracted widespread attention as a green and sustainable method for air and water purification. The mechanism of photocatalytic processes occurs in three main steps:

Catalyst activation and charge carrier generation

By irradiating photons with energy equal to or greater than the energy gap (E_g) of the photocatalyst, the valence-level electrons (VB) are excited to the conduction level (CB) and an electron-hole pair (e⁻/h⁺) is created.

Generation of active oxidizing species

- Positively charged holes (h⁺) that can react with water molecules adsorbed on the surface and produce hydroxyl radicals (•OH).
- Conduction level electrons also interact with molecular oxygen (O₂) to form superoxide ion (•O₂⁻) and other reactive species (e.g., H₂O₂).
- Degradation of pollutants: Active species (especially •OH) attack the C-H and C-C bonds in BTEX molecules, oxidizing them to less hazardous intermediates and ultimately to CO₂ and H₂O.

The advantages of this method include high efficiency of VOC destruction, operation at ambient temperature, environmental friendliness, no production of hazardous residues, and the ability to be used for continuous purification of air streams (65,77).

Challenges and solutions

- Low quantum efficiency due to fast e⁻/h⁺ recombination → Surface modification by metal/n-type doping or creation of structural heterogeneities.
- Limited visible light absorption in TiO₂ → Use of modified photocatalysts with photosensitization (e.g. CdS/TiO₂) (1,57,61,64,69,75,78).

Types of applicable catalysts in photocatalytic processes

Several studies have shown that different photocatalysts (TiO₂, ZnO, BiVO₄, etc.) are effective in removing toluene, benzene, and other BTEX compounds, sometimes achieving up to 90% removal under controlled conditions (44,71).

Advanced oxidation process in the presence of TiO₂ and UV

In this method, UVC/UVA radiation with sufficient energy (wavelength between 254 and 387 nm) excites TiO₂ and produces electron-hole pairs (e⁻/h⁺) on the catalyst surface. The electrons produced react with O₂ and produce active radicals O₂⁻•. On the other hand, the holes created on the catalyst surface can also react with water molecules or water vapor and produce highly oxidizing radicals •OH. These radicals can readily oxidize BTEX to CO₂ and H₂O.

Although this method has advantages such as high efficiency under UV irradiation, cheapness, and availability of TiO₂, the rapid recombination of e⁻/h⁺ reduces the efficiency of the process (60,64).

Photocatalysis with Metal-doped TiO₂

To increase the efficiency of the advanced oxidation process for single metals such as TiO₂, metals such as Fe, Cu, and Ag are added to the TiO₂ structure. These metals reduce the e⁻/h⁺ recombination, facilitate charge transfer, increase the sensitivity of TiO₂ to visible/ultraviolet light, improve the photocatalytic activity under ambient conditions, and consequently increase the efficiency of BTEX degradation. The higher cost of manufacturing this photocatalyst and the possibility of degrading the highly doped crystal structure can be considered disadvantages of this method (61,79).

Ag/TiO₂ filters

Dielectric barrier (or electric arc) discharge coupled with catalysis is a new method that has attracted much attention for the removal of volatile organic compounds from the air due to its characteristics such as moderate operating conditions, high oxidation efficiency, and low energy costs. The synthesis of Ag/TiO₂ nanoparticle filters is carried out by depositing silver nanoparticles onto a commercially stabilized TiO₂ sheet via impregnation. Previous studies showed that the performance of these filters in removing volatile organic compounds has two stages. In a study by Wu Zhou et al. (2019), it was reported that the performance of these filters in removing volatile organic compounds was two-stage. The first step was a partial absorption step in the dark, with approximately 15% toluene removal in less than 60 min, and the second step was a photooxidation step under UV irradiation, with a toluene removal efficiency of 97%. Another advantage of these filters is their high ability to remove microorganisms from the air (100% efficiency). These filters can be effectively implemented as an air-purification system in industrial, hospital, and domestic applications. Also, in this regard, Ag/TiO₂ filters were used to remove 26 mg/L toluene in laboratory conditions, which is 1000 times higher than the actual concentration in indoor air. According to the reported results, this filter showed high performance at the highest reported indoor toluene level. According to the reported results, this filter showed high performance at the highest reported indoor toluene level. These filters have a promising ability to remove very high concentrations of volatile organic compounds in industrial environments (80,81).

Photocatalysis with TiO₂ doped with non-metallic elements (S, C, N)

To make this type of photocatalyst, atoms such as N, C, or S are substituted for Ti or O in the TiO₂ crystal structure. This method changes the energy bandgap of TiO₂ and increases its sensitivity to visible light. This allows the photocatalyst to be activated by visible light (such as sunlight) and could make it suitable for outdoor applications without the need for artificial UV. However, this method has lower efficiency than metal doping and

requires more precise control of the synthesis conditions (68,70).

Plasmonic Photocatalysis

This method uses metal nanoparticles, such as Ag or Au, that exhibit surface plasmon resonance. These nanoparticles absorb visible light and transfer its energy to TiO₂, which ultimately leads to the production of active radicals. However, the high cost of metal nanoparticles and lower stability in some conditions are its disadvantages (82).

TiO₂/graphene oxide nanocomposite

Since graphene exhibits synergistic effects and enhances VOC removal in gaseous and aqueous environments, it is currently used in catalyst manufacturing. In a study, Azimi et al. (2019) synthesized a graphene-based nanocomposite with a TiO₂ photocatalyst for the removal of toluene from air. The results showed that graphene oxide in the composite structure increases dispersion and, as a result, reduces particle aggregation. The highest toluene removal efficiency using these catalysts and under ultraviolet and visible light is 97.7 and 77.2%, respectively. Studies have shown that toluene removal efficiency increases significantly with reactor length, decreasing flow rate, and increasing initial concentration. The reason for the high efficiency under UV irradiation was attributed to the higher light intensity and, as a result, the production of more electron-hole pairs (78). In another study, Azizi et al. (2016) investigated the effect of 4-aminodiphenylamine-modified graphene oxide nanoparticles (GO-A) on the removal of toluene, ethylbenzene, and para, meta, and ortho-xylene (TEX). The results showed that 1 g of nanosorbent removed 56, 70, 72, and 66% of toluene, ethylbenzene, para-xylene, and o-xylene in 5 min at pH 4, respectively. The adsorption capacity of the adsorbent decreased for para-xylene, ethylbenzene, o-xylene, and toluene, respectively. The adsorption process followed the Langmuir isotherm and pseudo-second-order kinetics. Finally, GO-A was reduced in seven cycles for TEX removal, which confirms its good reduction capacity. The results indicate that GO-A can be proposed as an economical and reproducible adsorbent (83).

TiO₂ loaded on ACF1 modified by Zn(CH₃COO)₂

Bi et al. (2021) presented a new approach to overcome the disadvantages of TiO₂ and improve its efficiency for the degradation of volatile organic pollutants, including the preparation of dual-purpose catalysts with photocatalytic adsorption and oxidation functions. Their proposed route was to use activated carbon fiber (ACF). ACF is an advanced porous fibrous material with many advantages, including high adsorption efficiency, large adsorption area, a prominent porous structure, and abundant surface functional groups. Previous studies have shown that these

compounds perform well at removing heavy metals, organic pollutants, and, especially, waste gases. However, to increase efficiency, it is necessary to modify the surface properties and pore structure of these materials. For this purpose, oxidation, surface reduction, microwave modification, or metal/metal oxide loading can be used. In accordance with the findings of previous studies, it was found that, after loading metal oxides onto the ACF surface, additional binding sites are provided, resulting in improved adsorption performance of the aforementioned fibrous materials.

Therefore, the high porosity and adsorption capacity of ACF can play an important role in increasing the removal efficiency of volatile pollutants and, in addition, in adsorbing and removing toxic intermediate products. Therefore, these materials have the potential to improve the photocatalytic performance of TiO_2 and support the recyclability of these photocatalytic materials. Since very few studies have reported TiO_2 loading on zinc salt-modified activated carbon fibers for the removal of volatile organic compounds and BTEX, the above research first modified the activated carbon fibers with ZnCl_2 and $\text{Zn}(\text{CH}_3\text{COO})_2$ using ultrasonic-vacuum deposition. Then, TiO_2 was loaded onto the modified activated carbon fibers. The target pollutant in this study was toluene, which is representative of BTEX and other volatile organic compounds. The results of this study showed that $\text{TiO}_2/\text{ACF-Ac}$ composites contain a large amount of oxygen-containing functional groups, which are useful for toluene adsorption and photocatalytic oxidation. The optical properties results showed that the modified ACFs significantly improved the efficiency of sunlight utilization and enhanced charge transfer and electron-hole pair separation. The photodegradation rate of toluene in this method was reported to be 70% (84-86).

Zn-Ti-LDH photocatalyst

Studies have shown that TiO_2 and other traditional catalysts alone are not able to mineralize volatile organic pollutants, leading to the accumulation of intermediates such as benzaldehyde and the catalyst's neutralization during the process, increasing the possibility of secondary pollution. Therefore, improving the selectivity of photocatalytic processes for toluene and other BTEX compounds and increasing their mineralization rate has become a key issue. To solve this problem, a large number of semiconductor catalysts with wider band gaps, higher positive charge capacities, and stronger oxidation abilities have been designed and produced to replace conventional TiO_2 catalysts. However, during the decomposition process of toluene, mainly due to the high stability of the benzene ring, it is challenging to break/oxidize the ring to its linear intermediates. Also, if only strong oxidation ability is provided without selectivity, it is likely that some new aromatic intermediates will be produced during the

process.

Layered hydroxides (LDHs) are a class of photocatalysts that are mainly used in the photodegradation of VOCs. Due to their high content of hydroxyl groups, these compounds can provide potential hydroxyl groups for the opening of the toluene ring, making them suitable candidates for the removal of toluene and other mentioned compounds. The band gap of these materials can also be tuned from 2 to 5 eV by incorporating specific photoactive metal cations into their structure. Liu et al. (2021) prepared Zn-Ti-LDH catalysts via hydrothermal synthesis for toluene removal in air. It was found that this photocatalyst produced fewer intermediates and showed a higher toluene degradation efficiency (75.2%) and better stability. During the photochemical degradation of toluene, benzaldehyde and benzoic acid were reported to be the central intermediates in the gas phase and on the catalyst surface, respectively. In these photocatalysts, hydrogen atoms in LDH selectively adsorb oxygen atoms in the carbon-oxygen double bonds. In addition, the electronic structure of the ZT-LDH surface facilitates the benzene ring opening reaction and ultimately maintains high activity and stability. On the other hand, this catalyst has a lower activation energy for the ring-opening reaction of intermediates and its surface electronic structure is more favorable for the photochemical degradation of toluene (87-89).

Micrometric TiO_2 Sample Powders

Stuchi et al. (2017) conducted a study on nanometric TiO_2 powders. The results showed that the removal of VOCs such as benzene and toluene by this photocatalyst was 54%. However, micrometric TiO_2 could be a safer and cheaper alternative to nanometric TiO_2 (P25). In general, this photocatalyst was affected by humidity, and due to the mixture of VOCs and the competition between them, the reaction synthesis was considered as an effective factor (71).

Mn- TiO_2 photocatalysts in fiber-optic honeycomb reactors

Studies have shown that the use of photoreactors is highly significant in photocatalytic reactions due to the increased surface area of the doped catalyst and the improved uniform transmission and distribution of light energy, and is useful for overcoming the disadvantages of TiO_2 . Wu et al. (2013) presented a system for more uniform irradiation of photocatalysts. Since the surface area covered by the optical fiber photocatalyst is relatively small and the optical fiber reactor does not effectively utilize the entire reactor, researchers have proposed honeycomb reactors instead of optical fiber reactors. These reactors consist of a large number of straight channels with small internal diameters. Low pressure drop and high surface area are advantages of this reactor type. However, one

disadvantage of these reactors was that the honeycomb length could not be very long, because the photocatalyst could not effectively radiate from the beginning to the end of the channel. To overcome this problem, Wu and colleagues designed a new type of photoreactor, called the fiber-illuminated honeycomb reactor (FIHR). These optical fibers are similar to small tube lamps, which increase the light transmission. In general, these photoreactors, in addition to reducing system costs, increase the photocatalyst surface area and improve the uniform transmission and distribution of light energy within the fiber-optic reactor module. FIHR has been shown to have very high removal efficiency for xylene at very low concentrations (ppb) at ambient temperature. The FIHR showed very high removal efficiency for xylene at very low concentrations (ppb) at ambient temperature, and the removal efficiency of m-xylene increased significantly from 22% to 96.5% under UV irradiation. The use of FIHR with the Mn-TiO₂ photocatalyst not only increases the efficiency of m-xylene removal but also improves the selectivity for CO₂. Mn-TiO₂ in FIHR has excellent recovery and reuse capabilities, maintaining a removal efficiency of 93% after 72 hours of reaction. Among the challenges of these reactors, one can mention the reduction in process efficiency as humidity increases. However, during this reaction, a large part of the m-xylene is converted to CO₂ and other reaction by-products are hydrophilic, which are easily washed away by water, and in addition, Mn-TiO₂ in FIHR has good reuse capabilities after several regenerations (90,91).

Acidic F-TiO₂/SiO₂ Catalyst

The use of non-metallic compounds such as nitrogen, carbon, sulfur, and fluorine is approved to overcome the problems of the TiO₂ catalyst. Improving photocatalytic activity leads to an increase in Ti³⁺ ions, the creation of surface oxygen vacancies, and an increase in surface acidity. The increase in acidic sites provides more surface chemical adsorption centers for reactants, which increases the adsorption of organic molecules and oxygen. Research has shown that a catalyst with an acidic surface can efficiently adsorb polarized reactants and subsequently enhance photocatalytic degradation. For this purpose, Qiu et al. (2019) prepared F-TiO₂/SiO₂ catalyst by the sol-gel method and investigated its BTEX removal efficiency. The adsorption and photocatalytic degradation performance of the F-TiO₂/SiO₂ catalyst has been studied for a group of benzene compounds. The results showed that the aforementioned catalyst is superior to TiO₂ (P25) in photocatalytic adsorption and degradation capacity under simulated sunlight. The increase in the number of organic molecules adsorbed on the acidic catalyst contributes to photocatalytic degradation. The results also showed that the enhancing effect of acidic sites on benzene compound adsorption depends on

the electronic properties of the functional groups. The electron-donating groups of benzene compounds (-OH and NH₂) are adsorbed on the weakly acidic sites of the catalyst due to competitive adsorption with H₂O, while the electron-accepting groups (-Cl and NO₂) are adsorbed on the stronger acidic sites. Monosubstituted chlorobenzenes prefer vertical adsorption on the acidic surface, while disubstituted benzenes prefer horizontal adsorption, which further reduces the adsorption rate. The photocatalytic rate depends mainly on the electron-donating properties of the functional group and the amount of organic molecules adsorbed. It is not related to the electron density of the benzene ring (92-94).

CuO-TiO₂ nanoparticles synthesized with blackening route

Although photocatalytic methods using TiO₂ are effective for removing volatile organic compounds, the light sources used in the process are mainly concentrated in the ultraviolet band below 400 nm, and 95% of non-ultraviolet light is wasted. This is important because most of the sunlight is in the visible range. On the other hand, TiO₂, as a common photocatalyst, faces limitations such as a wide band gap and rapid electron recombination. One solution to improve TiO₂ performance and increase process efficiency is to load active metal components onto it. Copper in particular is best suited for this purpose. This metal facilitates electron transfer to the interface and also narrows the catalyst band gap. However, traditional loading methods, such as impregnation and precipitation, although easy, have less control over particle size. On the other hand, advanced methods such as vapor phase deposition are complex and difficult to control. Another limitation of these methods is that some metal oxides, such as CuO, cannot disperse on the surface, significantly inhibiting catalyst activity. To overcome these limitations, Zhou et al. (2020) and Tan et al. (2014) introduced a new method for the synthesis of these dispersed nanoparticles, which was a type of self-doping that formed a significant amount of Ti³⁺ with oxygen vacancies through hydrogenation, leading to the creation of a black color (95,96). Choosing a suitable method for dispersing the catalyst is an important factor in this process. Metal-based framework (MOF) has attracted attention as an adsorbent due to its properties, such as regular flexible topology and large specific surface area, and it can be used to disperse catalysts. Also, Liu et al. (2015) reported the use of these materials in photocatalyst production processes (97). Zhuo et al. (2020) studied the photocatalytic activity of these catalysts for xylene removal. It was found that the synthesis of CuO-TiO₂ nanoparticles with Cu-MOF by the blackening method showed a significant improvement in photocatalytic performance compared to TiO₂ nanoparticles or CuO-TiO₂ nanoparticles synthesized by the saturation

method. The xylene removal efficiency of these catalysts was 3.45 times higher than that of the conventionally synthesized samples and 12.12 times higher than that of TiO_2 alone. On the other hand, the presence of Cu-MOF on the catalyst surface leads to the formation of smaller CuO- TiO_2 nanoparticles than TiO_2 nanoparticles and nanoparticles synthesized by the saturated method, which is very important for the photocatalytic performance. The blackening process, achieved by mixing with NaBH_4 , greatly improves the photocatalyst's light response to ultraviolet and visible light. On the other hand, the coexistence of Ti^{4+} , Ti^{3+} , Cu^{2++} , and Cu^+ in the new CuO- TiO_2 photocatalysts reduces e-h⁺ recombination rate, which is another important factor in improving the photocatalytic performance. In addition, the blackening process narrows the band gap, reducing it from 2.95 eV to 1.32 eV (95).

Cobalt-Iodine-Doped TiO_2

To overcome the limitations of TiO_2 as the most common photocatalyst, Chen et al. (2022) modified it with cobalt and iodine to reduce the band gap and electron-hole recombination rate, increase the spectral response, and extend its lifetime as a photocatalyst. This group of photocatalysts is titanium dioxide nanocrystals doped with cobalt and iodine, which were synthesized and modified by the sol-gel method, and lead to increased absorption of visible light. This is very important because ultraviolet radiation, which accounts for a small portion of sunlight, is mainly used to activate TiO_2 . In this method, both the particle size and band gaps of TiO_2 are significantly reduced by Co/I doping. Also, with the addition of Co/I, the lattice defects and specific surface areas of TiO_2 increase significantly due to the increase in oxygen vacancies, especially for Co-I- TiO_2 . The benzene removal capacity of Co-I- TiO_2 , Co- TiO_2 I- TiO_2 , and pure TiO_2 is 441.46, 424.36, 388.06, and 51.25 μg , respectively, indicating that the photocatalytic degradation of gaseous benzene is improved by Co/I doping due to the increase in catalyst lifetime and response range to visible light-enveloping light (98).

Arrayed Dielectric Double Barrier Discharge (DDBD) Reactor with $\text{TiO}_2/\text{Al}_2\text{O}_3$ Catalyst

The initial toluene concentration, energy density, and gas flow rate are factors affecting the efficiency of these reactors. Thus, the toluene removal efficiency in the exhaust gas decreased with increasing initial toluene concentration and gas flow rate, but increased with increasing specific energy density. On the other hand, increasing the relative humidity of the air decreased the efficiency of toluene removal. The results showed that the main intermediate products of toluene removal by DDBD- $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst were phenol, benzaldehyde, benzyl alcohol, benzoic acid, N-benzylformamide,

dimethyl terephthalate, dimethyl isophthalate and other materials (80).

Use of Zn-Mn (S-AZMB) in alkaline batteries in TiO_2 compound

Another way to overcome the disadvantages of TiO_2 as the most common photocatalyst is to combine semiconductors with narrow band gaps to form a Z-scheme system. It can be said that the addition of a narrow-band-gap material to the photocatalytic system can create intermediate states in the gap, effectively extending the light response range into the visible region. In this situation, by eliminating some of the generated carriers, the Z-design photocatalytic system has the potential to significantly improve the efficiency of light-induced e-h pair separation and maximize the redox potential. Despite their advantages, these catalysts have drawbacks, including high cost and complex preparation and purification processes, which seriously hinder their development. Therefore, Zhao et al. (2020) proposed a low-cost method for designing these efficient photocatalysts using Zn-Mn batteries (S-AZMB), which are among the most widely used battery types worldwide. Unpurified S-AZMB can be used as a starting material for the preparation of a Z-scheme photocatalytic system in combination with TiO_2 . These photocatalysts are easily prepared via simple ball milling and annealing processes. A series of characterization analyses confirmed that the incorporation of S-AZMB enhanced TiO_2 's response to visible light and significantly improved its ability to separate photogenerated electron-hole pairs. In the toluene removal experiment, the degradation kinetics of the Z-scheme TiO_2 @S-AZMB photocatalyst are 21 and 10.5 times higher than those of pure TiO_2 and S-AZMB, respectively. The S-AZMB-based Z-scheme photocatalysts can also maintain their structural stability and photocatalytic performance in cyclic catalytic reactions and show higher hydrogen evolution efficiency (99-101).

Cu_2O nanowire catalysts

Cu_2O , as one of the rare metal oxides, is very efficient in photocatalytic processes due to its narrow band gap (about 2 eV). Also, due to the abundance of copper in nature, the fabrication of this oxide on a large scale is cost-effective and straightforward. In general, three-dimensional and oriented structures can facilitate efficient photon absorption and rapid VOC release, which are superior to powder catalysts. Yang et al. (2021) proposed replacing $\text{Cu}(\text{OH})_2$ nanowires to overcome the disadvantages of conventional photocatalysts, such as the diffusion and contact of target VOCs with photocatalyst surfaces, which hinder photocatalytic degradation and stabilization processes. Uniform Cu_2O nanowire arrays can be formed by thermal treatment of $\text{Cu}(\text{OH})_2$ nanowires, which are spontaneously grown on copper grids. These nanowires

have high orientation and low energy consumption, and are easy to operate. Cu₂O nanowires showed high efficiency in degrading 30 mg L⁻¹ toluene (99.9% after 120 min) and high stability (no decrease after ten reuses). These nanowires were able to degrade toluene under natural sunlight completely. During photocatalysis, toluene is attacked by light-generated holes and hydroxyl radicals (\bullet OH), and is finally oxidized to non-toxic small molecules. Photocatalytic removal of toluene with Cu₂O nanowires/copper mesh also offers advantages of low cost, high efficiency, stability, and convenient operation, and has promising application prospects (102,103).

TiO₂/UV/O₃ Photocatalyst

Marchiori et al. (2019) presented a new device configuration that achieved high efficiency in the photocatalytic degradation of VOCs in a short time and space. In this study, ozone was also used to enhance the degradation of cyclohexanes and BTEXs. The results of this study showed that the addition of ozone is a useful technique for improving the photodegradation of VOCs and can effectively increase their conversion, raising the removal efficiency by 9% compared to the absence of ozone. This helps reduce reaction time, which also reduces equipment size. According to the results, the toluene degradation process was accompanied by no catalyst deactivation. This is a significant advantage, especially for toluene, since catalyst deactivation leads to the formation of toxic by-products (104).

TiO₂ photocatalytic reactor

Previous studies have shown that the TiO₂ photocatalytic coating agent can degrade toluene. The efficiency of this process can be increased as a primary function of changes in UV-A irradiation and reactor volume. However, since toluene is decomposed in this process, additional organic pollutants such as benzene and butadiene can be produced. TiO₂ photocatalysts decompose these pollutants. So, the overall reduction performance may change. However, TiO₂ photocatalysts can be used to investigate the effect of reducing indoor pollutants in indoor ventilation systems and building materials. In general, in a study conducted in this field, the appropriate titanium content for reducing toluene concentration in the coating was 29.51%, and increasing UVA light intensity and reactor volume led to higher toluene removal. The toluene concentration was reduced between 55.22% (0.23 ppm) and 32% (0.32 ppm) under the conditions of UV-A radiation intensity and reactor volume (UV-A: 15 and 20 W/m², reactor volume: 20 and 15 cm³). In addition, this method faced limitations, including the difficulty of providing sufficient UV-A light in indoor environments and the production of possible by-products from the photocatalytic reaction (66,67).

Fe-TiO₂ rotating flow packed bed reactor

Among the activities carried out to overcome the limitations of TiO₂ catalysts is the production of TiO₂ nanoparticles with appropriate dispersion and uniform particle size. In addition to dispersion, increasing the sensitivity of TiO₂ to visible light and reducing electron-hole recombination generated by light are important goals in the large-scale production of nano-TiO₂. Since the sol-gel method, as a standard method for synthesizing this nanocatalyst, has disadvantages such as the use of expensive raw materials (titanium alkoxide), the production of large volumes of waste organic compounds and solvents, the need for precipitation is considered an alternative method. This traditional method is cheaper and, with low-speed intermittent stirring, results in non-uniform mixing, leading to nucleation, non-uniform particle growth, and the formation of large, agglomerated particles. Zeng et al. (2019) introduced Fe-TiO₂ circulating-flow-packed-bed reactors with these considerations. In the production of these catalysts, TiO₂ nanoparticles are prepared using the high-gravity technique and the direct deposition method in an impinging-flow rotating packed-bed reactor (IS-RPB), followed by in situ doping with Fe⁺³. Iron ions can act as electron-trapping centers and prevent electron-hole recombination. This leads to an increase in the lifetime of electrons and holes and consequently to an increase in photocatalytic activity. Fe⁺³ ions also increase the optical response amplitude and reduce the band gap energy. The efficiency of gaseous toluene degradation by Fe-TiO₂ under UV light is higher than that of pure TiO₂ and commercial P25, because Fe⁺³ effectively prevents the recombination of electrons and holes (105-107).

Pt single-atom catalyst on nanoporous TiO₂ film

Studies have shown that deposition of noble metals such as gold, platinum, and palladium on semiconductor catalysts improves performance. In recent years, many studies have been conducted on single-atom catalysts with active metal centers and atomic distribution due to their maximum atomic efficiency and excellent activity. Studies have shown that single noble metal atoms can significantly increase the number of active sites on the catalyst surface, enhance contact opportunities between VOCs and the catalyst, and accelerate the generation of active radicals and the subsequent separation of carriers. Since the research on these catalysts has mainly focused on hydroformulation, gas-water displacement reaction, water splitting, and oxygen reduction reaction, Xu et al. (2019) fabricated a novel photocatalyst with single-atom platinum sites doped on nanoporous TiO₂ film using a facile immersion and reduction method. The results of this study showed that Pt shows significant potential for photocatalytic removal of low-concentration VOCs in indoor environments. These catalysts have very high photocatalytic activity and are also stable and selective. The toluene removal rate of these catalysts under UV

irradiation was reported to be 48.88% at a toluene input concentration of 200 ppb and a reaction time of 0.3 s. This value is 5.94 times higher than that of a pure nanoporous TiO₂ film (108,109).

Sr₂Sb₂O₇ Photocatalyst

Among various photocatalytic materials, transition metal oxides are widely used in the photocatalytic degradation of volatile organic compounds. These materials have a surface oxygen in their lattice, which plays a vital role in photocatalytic processes. Many researchers have shown that surface lattice oxygen acts as an important redox site for the activation of molecular oxygen in transition metal oxides. Since the activation of surface network oxygen on the catalyst surface is of great importance for improving catalytic activity and further identifying the activation mechanism for surface network oxygen, Chen et al. (2021) investigated the critical role of surface network oxygen in transition metal oxide catalysts in a study and aimed to improve its role in photocatalytic processes. Considering that the efficient decomposition and removal of toluene remains a significant challenge due to the high stability of conjugated bonds in the benzene ring, they investigated the Sr₂Sb₂O₇ photocatalyst. This is because the methyl group in toluene is more easily oxidized than the benzene ring is. For this reason, toluene is gradually converted into benzyl alcohol, benzaldehyde, and benzoic acid, and then enters the ring-opening and mineralization stage. Previous studies have shown that the formation of benzoic acid reduces the energy barrier required for ring opening and facilitates toluene mineralization. In general, the selectivity for the formation of specific intermediates depends on the reaction pathway and the degradation efficiency. In addition, to achieve complete mineralization, the final reaction products (CO₂ and H₂O) must be effectively released from the catalyst surface. In Sr₂Sb₂O₇ photocatalysts, the surface lattice oxygen promotes the adsorption and subsequent activation of O₂ and H₂O molecules for further ROS production. On the other hand, the adsorbed H₂O molecules can reactivate the lattice oxygen. Active lattice oxygen is favorable for the adsorption and activation of toluene and its intermediates. Subsequently, it induces an intermediate conversion, especially for benzoic acid, leading to the opening of the benzene ring and the final mineralization. The CO₂ removal and reactivation of lattice oxygen by H₂O can prevent competitive adsorption between the final products and confidence intermediates. Due to the enhanced activation of lattice oxygen, Sr₂Sb₂O₇ exhibits excellent activity and stability in the photocatalytic mineralization of toluene. Compared to the conventional P25 photocatalyst, although P25 showed higher efficiency at the beginning of the process (10 min after light irradiation, the toluene conversion ratio in P25 and Sr₂Sb₂O₇ was 1.74 and 3.72%, respectively, at a concentration of 45 ppm toluene),

after 1 hour of reaction time, its activity decreased to 4.32. Meanwhile, Sr₂Sb₂O₇ still maintains a high toluene conversion activity of about 73.3%. The toluene mineralization ratios for P25 and Sr₂Sb₂O₇ are 23.3% and 72.2%, respectively, and both still maintain efficiency after 7 hours. The toluene mineralization ratio after 7 hr in P25 and Sr₂Sb₂O₇ was 23.3 and 72.2%, respectively. This is because the low conversion ratio for toluene and the refractory intermediates accumulated in P25 leads to gradual deactivation. After 5 test cycles, P25 becomes almost inactive, and its color darkens, indicating the formation and accumulation of refractory intermediates on the surface. Also, in this process, toluene gas is mainly converted to CO₂, and simple absorption or conversion to other refractory intermediates does not occur. So that the CO₂ production efficiency of P25 and Sr₂Sb₂O₇ is 79.2% and 98.8%, respectively. The mechanism of lattice oxygen activation and its dominant role in the effective photocatalytic mineralization of toluene have been proposed at the atomic level. It is believed that this work provides new insights into the origin of lattice oxygen activation for the effective degradation of VOCs (69,110,111).

The study evaluated the photocatalytic degradation of gaseous toluene using SrTiO₃ and SrTiO₃/rGO catalysts under UV light. Results showed that incorporating graphene enhanced removal efficiency due to improved adsorption and charge transfer, achieving maximum efficiencies of 27.2% and 32%, respectively. Relative humidity had the most substantial negative impact on performance, followed by flow rate and concentration effects (112).

TiO₂ composites loaded with CaCO₃

One of the most important problems with TiO₂, as the most commonly used photocatalyst, is that it rapidly deactivates and exhibits low conversion efficiency in the photocatalytic degradation of volatile organic compounds, especially aromatic compounds. To date, there has been little research on preventing TiO₂ deactivation, which is mainly observed during VOC degradation. Cui et al. (2020) investigated this issue and presented new composites to address it. The researchers in this study pointed out that the rapid deactivation of TiO₂ is due to strong complexes and the accumulation of carbon products formed on the catalyst during the decomposition of volatile organic compounds. Therefore, proper transport of the accumulated end products from the TiO₂ surface during the photocatalytic process can relieve blocked active sites, prevent deactivation, and maintain high efficiency. In the above study, the researchers fabricated nanosized composites in a cost-effective and facile manner, capable of large-scale fabrication and exhibiting highly efficient photocatalytic stability for toluene mineralization. These samples have some special stalactite properties and can

therefore spontaneously transport the end products of CO_2 and H_2O from the photocatalyst surface and liberate the active sites on the surface. In this study, Wen et al. concluded that the application of CaCO_3 promoted the interaction between TiO_2 and CaCO_3 , thereby generating abundant active electrons that improved the adsorption and activation of reactants and the conversion of photogenerated carriers. More importantly, it facilitated the transfer of end products, thereby liberating active sites and suppressing TiO_2 deactivation. This nanocomposite is also highly efficient, durable, and inexpensive, thereby improving the adsorption and activation of reactants and facilitating the transfer of end products. Therefore, it can prevent TiO_2 from deactivation and significantly reduce costs. In this way, the problem of the accumulation of reaction products on the TiO_2 surface and the reduction in catalyst efficiency and life was also solved. Also, the use of photocatalyst powder poses problems due to its dispersion by air flow and inactivation. However, by immobilizing CCT21 on a flexible sponge, its dispersion is prevented and it provides numerous other advantages, including easy installation, a large reaction surface, and easy recycling (113,114).

ZnO nanoparticles immobilized on modified natural zeolite

Studies have shown that ethylbenzene, as one of the BTEX compounds, can be removed from the air by combined adsorption-photocatalysis processes. In a study, Rangkooy et al. (2021) used zinc oxide nanoparticles immobilized on modified natural zeolite for the removal of ethylbenzene. Then, ZnO nanoparticles were immobilized on the natural zeolite substrate by the wet inoculation method. Ethylbenzene vapor at concentrations of 25, 50, 100, and 200 ppm was passed over zinc (Zeolite Modified: MZe) under UV irradiation. Photocatalytic experiments were performed at ambient temperature and 35% humidity. Based on the results, modification of natural zeolite with dichlorosilane increased the porosity and specific surface area of the zeolite. As a result, this surface adsorbent can be a suitable substrate for improving the efficiency of photocatalytic removal of ethylbenzene pollutant. Due to its high physical strength and higher heat tolerance than adsorbents such as activated carbon, as well as its abundance of resources, it can be an alternative substrate for the removal of air pollutants. Immobilization of nanoparticles on a modified natural zeolite can be a suitable method for removing ethylbenzene vapor from the air, and the ZnO/MZe/UV process showed greater efficiency in its removal. Therefore, the ZnO/MZe/UV process can be a suitable technology for removing volatile organic compounds from the air stream. The results showed that as the initial concentration of ethylbenzene increased, the decomposition efficiency decreased. And the highest removal efficiency (about 55%) is observed at

a concentration of 25 ppm, which is attributed to substrate blockage (115). In another study, Tu et al. (2019) specifically addressed the challenge of benzene's slow degradation compared to other BTEX compounds. The researchers sought to combine the advantages of high adsorption (by zeolite) and photocatalytic activity (by TiO_2) by synthesizing a TiO_2 /zeolite Y nanocomposite. The results showed that the zeolite substrate, due to its high specific surface area and selective adsorption properties, effectively concentrates benzene molecules in the vicinity of the TiO_2 photocatalytic sites. This "synergistic effect" between adsorption and photocatalyst resulted in a significant increase in the benzene degradation rate and a reduction in the formation of toxic byproducts compared to pure TiO_2 . The proposed mechanism is the initial adsorption of benzene onto the pores of zeolite Y and then its transfer to TiO_2 nanoparticles for photodegradation (116).

Fe/Bi₂WO₆/TiO₂-N composite

Studies have shown that the use of metal complexes or plasmonic metals to modify the TiO_2 surface is highly efficient and expands its absorption spectrum by creating a sensitization effect. However, the production of active species and the light-absorption efficiency in this case are usually not high enough due to the nature of electron excitation and the need for charge transfer to the energy bands of TiO_2 . In such situations, doping TiO_2 with nitrogen is used to modify it. As a result, additional energy levels form within the TiO_2 band gap, leading to a decrease in the minimum energy required for photoexcitation of electrons.

TiO_2 -N photocatalysts exhibit high photocatalytic activity in visible light, especially under blue light. However, the quantum efficiency of this photocatalyst in the visible region is usually not high enough due to the fast electron-hole recombination. To overcome this problem, the photocatalyst surface can be coated with noble metals or other transition metals to increase visible-light activity, create an energy barrier, and improve charge separation.

Noble metals also accelerate electron transfer to adsorbed oxygen molecules, thus increasing the activity compared to the activity of the photocatalyst alone. Some studies have shown that the $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ -N heterostructure prepared by the hydrothermal method exhibits high activity for the degradation of gaseous organic pollutants under visible light and high stability against radiation. Lyulyukin et al. (2023), considering the above findings, investigated the ability of photocatalysts on the kinetic aspects of the degradation of volatile organic compounds. They used benzene as a representative aromatic compound and investigated its removal efficiency by $\text{Fe}/\text{Bi}_2\text{WO}_6/\text{TiO}_2$ -N composite. As previously noted, the incorporation of TiO_2 -N into a composite system and subsequent surface modification with iron species significantly enhances the catalytic activity. These composites are based on nitrogen-

doped nanocrystalline TiO_2 and bismuth tungstate, synthesized using a hydrothermal method. The $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-N}$ heterostructure reinforced with iron species effectively utilized visible light in the blue region and showed much higher activity in ethanol vapor degradation than $\text{TiO}_2\text{-N}$ alone. However, increasing the activity of $\text{Fe}/\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-N}$ can adversely affect benzene vapor degradation. Temporary deactivation of the photocatalyst can occur at high benzene concentrations due to the rapid accumulation of non-volatile intermediates on its surface. The formed intermediates suppress the adsorption of primary benzene and significantly increase the time required for its complete removal from the gas phase. Increasing the temperature to 140°C enables faster overall oxidation without increasing the production of hazardous by-products such as carbon monoxide. The use of $\text{Fe}/\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-N}$ composite improves the oxidation selectivity compared to pure $\text{TiO}_2\text{-N}$ (117,118).

$\alpha\text{-Fe}_2\text{O}_3/\text{Cu}/\text{g-C}_3\text{N}_4$ & $\alpha\text{-Fe}_2\text{O}_3/\text{Cu}/\text{g-C}_3\text{N}_4$ nanocomposites

In some studies, two novel $\alpha\text{-Fe}_2\text{O}_3$ -based nanocomposites— $\alpha\text{-Fe}_2\text{O}_3/\text{Cu}/\text{g-C}_3\text{N}_4$ and $\alpha\text{-Fe}_2\text{O}_3/\text{Ag}/\text{g-C}_3\text{N}_4$ —were designed and synthesized via simple preparation routes to enhance photocatalytic degradation of ethylbenzene in continuous air flow systems under visible light irradiation. Comprehensive characterization (XRD, FT-IR, SEM-EDS, elemental mapping, PL, DRS, and N_2 adsorption-desorption) confirmed the successful formation of core-shell and core-discontinuous shell architectures with efficient charge separation and extended visible light absorption. Both Cu- and Ag-modified composites exhibited superior photocatalytic performance and stability compared to pristine $\alpha\text{-Fe}_2\text{O}_3$, $\text{g-C}_3\text{N}_4$, and $\alpha\text{-Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$, attributed to effective Z-scheme charge-transfer mechanisms. The $\alpha\text{-Fe}_2\text{O}_3/\text{Ag}/\text{g-C}_3\text{N}_4$ system was further optimized using response surface methodology (RSM) based on the central composite design (CCD) to determine the optimal operational parameters. In both systems, complete mineralization of ethylbenzene occurred without formation of organic byproducts, producing CO_2 as the only inorganic product. These results demonstrate that $\alpha\text{-Fe}_2\text{O}_3/\text{Cu}/\text{g-C}_3\text{N}_4$ and $\alpha\text{-Fe}_2\text{O}_3/\text{Ag}/\text{g-C}_3\text{N}_4$ nanocomposites are highly promising visible-light photocatalysts for efficient and continuous removal of airborne pollutants (119,120).

VUV/ TiO_2

Recent studies have shown that the removal efficiency of volatile organic compounds under VUV irradiation is much higher than that under ultraviolet radiation alone. The reason for this superiority lies in the roles of hydroxyl and oxygen radicals. However, most research in this field has focused on increasing the removal efficiency, and attention has not been paid to the complete mineralization

of pollutants or the type of intermediate product produced. Therefore, Liang et al. (2020) conducted a study to identify intermediate products and degradation mechanisms, focusing on preventing catalyst deactivation and designing the necessary catalysts. Overall, this study aimed to change the degradation chemistry of VOCs, especially toluene, in the VUV-PCO process and to identify intermediate products in the gas phase. The results show that the VUV-PCO process greatly increases the efficiency of photocatalytic degradation and mineralization of toluene. On the other hand, VUV/ TiO_2 significantly contributes to the mineralization of most pollutants and their intermediates. Various factors, such as direct photolysis by high-energy photons produced (6.7 eV) from 185 nm radiation, use of O_3 in the UV-PCO process, degradation by reactive species produced by O_2 , H_2O , and TiO_2 photocatalyst under VUV irradiation, make the toluene degradation pathways in the VUV-PCO process (P25) proposed as an efficient pathway (121-123).

Kamaei et al. (2017) investigated the photocatalytic degradation of ethylbenzene in air using photocatalytic oxidation in a ring photoreactor filled with glass beads coated with TiO_2 nanoparticles. Removal efficiencies of about 75–100% were achieved for initial ethylbenzene concentrations up to 0.6 g/m³ in the reactor under UV irradiation at relatively low residence times. Inlet flow rate and initial ethylbenzene concentration were the parameters affecting removal efficiency; increasing them decreased it. CO_2 production in the photoreactor indicated mineralization of the pollutant during the photocatalytic degradation of ethylbenzene (124).

Carbon boron nitride

Qu et al. (2020) investigated the potential of new catalysts in the presence of boron nitride to overcome the limitations of TiO_2 catalysts in VOC removal, including UV radiation limitations, rapid deactivation, and the accumulation of carbon intermediates on its surface. Boron nitride is a promising metal-free two-dimensional catalyst that is resistant to coke and carbon intermediates. This insulating material, after carbon doping, is converted into a carbon boron nitride photocatalyst that responds to visible light and is highly effective at stabilizing and mineralizing pollutants into CO_2 and water. Accordingly, carbon boron nitride has significant potential for use in photocatalytic processes for pollutant control and removal. In this study, the researchers successfully designed and characterized a ring-opening pathway for toluene removal using carbon boron nitride. They found that the overall arrangement and bonding of carbon atoms in the catalyst structure play a key role. The ring-opening process is usually the rate-determining step in the photocatalytic degradation of VOCs. This process, which involves electron delocalization in a carbon boron nitride photocatalyst, is more efficient than traditional

methods. In this process, the carbon chains in toluene are converted into carbon ring structures with pi-bonds. The unpaired electrons of carbon atoms in carbon boron nitride are converted into unstable electrons, which help facilitate the separation of positive and negative charges generated by light. Effective charge separation is essential to prevent recombination and extend their lifetimes. These electrons also play a role in the formation of reactive oxygen species, which are the main factor in the degradation of organic pollutants. The results showed that the removal and mineralization of toluene were facilitated without the formation of additional intermediate species, and by adjusting the dopant coordination configuration and electron geometry in the catalyst, the lone electrons of carbon were converted to delocalized counterparts. This enhances the interaction between toluene molecules and the photocatalyst. The aromatic ring of toluene can be directly attacked by electron delocalization. This unprecedented pathway-control strategy changes the behavior of the aromatic ring-based reaction from toluene to CO₂. This opens up a new route for BTEX purification (125-127).

ZnO coated on glass plates

Jafari et al. (2018) developed a photocatalyst that was satisfactory in removing BTEX compounds. For this purpose, the thermal-bonding method was used to fix ZnO powder on glass plates. Before fixation, the plates mentioned were washed in 0.01 M NaOH to increase the number of OH groups and improve contact between ZnO and the plates. After that, the prepared ZnO suspension was poured onto glass plates. The ZnO-coated plates were calcined for 3 h at 450 °C in an electric furnace at 50 Hz. The stabilization process was performed three times to increase the amount of ZnO loaded on the plates. The photocatalytic oxidation of benzene and toluene was carried out in a Plexiglas reactor under the irradiation of a metal halide lamp (150 W, 345-800 nm). The UV intensity in all experiments was 139 μW/cm². The results showed that coating glass surfaces with ZnO suspension resulted in the removal of 46% of benzene and 57% of toluene at a concentration of 50 ppm at 45°C and 40% relative humidity after 240 minutes of metal halide lamp irradiation (128).

W/TiO₂ nanoparticles

Pourkarimi et al. (2017) introduced tungsten-doped TiO₂ nanoparticles, which alone solved the problems of TiO₂ catalysts. In these catalysts synthesized by the sol-gel method, tungsten played a key role in improving the photocatalytic activity of TiO₂ under visible and UV light irradiation by reducing the electron/hole recombination rate. The maximum toluene removal efficiency depended on the tungsten percentage, reaction time, and to some extent on the initial toluene concentration. At a

concentration of 4000 ppm toluene, a temperature of 500°C, 0.52 wt% tungsten, and 8 h reaction time, a toluene removal efficiency of 59% was obtained (129).

Bi₂O₂CO₃ (BOC) composites modified with carbon quantum dots (CQDs)

In recent years, bismuth (Bi)-based photocatalysts have attracted much attention due to their chemical stability, high activity under visible light, and unique electronic band structure. The hybridization of O₂p and Bi6s orbitals in Bi-based photocatalysts leads to a well-dispersed valence band. Also, the lone-pair deviation of the Bi 6s orbitals increases charge-carrier mobility and reduces electron-hole pair recombination. Bi₂O₂CO₃ is considered a suitable catalyst due to its special layered structure, suitable band gap, excellent photocatalytic activity, and long-term stability. However, it has a wide band gap (2.8-3.5 eV) and can only be fully stimulated by ultraviolet light, severely limiting its application under sunlight. To overcome the problems of this photocatalyst, several methods such as crystal surface modification, metal doping, and heterogeneous structure have been used. Carbon quantum dots, as a high-conversion material, can absorb ultraviolet light at specific wavelengths and emit ultraviolet or visible light. This will create an indirect path for visible light in the photocatalytic process. Therefore, Ding et al. (2020) investigated and reported a facile hydrothermal method for fabricating the aforementioned composites. Experiments showed that modifying BOC with CQDs is a relatively simple and efficient method that enhances its photocatalytic activity. On the other hand, the specific crystal orientation (002) of BOC plays an important role in improving the photocatalytic performance. Also, the specific morphology (flower-like) of BOC provides a high specific surface area, which is beneficial for the adsorption of pollutants and light. The results showed a toluene removal rate of 96.62% in 3 h and excellent stability. It was confirmed that CO₂ was the main product. Oriented flower-like Bi₂O₂CO₃ with carbon quantum dots on the surface shows outstanding potential in the field of solar-powered air purification (130-132).

Comparison of metal- and non-metal-based TiO₂ photocatalysts from a chemical perspective

From a chemical perspective, TiO₂ photocatalysts modified with metals (e.g. Ag/TiO₂, Fe/TiO₂) and TiO₂ modified with non-metals (e.g. N-TiO₂, C-TiO₂) have significant differences in terms of energy consumption, environmental compatibility, VOCs removal efficiency, and photoactivation range (Table 3):

Energy Consumption & Activation Wavelength Metal-doped photocatalysts (e.g., Ag-TiO₂, Fe-TiO₂)

Extends light absorption into the visible range (400–700 nm) due to dopant-induced intermediate energy states,

Table 3. Comparison of Photocatalysis with Metal-doped TiO₂ vs. Non-metal Doped TiO₂ (43,69,105,113,117,121,125,129)

Aspect	Metal-doped TiO ₂	Non-metal doped TiO ₂ (N, C, S)
Band Gap Modification	Effective narrowing of the band gap through introduction of impurity levels, enhancing visible-light absorption.	Band gap narrowing by introducing localized states, especially around valence band. Visible-light activity significantly improved.
Charge Carrier Dynamics	Metal dopants can act as electron traps, reducing recombination rate of electron-hole pairs. However, excess metal can act as recombination centers.	Non-metals generally reduce recombination through surface modification; less effective than metals in trapping electrons.
Photocatalytic Efficiency	High, especially under visible light. Enhanced redox potential with proper doping levels.	Moderate to high. N-doping is particularly effective under visible light; C and S show variable results depending on synthesis method.
Thermal Stability	Generally stable, though some metal dopants (e.g., Fe, Cu) can catalyze undesired reactions at high temperatures.	Better thermal and chemical stability; less reactive at elevated temperatures.
Synthesis Complexity	More complex, requiring precise control over dopant concentration and dispersion to avoid nanoparticle agglomeration or recombination centers.	Simpler and often more cost-effective, non-metals can be introduced via sol-gel, hydrothermal, or annealing methods.
Environmental Impact	Potential toxicity and environmental risks due to metal leaching, especially heavy metals.	More environmentally friendly; no risk of metal contamination.
Cost	Generally, more expensive due to the use of noble or transition metals.	Lower cost; abundant and less hazardous raw materials.

reducing reliance on UV light.

However, some metals (e.g., Pt, Au) increase production costs and energy input for synthesis.

Some metals (e.g., Cu, Fe) may act as recombination centers and reduce catalytic efficiency.

Non-metal-doped photocatalysts

- Doping with elements such as nitrogen (N) or carbon (C) also improves visible light absorption, but is usually less energy-intensive and less cost-effective to synthesize.
- Non-metallic photocatalysts may have lower activity in the visible region compared to some metal-doped examples.

Environmental Friendliness

Metal-doped

- Risks of metal leaching (e.g., Ag⁺, Cu²⁺) causing secondary pollution, particularly in aqueous systems.
- Some transition metals (e.g., Fe, Co) may generate reactive oxygen species (ROS) excessively, harming ecosystems.

Non-metal-doped

- More eco-friendly, as dopants (N, C, S) are non-toxic and minimize secondary contamination.
- Generally, more sustainable for large-scale applications.

BTEX Degradation Efficiency

Metal-doped

- Often shows higher initial degradation rates for VOCs due to enhanced charge separation (e.g., Ag-TiO₂ for formaldehyde degradation).
- However, long-term stability can be compromised by photocorrosion or dopant deactivation.

Non-metal-doped

- Provides more stable performance over time with minimal deactivation.

- May exhibit slower kinetics for some refractory VOCs due to less aggressive redox potential.

Therefore, if high efficiency and visible-light activation are the goals, metal-doped photocatalysts (especially with selected metals such as Ag or Fe) are a better option, provided that their stability is improved. Also, if environmental compatibility and stability are the priority, non-metal-doped photocatalysts (such as N-TiO₂) are more suitable, as they do not pose a risk of secondary pollution and are less expensive to synthesize.

Photocatalyst synthesis methods

In addition to the type of photocatalyst, synthesis methods also play a role in improving BTEX degradation efficiency. For example, hydrothermally prepared Nd-TiO₂ catalysts contain three times more hydroxyl groups in the surface layer and two times more surface defects than sol-hydrothermal catalysts. In addition, the modification of rare-earth metals (RE) has been recognized as a practical approach in recent years to address issues with TiO₂ catalysts and to expand the range of the solar spectrum they absorb. The presence of RE ions slows down the rate of charge carrier recombination processes and acts as a luminescence conversion media. Nd-TiO₂ catalysts can also convert light from the near-infrared and visible spectral ranges to ultraviolet wavelengths (133,134). Patrycja et al. (2018) showed that the synthesis method for TiO₂ nanoparticles significantly affects the catalyst's properties and final morphology. In general, careful control of the synthesis conditions is essential to achieve the desired properties and, consequently, improve photocatalytic performance. Another factor affecting the efficiency of the BTEX removal process is the two-phase solid-liquid (LPCO) or solid-gas (SPCO). Possible pathways for toluene degradation include the addition of an OH group to the benzene ring and the removal of a hydrogen atom from the methyl group. The liquid-gas method produced more hydroxyl radicals than the conventional solid-gas method, thereby contributing to more effective toluene

degradation (the toluene removal efficiency in LPCO is about 6 times higher than in traditional SPCO). Also, in the LPCO method, no intermediates are detected in the exhaust gas, indicating that degradation is more complete and by-product emissions are reduced. On the other hand, continuous washing of the catalyst in LPCO prevents the precipitation of intermediates on it and prevents catalyst deactivation (135). Tables 4 and 5 review the types of BTEX removal methods and their advantages and disadvantages.

The photocatalytic degradation of toluene on TiO₂ involves electron-hole generation under UV light, producing hydroxyl and oxygen radicals. These reactive species break C-C and C-H bonds, converting toluene into intermediates such as benzyl alcohol, benzaldehyde, benzoic acid, phenol, dimethyl isophthalate, and N-benzylformamide. Finally, all intermediates are mineralized into CO₂, H₂O, and CO (121,140-146). A schematic of the pathway for toluene breakdown and the production of intermediates under photocatalytic conditions is presented (Supplementary file, Figure S1).

Conclusion

In this study, various methods for removing BTEX from air were reviewed and compared, including both destructive and non-destructive techniques. The findings indicate that while non-destructive methods—such as adsorption on solid or liquid media—can be effective in the short term, their inability to eliminate pollutants

and their merely transfer-based nature make them less suitable as sustainable solutions for air pollution control. On the other hand, destructive methods such as thermal oxidation and cold plasma offer higher degradation efficiency but are often associated with high energy consumption and the potential formation of undesirable by-products. Photocatalytic degradation emerged as a promising, environmentally friendly, and energy-efficient approach for VOC removal. The use of semiconductor nanoparticles, particularly TiO₂, demonstrated significant improvements when doped with metal (e.g., Ag, Fe, Cu) or non-metal elements (e.g., N, C, S). These modifications enhanced photocatalytic performance by extending light absorption into the visible range, improving pollutant degradation rates, reducing energy demand, and increasing photocatalyst stability. Finally, the evaluation of energy consumption and environmental compatibility confirmed that doped photocatalysts not only offer superior performance but also align well with the principles of green chemistry and sustainable environmental management. Overall, the study highlights the potential of optimized photocatalytic systems as practical and effective solutions for BTEX abatement and air quality improvement. However, this method also has some limitations. A key limitation of the large-scale application of photocatalysis is rapid catalyst deactivation, where reactive intermediates (e.g., benzaldehyde, carboxylic acids) strongly adsorb to active sites, blocking them and halting degradation. Furthermore, process efficiency is

Table 4. summarizes the comparison of BTEXs removal methods (66,78,98,104,136-139)

Processes	Types of Classification	General Mechanism	Advantages	Disadvantages	Removal Efficiency (Relative)
Destructive	Thermal oxidation	Burning BTEX at high temperature and converting it to CO ₂ and H ₂ O	High efficiency Simple	High energy consumption, NO _x production	90-99%
	Catalytic oxidation	Use of catalyst to reduce BTEX combustion temperature	Lower temperature, Lower energy consumption	High sensitivity to toxins Sediments	80-95%
	Advanced Oxidation Process (AOP)	Production of OH radicals for BTEX degradation	No need for high heat Can be combined with other methods	High operating cost Requires maintenance	75-95%
	Photocatalytic plasma	Gas ionization and generation of active electrons to break down BTEX molecules	Rapid, no need for temperature or catalyst	Production of toxic by-products Equipment cost	60-90%
	Photocatalytic	Light excitation of a catalyst (TiO ₂) and generation of active radicals	High efficiency Use of sunlight	Low efficiency in low light Humidity dependence	70-95%
Non-destructive	Adsorption	Adsorption of BTEX molecules on a solid surface (activated carbon, zeolite)	Recyclable Low cost	Rapid saturation Requires continuous recycling	80-95%
	Absorption	BTEX dissolution in absorbent liquids	Simple implementation Suitable for wet streams	Produces contaminated effluent Limited efficiency	50-80%
Biological	Biofiltration	Degradation of BTEX by microorganisms in a solid bed	Low cost Ecofriendly High efficiency	Sensitive to environmental conditions	70-95%
	Bioscrubber	Dissolution of BTEX in liquid and degradation by bacteria	Better control of process conditions	Need for biological sludge treatment	60-85%
	Biotrickling Filter	Air passage through wet bed with active biofilm	High stability Suitable for harder contaminants	complex and expensive	75-95%

Table 5. Summary of the advantages and disadvantages of the mentioned photocatalytic BTEX removal methods

Photocatalytic processes	Advantage	Disadvantage	Removal efficiency
Zn-Ti-LDH	High efficiency Less intermediate production High stability	Relatively high production cost	75.2%
Fe-TiO ₂ (IS-RPB)	Prevent electron-hole recombination High stability	Requires special reactor concentrations	95.7%
FHR + Mn- TiO ₂	High efficiency Reusability Suitable for industrial environments	Sensitivity to humidity	96.5%
TiO ₂ /UV/O ₂	Increase VOCs degradation efficiency Reduce retention time	High energy consumption	98.5%
Fe/Bi ₂ WO ₆ / TiO ₂ -N	Use of visible light Increase in photocatalytic activity	Sensitivity to high benzene	92%
GO- TiO ₂	High efficiency under UV irradiation Increase the surface area of pollutant absorption	Strong dependence on UV light	97.7%
TiO ₂ /ACF + Zn(CH ₃ COO) ₂	Improved charge transfer Increased degradation efficiency	High synthesis cost	70%
CuO- TiO ₂	Better visible light absorption Higher efficiency than pure TiO ₂	Less stability compared to some catalysts	3.45 times more than pure TiO ₂
Pt/TiO ₂ Nanoparticles	High performance at low concentrations Higher stability	Expensive	48.88%
Sr ₂ Sd ₂ O ₇	More efficient mineralization High stability High CO ₂ conversion	Complexity of synthesis	98.8%
ZnO coated on glass plates	Low cost Relatively high toluene removal	Poor performance in low light	57%
Co-I- TiO ₂	Increase visible light absorption Improve benzene degradation	Complexity of synthesis Sensitive to surface contamination	90%
TiO ₂ + CaCO ₃	Prevent catalyst deactivation Reduce cost	Lower efficiency than some superior options	85%
VUV/ TiO ₂	Better mineralization Reduction of toxic intermediates	Requires strong and expensive light source	95%
g-C ₃ N ₄	Effective removal without producing organic intermediates	Sensitivity to environmental conditions	91%
TiO ₂ -(DBD + UVP)	Complete removal of BTEX and formaldehyde Reduction of side pollutants	High cost for industrial scale	100%
BOC + CQDs	High stability Relatively high removal rate	Limitations in removing some contaminants	96.62%
TiO ₂ (P25) Metrometric	Cheaper alternative Simplicity of synthesis	Lower efficiency than nanostructures Sensitive to humidity	54%
Cu ₂ O nanowire catalysts	Very high removal Stable performance	Limitations in scalability	99.9%
TiO ₂ reactor in indoor ventilation	Application in building systems Simplicity of use	Generation of side contaminants Lower efficiency	23-55%

often limited by slow mass transfer of BTEX from the air stream to the catalyst surface and the rapid recombination of photogenerated electron-hole pairs. The cost of developing and immobilizing advanced photocatalysts, coupled with the energy consumption of UV irradiation, challenges their economic viability. Maintenance is a persistent issue, as catalyst surfaces foul and deactivate, requiring frequent cleaning or replacement, which increases downtime and operational costs. A critical environmental challenge is the potential for secondary emissions; incomplete mineralization can release hazardous intermediate compounds (such as aldehydes and ketones) that are more toxic and persistent than the original BTEX, posing a greater health risk if not managed properly. Future research must pivot towards integrated process engineering for complete air purification. The focus should be on developing robust, visible-light-active photocatalytic materials resistant to fouling and

poisoning. Furthermore, combining photocatalysis with ancillary technologies such as adsorption or non-thermal plasma in a hybrid system is a promising approach. This would allow for the initial concentration of BTEX and subsequent efficient mineralization, ensuring both high energy efficiency and the prevention of secondary emissions, enabling practical deployment.

Despite the promising potential of photocatalytic oxidation (PCO) for removing gaseous aromatics such as benzene, toluene, ethylbenzene, and xylenes (BTEX), several critical limitations hinder its practical deployment in air-treatment applications. First, the kinetic efficiency under real-life conditions remains challenging. Many studies report fairly rapid removal at elevated concentrations in laboratory settings, but at low concentrations (ppb to low ppm) typical of ambient air or indoor environments, reaction rates drop considerably. For example, the oxidation of benzene in a

BTEX mixture was found to proceed much more slowly, resulting in prolonged exposure times (33,147-149). Second, incomplete oxidation and the formation of secondary pollutants are significant concerns. During PCO of BTEX on photocatalysts such as TiO_2 , strongly adsorbed intermediates, such as benzaldehyde, benzoic acid, or even benzene (from toluene oxidation), may accumulate and themselves pose health risks (149,150). Third, the sensitivity to operating conditions (humidity, temperature, oxygen concentration, pollutant mixture, light intensity/wavelength) adds complexity to practical systems. For instance, high humidity can block adsorption of BTEX on catalyst surfaces through competition with water molecules, or change the radical-generation pathways (62,149). Fourth, mass-transfer limitations and reactor design issues frequently govern real-world performance more than intrinsic catalyst kinetics. In the gas phase, delivery of BTEX molecules to the catalyst surface, and removal of products, can be rate-limiting — especially in fixed-bed or monolithic reactors under flow conditions. Fifth, catalyst deactivation and operational durability remain key obstacles. Accumulation of firmly bound intermediates on catalyst surfaces may block active sites and reduce longevity (149,150). Further, exposure to real-air contaminants (dust, NO_x , VOC mixtures) may impair performance over time. In summary, while PCO of BTEX holds significant promise, addressing these limitations — namely, low-concentration kinetics, safe handling of intermediates, stable catalyst operation, and validated reactor designs in real environments — is essential before widespread application.

Improving the efficiency of photocatalytic oxidation (PCO) of BTEX requires both material and process optimization.

1. Band-gap engineering through metal or non-metal doping (e.g., N, Fe, W) and constructing heterojunctions ($\text{TiO}_2/\text{g-C}_3\text{N}_4$, ZnO/CdS) extends light absorption into the visible region and suppresses charge recombination.
2. Incorporating plasmonic nanoparticles (Ag, Au) enhances light harvesting and charge transfer.
3. Combining adsorption–photocatalysis (e.g., TiO_2 -activated carbon composites) concentrates pollutants near active sites and increases removal efficiency.
4. Hybrid oxidation systems such as PCO–ozonation or PCO– H_2O_2 improve mineralization by generating additional $\bullet\text{OH}$ radicals.
5. Optimization of reactor design (monolithic supports, LED-based illumination, controlled humidity) minimizes mass-transfer resistance and improves quantum.
6. Finally, developing stable and regenerable catalysts with anti-fouling surfaces and testing them under realistic air matrices is essential for practical application.

Acknowledgments

Acknowledgements: The authors would like to thank the Environmental Health Engineering Research Center at Kerman University of Medical Sciences for their scientific support. Finally, the authors acknowledge to Dr Hamid Shirkhanloo for professional English language editing and proofreading of the manuscript.

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Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical issues

There is no ethical issue. The authors declare that all data collected during the study are as stated in the manuscript and that no data from the survey have been or will be published separately elsewhere.

Funding

This study was conducted at the Environmental Health Engineering Research Center, Kerman University of Medical Sciences. Also, it was financially supported by the Vice-Chancellor for Research and Technology at Kerman University of Medical Sciences (Reg. No. 404000550).

Supplementary files

Supplementary file 1 contains Table S1-S2 and Figure S1.

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