

CHAPTER:13

CHLOROPHENOL PHOTODEGRADATION IN WATER BY USE OF TITANIA BASED NANOMATERIALS

Azad Kumar*, Ankur Prajapati

Department of Chemistry, Siddharth University, Kapilvastu, Siddharthnagar

Corresponding author email: kumarazad20@gmail.com

Abstract

Many of the harmful pollutants such as organic compounds in water are generated diseases in human beings and contaminated our environment. Many industries produce these chemical waste and release into our environment. These chemical compounds created the many problems for the human and environment due the increasing of diseases and contamination of natural water bodies. Therefore, it is not possible to remove 100 percent of these toxic chemicals from the water bodies. We need the green technology which can remove 100 percent of toxic chemicals from the environment. A photocatalyst is defined as "a substance able to produce, by absorption of ultraviolet (UV), visible, or infrared radiation, chemical transformations of the reaction partners, repeatedly coming with them into intermediate chemical interactions and regenerating its chemical composition after each cycle of such interactions. Due to its exceptional qualities like nontoxicity, high photocatalytic degradation ability, and superior thermal and chemical stabilities, TiO₂ based photocatalysts demonstrate excellent absorption behavior toward organic molecules in wastewater. Significant environmental contaminants known as chlorophenols have caused major issues for both aquatic and terrestrial life. Therefore, to protect our ecosystem for future generations, their eradication requires urgent, efficient, and cutting-edge solutions. This paper includes a thorough investigation of the uses of chlorophenols, their negative effects, and their photocatalytic breakdown.

Keywords: photo degradation of toxic chemicals, photocatalyst, removal of toxicity

Introduction: -

Traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.) have been used for the removal of dye pollutants, but these techniques only succeed in transferring organic compounds from water to another phase, the degradation of dyes in industrial wastewaters has therefore received increasing attention and some methods of remediation have been proffered [1]. The dye might be reduced by the photo generated electrons, or they may interact with electron acceptors like O₂ adsorbed on the Ti(III)-surface or water, reducing it to superoxide radical anion O₂⁻ [2]. The organic molecule can be oxidized by the photo generated holes to make R⁺, or they can react with OH or H₂O to oxidize them into OH radicals.

They are said to be responsible for the heterogeneous TiO_2 together with other highly oxidizing species (peroxide radicals) [3]. One such heterogeneous catalysis technique is photocatalysis, which takes place between a solid catalyst—in the system we studied, a nanocomposite consisting primarily of a semiconductor containing TiO_2 —and the gas or liquid phase of the pollutant. Irradiation that produces electron-hole pairs in the semiconductor region prompts the photocatalyst to activate. Various and numerous kinds of volatile organic compounds (VOCs), including benzene, toluene, methyl/ethylbenzene, dichloromethane, etc., have been suggested for the degradation using these procedures. Due to the extensive contamination of natural resources like soil, air, and water bulk manufacturing of garbage. Both on humans and the ecology, their undesirable and varied effects are very evident. A significant amount of water contamination brought on by petrochemical wastes poses this concern [4]. Many organic pollutants, including halogenated phenols, are highly stable and are primarily used in numerous industrial applications, including dyes, medications, antibiotics, fungicides, herbicides, pesticides, rodenticides, germicides, de foliants, disinfectants, and atmosphere, soil, ground water, sea water, and even sweet drinking water to further add fuel to the fire [5].

2. Photo degradation of toxic chemical

(I). Chlorophenols

Given the potentially harmful consequences of chlorophenols, it is crucial to use green and sustainable solutions to minimize the build-up of these substances in drinking water. As a low-cost green technique, photocatalysis is frequently used to oxidize a variety of organic contaminants with the help of only solar energy and the right kind of nano photocatalyst. According to this method, chlorophenols are converted to low-molecular-weight compounds, CO_2 , and water while being protected against the creation of secondary dangerous chemicals during photocatalysis. The many photocatalysts currently in use each have advantages and disadvantages of their own. Due to their enormous band gaps, some of them are UV-responsive and need high energy photons to excite them for the necessary redox reaction, whilst others are visible light-responsive and may be activated with relatively low energy photons to bring about the oxidation of harmful contaminants. We discussed a few of the well-known photocatalysts used for the photocatalytic degradation of chlorophenols in the section that follows. This section provides a thorough explanation of the photocatalytic decomposition processes of several chlorophenols when exposed to various photocatalysts under prescribed conditions. Degradation of monochlorophenols through photocatalysis Monochlorophenols comprise 4- and 2-chlorophenols, also known as o- and p-phenols. photodegradation of monochlorophenols using a variety of photocatalysts and extensively highlighted the real mechanisms of photodegradation. It is interesting to observe that different photocatalysts delivered various intermediates when monochlorophenols were

degraded. Yang et al. suggested measuring the amounts of chloride ions released and total organic carbon to determine the photoelectrodegradation of p-chlorophenol using TiO₂ as photoanode. According to charge trapping tests, hydroxyl attack in the presence of dissolved oxygen molecules actually started the destruction of p-chlorophenol. The hydroxyl assaults during the photodegradation reaction were further supported by isotopic tracer tests utilizing labelled H₂O₁₈. P-hydroxyphenol is created when the chlorine at the para position is replaced by a hydroxyl radical, creating 1,4-benzoquinone. In the presence of dissolved oxygen and hydroxyl radicals [6].

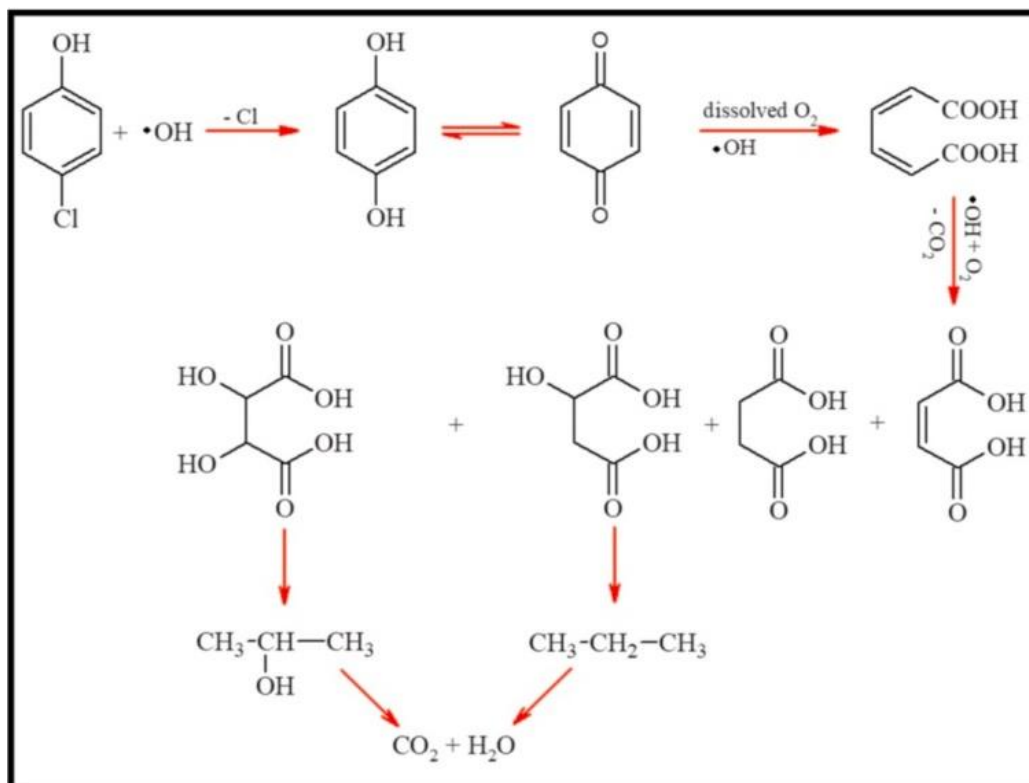


Fig [1] Hydroxyl based degradation mechanism of 4-chlorophenol [6]

the benzoquinone undergoes dissociation, rupturing the benzene ring and forming various compounds, such as unsaturated dicarboxylic acids, saturated dicarboxylic acids, and hydroxy dicarboxylic acids. The end products of photocatalytic degradation of dangerous compounds are simple CO₂ and H₂O, which are produced in the second stage of assaults when both saturated and unsaturated carboxylic acids are transformed. (Yang et al., 2009) depicts the entire degradation mechanism. Real-time analysis of the sequential evolution of complete molecular structures during photocatalysis provides exceptional opportunities to classify the reaction intermediates TiO₂ nanoparticles, and they identified the real intermediates produced during the decomposition procedure. Based on the two pathways they proposed, hydroxyl radical assault and derived intermediates. In the first pathway, the formation of p-hydroxyphenol or hydroquinone occurs simultaneously with the

elimination of chlorine and the entry of the hydroxy radical. When more hydroxyl radicals attack the newly acquired hydroquinone, it rapidly transforms into 1,4-benzoquinone, which ultimately breaks down into CO₂ and water. In the second pathway, the hydroxyl radical hits the ortho site first to create 4-chlorobenzene-1,2-diol, which, upon dechlorination, produces 2-hydroxyphenol or pyrocatechol in the subsequent step [7].

Data analysis

In chlorophenols' photocatalytic breakdown in this investigation could be modelled using pseudo-first-order kinetics. The following calculation [8] was used to calculate the rate of reaction for each set of experimental conditions:

Pollutant	Catalyst	k (min ⁻¹)	$t_{1/2}$ (min)	R^2	References
PCP	PorphyrinTiO ₂	4.23×10^{-2} 0.46×10^{-2}	15.1	0.9999	This research[30]
2,4,6-TCP	Porphyrin	1.30×10^{-2} 0.33×10^{-2}	106	-0.9634	This research[31]
	TiO ₂ FeR ₄ P-SiO ₂	0.66×10^{-2} 0.13×10^{-2}	53.3	-	[24]
2,4.-DCP	Porphyrin	0.13×10^{-2}	179.1	-0.9825	This research

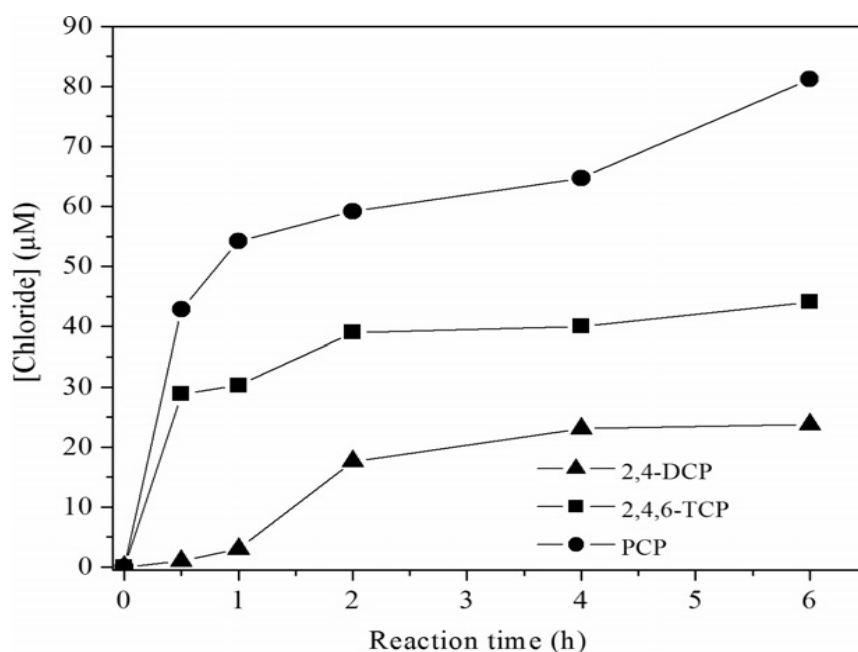
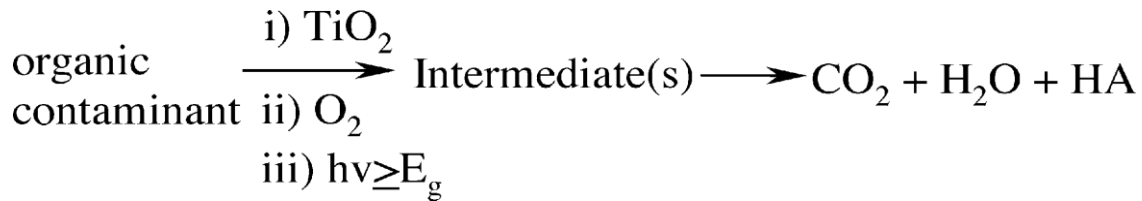


Fig. 5. Chloride released during P-PSD catalysed photocatalytic degradation of chlorophenols (reactor volume: 40 mL, chlorophenols concentration: 30 IM, star block copolymers concentration: [8,9])

2.2 Titania-assisted photo catalytic degradation: -

In order to produce charge carriers and hence trigger reductive and oxidative processes, titanium has been widely utilized as a photocatalyst [10]. In contrast to

a photosynthetic reaction, G is often negative for Titania-assisted aerobic photocatalytic reactions [8]. The non-metal substituent's equivalent acid, HA, is created as a byproduct:



The photocatalytic breakdown of organic molecules over a TiO₂ surface has been characterized in terms of numerous simple mechanistic processes. Surface-trapped valence band electrons are represented by the >Ti(IV)OH•+ and >Ti(III)OH, respectively, whereas surface-trapped conduction band electrons are represented by the >Ti(III)OH. Because the surface-bound OH radical, represented by >Ti(IV)OH•+, and the surface-trapped hole are chemically similar, the names can be used interchangeably [11]. The trapped hole and a surface-bound OH radical, according to Lawless and Serpone [12], are indistinguishable species. Charge carrier dynamics, their surface densities, and the effectiveness of photocatalytic degradation over TiO₂ are well correlated. Aqueous suspensions of TiO₂ have been studied over the past 20 years using picosecond and, more recently, femtosecond absorption spectroscopies [13].

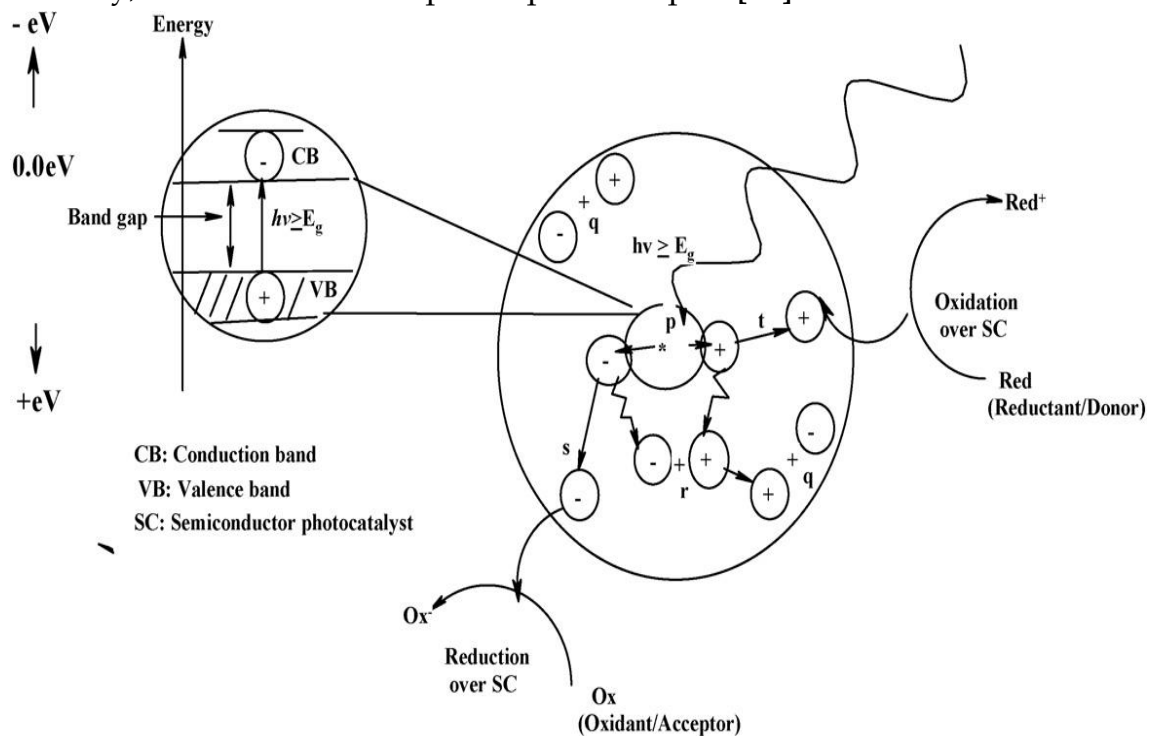


Fig. 2 A schematic representation of the photophysical and photochemical processes that occur over a photon-activated semiconductor cluster shows the following: (p) photogeneration of an

electron/hole pair; (q) surface recombination; (r) recombination in the bulk; (s) diffusion of acceptor and reduction on the surface of the SC; and (t) oxidation of donor on the surface of the SC particle [13,14].

Historically, such research has used an electron scavenger. Colombo and Bowman's femtosecond spectroscopy analysis of the TiO₂/SCN aqueous system] revealed a substantial rise in the population of trapped charge carriers within the first few picoseconds. Additionally, the outcomes demonstrated that for species adsorbing on TiO₂, In most applications, photocatalytic degradation reactions are carried out in presence of water, air, the target contaminant and the photocatalyst. The presence of water is indispensable in TiO₂ photocatalysis. Earlier work on 2-propanol photooxidation showed that the reaction did not proceed in the absence of water [13] shows the stages in the photoinduced processes of the photomineralisation of organic contaminant in presence of TiO₂.

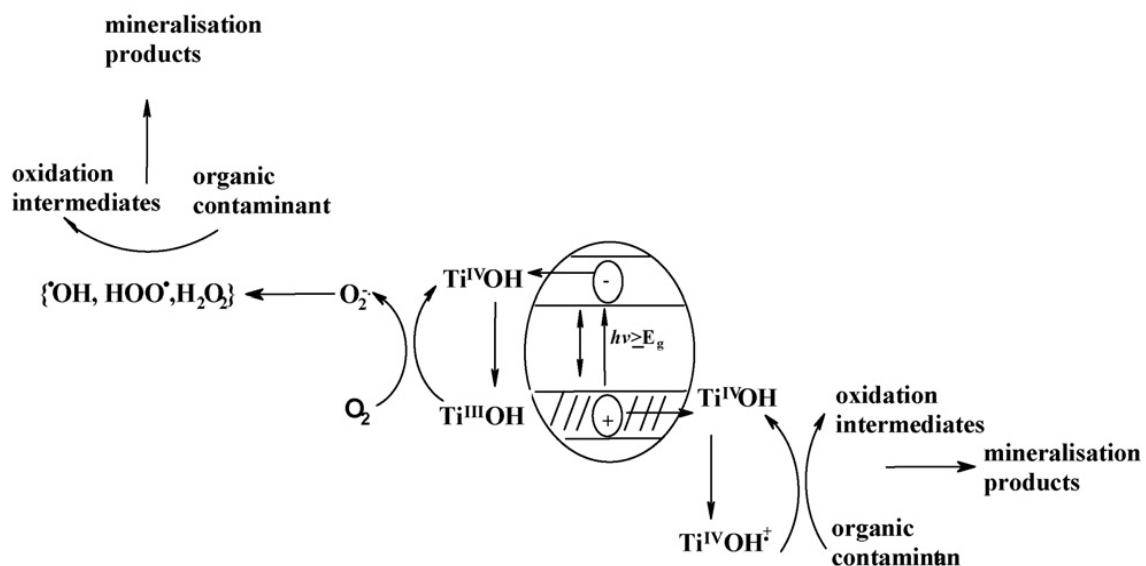


Fig 3 Conceptual diagram for the primary processes involved in photomineralisation of organic compound [15].

Photo-Oxidation Process

For aqueous solutions of various detergents and their combinations, the ultraviolet photo-oxidation technique was utilized (without TiO₂ as a catalyst). Low pressure UV lamps (8 w) and medium pressure UV lamps (150 w) were both used. After a 5-hour photo-oxidation process, the following levels of COD and TOC value reduction were attained. Sulfapol 35 is required for Sulfarokanol L-327 above 30% COD and 32% TOC. - 25% COD and 5% TOC, and above 30% COD and 18% TOC for Cleentex and car cleaning shampoo combo. The aforementioned figures were discovered for UV light 8 W.

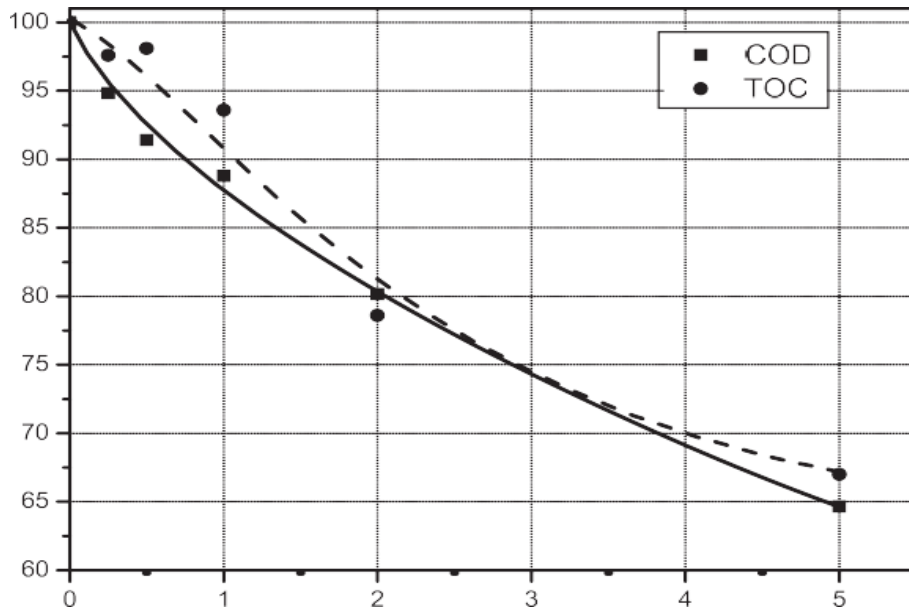


Fig. 4 shows the final COD and TOC values after 5 hours of photooxidation of Sulforokanol L-327 in water solution (lamp 8 w) [16]

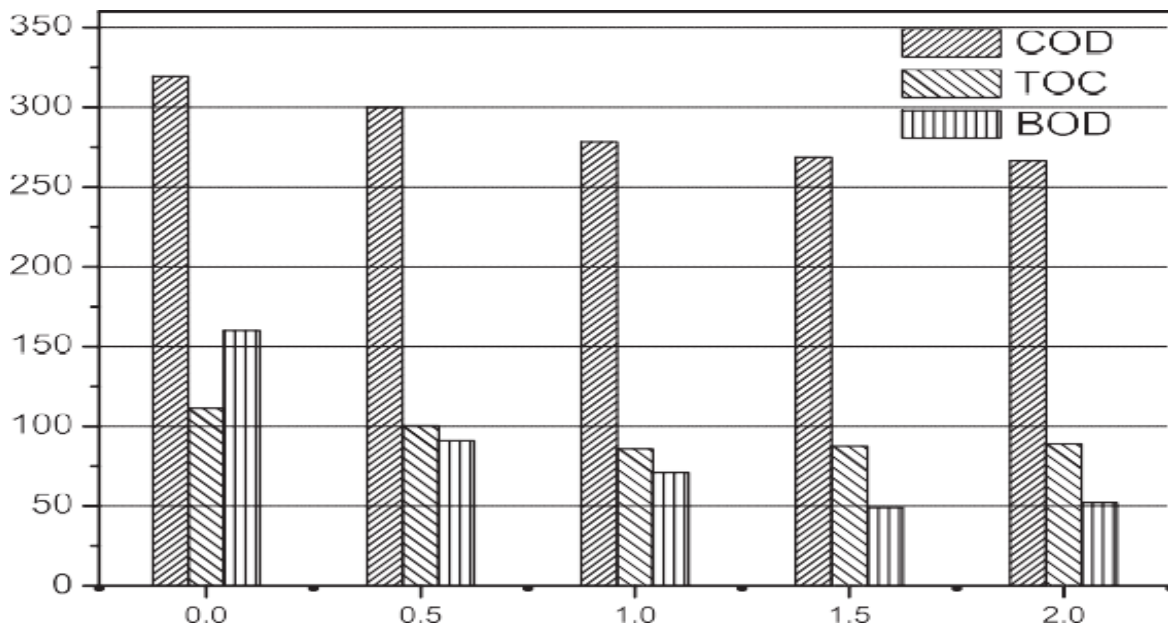


Fig. 5. The final changes of COD, TOC and BOD₅ obtained during photo-oxidation of Cleentex water solution for different applied doses of TiO₂ (lamp 150 w, pH = 10.9, 5 h)[16,17]

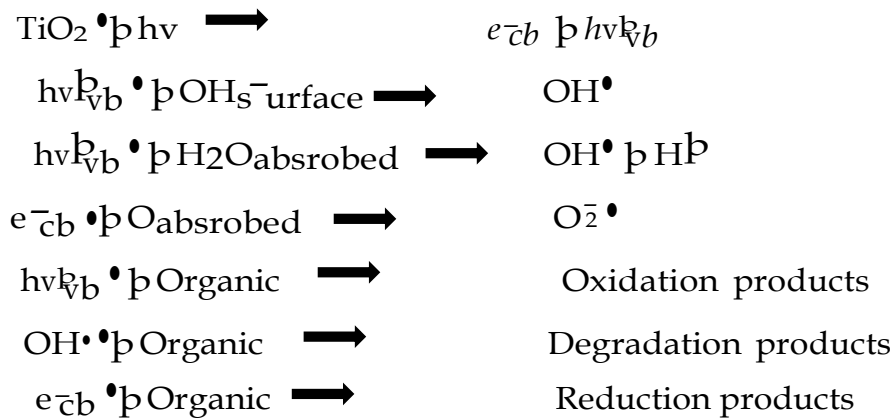
Photo catalytic degradation of dyes

Due to their color and toxicity, dye pollutants released in industrial wastewater frequently get a lot of attention. In several nations around the world, the dumping of these materials has caused major contamination. Because dyes can be seen by human eyes in water at even very low concentrations (as low as ppm for some colors), they

are regarded as an important class of contaminants in wastewater. Given that more than 10,000 commercially available dyes are inevitably employed in a variety of industries, including dyestuffs, textiles, paper, plastics, rubber, cosmetics, tanneries, paints, and leathers, dyes may significantly contaminate the environment Worldwide, more than 700,000 tons of dyes are generated each year; about 12% of that amount is lost in manufacturing or processing, and 20% of the dyes are lost [18].

TiO₂ photocatalyst: - Mechanism of TiO₂ photocatalytic reaction on organic pollutants

inside sewage, electrons and positive holes are produced in titanium dioxide's conduction (e⁻_{cb}) and valence band (hν_{vb}) under the influence of light (photons) According to Ahmad et al. (the holes can either directly interact with organic molecules or create hydroxyl radicals which then oxidize organic molecules show how the electrons can interact with organic molecules to produce reduction products. Since oxygen can interact with the photo generated electrons, its involvement is crucial.



Limitation of TiO₂ photocatalysis on organic pollutants in wastewater

The proportion of the articles for each restriction for TiO₂ photo-catalysis on organic wastewater is displayed in Fig 4 TiO₂ photocatalytic efficiency is inhibited by transfer limiting of electron and hole pairs, which occurs mostly on the surface of TiO₂. Titania is expected to experience electrode and hole charge carrier recombination, which will limit photocatalytic activity.

(2) Photocatalysts' poor affinity for organic pollutants (specifically hydrophobic organic pollutants)): Low organic pollutant adsorption on the TiO₂ surface led to delayed photocatalytic breakdown rates. Photocatalyst immobilization can offer a selective affinity toward target contaminants.

(3) Because nanoparticles are unstable, they may aggregate during photocatalytic degradation. This could prevent the active centers from receiving light radiation, which would impair the photocatalytic activities of TiO₂. TiO₂ aggregates as a result of particles being connected by organic compounds that are ionisable.

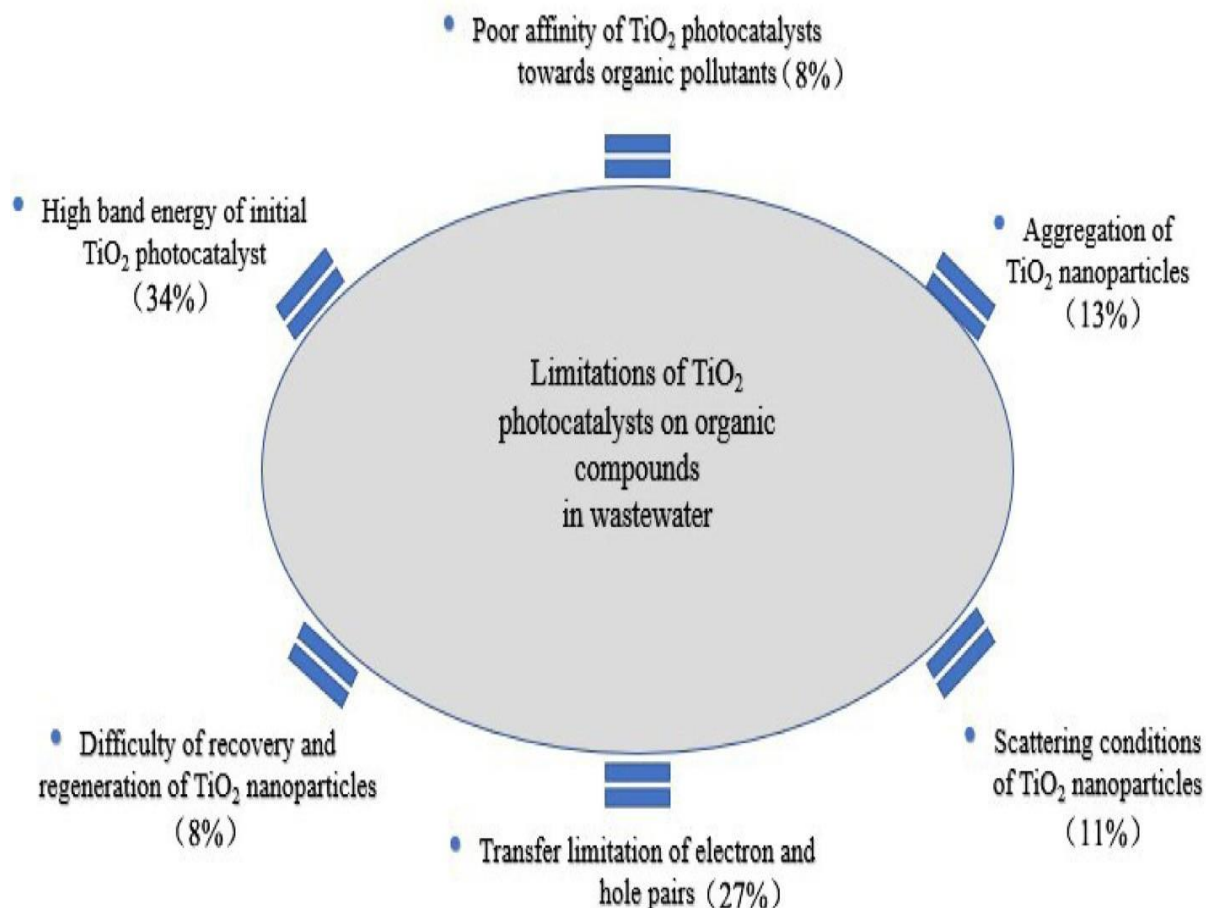


Fig4: Limitations of TiO₂ based photocatalysts on organic compounds in wastewater *the percentage of the articles related to each limitation is shown above [19].

Conclusion: - The destruction of persistent organic pollutants in both air and water can still be accomplished through heterogeneous photo catalytic degradation employing a TiO₂ photo catalyst. Environmentally friendly aerobic photocatalysis or methods that produce fewer intermediates still need to be developed to allow accurate development of models and successful application. Although the extent of photocatalytic degradation of organic pollutants is not entirely covered in this review, significant aspects of basic concepts and application have been touched upon.

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