The photocatalytic process in the treatment of polluted water

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Abstract
Wastewaters often contain toxic organic pollutants with a possible adverse effect on human health and aquatic life upon exposure. Persistent organic pollutants such as dyes and pesticides, pharmaceuticals, and other chemicals are gaining extensive attention. Water treatment utilizing photocatalysis has recently received a lot of interest. Photocatalysis is cutting-edge, alternative technology. It has various advantages, including functioning at normal temperatures and atmospheric pressure, cheap prices, no secondary waste creation, and being readily available and easily accessible. This review presented a comprehensive overview of the advances in the application of the photocatalytic process in the treatment of highly polluted industrial wastewater. The analysis of various literature revealed that TiO2-based photocatalysts are highly effective in degrading organic pollutants from wastewater compared to other forms of wastewater treatment technologies. The electrical structure of a semiconductor plays a vital role in the photocatalyst's mechanism. The morphology of a photocatalyst is determined by the synthesis method, chemical content, and technical characteristics. The scaled-up of the photoreactors will significantly help in curbing the effect of organic pollutants in wastewater.

Keywords Titanium (IV) oxide · Photocatalysts · Photoreactor · Wastewater · Organic pollutant

Introduction
The planet is mostly composed of water, which is the most crucial component of life. Water is necessary for the existence of all living beings on Earth. It accounts for 71% of the earth's surface (Panchal et al. 2019). Water has the physical traits of being clear, tasteless, odorless, and colourless (Sronsri et al. 2020). It might be polluted by a range of pollutants and pollution sources, including (Aarthye and Sureshkumar 2021). Dangerous substances are used in human activities (industrial wastes, fertilizers, pesticides, etc.) (Akhil et al. 2021) natural minerals and compounds such as arsenic, common salt, and fluorides Pathogens or disease-causing organisms such as amoebas, bacteria, and viruses, as well as pollutants that impact taste, odour, and colour. Water treatment is defined as the process of making water relevant and acceptable for a certain end-use, as well as eliminating and lowering the concentrations of water pollutants to match its intended purpose (Akpe et al. 2020). The amount and kind of wastewater treatment procedures used are determined by the original wastewater's quality, the numerous post-treatment needs, and the intended end-use. The purification of water sources is one of the most important concerns affecting the globe today. According to the World Health Organization (WHO), 844 million people lack access to safe drinking water, with 159 million relying on surface water (Al-Gamal et al. 2021). The scope of the water pollution problem is massive, with broad areas of the world suffering from poor water quality.

Water contamination has become one of the most pressing issues in recent years as a result of population increase and industrial development (World Health Organisation 2017). Separation is typically used to purify water contaminated with lipids, dissolved particles, suspended solids, organic ions, and radioactive compounds (Lin et al. 2020). Water treatment employs a variety of cutting-edge techniques, including membrane filtration, ion exchange, thermal distillation, reverse osmosis, and nanofiltration. These treatment procedures aid in the removal of suspended particulates as well as the majority of organic and inorganic components (Munirasu et al. 2016; Alzahrani and Mohammad 2014). Plankton and pollutants are
greatly decreased during wastewater treatment to improve the reusability of the water or before it is dumped into bodies of water. The treated water might be utilized as a drinking water supply, as well as in industrial, agricultural, medicinal, and other applications. The treatment method varies depending on the nature of the contaminated water (sewage, industrial, agricultural, and so on) and the purpose. Drinking water, for example, is treated with suspended particles, salts, and dissolved compounds (Medeiros et al. 2020). There are numerous therapy options available. Water may merely require sedimentation, or it may be contaminated to some extent. It is high and necessitates sophisticated processing. Many wastewater treatment technologies have been used to remove harmful substances from water (Devi 2011). Organic contaminants are removed using biological therapy (Pendashteh et al. 2010). For example, biological and chemical water treatment systems can release dangerous by-product toxins into the environment (Zare et al. 2015; Bechohra et al. 2015). Some pollutants, however, such as benzene, toluene, and ethylbenzene xylene (Jiménez et al. 2019), were not eliminated ((Fakhru’L-Razi et al. 2009; Jiménez et al. 2018; Butkovskyi et al. 2017).

Water treatment utilizing the photocatalytic approach has recently received a lot of interest. Because of its features such as excellent performance, functioning at ambient pressure and temperature, cheap costs, and the lack of secondary waste formation, the photocatalytic process is a contemporary and ecologically benign technology utilized in water treatment (Butkovskyi et al. 2017; Dewil et al. 2017). Table 1 displays the different pollution-control approaches, as well as their advantages and disadvantages. The photocatalysis approach demonstrates the distinction between older methods.

Using nanocatalysts, pollutants are transformed into CO₂ and H₂O during the photocatalysis process (Jiménez et al. 2019). Photocatalysis-based technologies play an important role in addressing major ecological shift challenges, such as environmental cleanup and renewable energy conversion. Photocatalysts can be used in hydrogen (H₂) synthesis, CO₂ reduction, pollution reduction, and water or air purification (through oxidation, for example, photo-reforming of organic substrates or water splitting). The photocatalytic method is based on a substance that speeds up the reaction without depleting or changing the reactants. This substance is known as a catalyst, and it accelerates a process by increasing the necessary activation energy and reaction rate without actively participating in the reaction. Semiconductors are utilized as photocatalysts because the energy gap between the valence and conduction bands is narrow. Because electrons go from the valence band to the conduction band, there is an electron in the conduction band and a positive gap in the valence band. The positive gap is a powerful oxidant capable of oxidizing compounds.

The energy corresponds to the energy of a photon with a wavelength of 388 nm, which is in the ultraviolet spectrum. TiO₂ is thought to be the best choice for use as a photocatalyst because of its benefits, which include corrosion resistance, inert properties, requiring less processing and preparation than other semiconductors, low toxicity, low cost, commercial availability, and photochemical stability (Nasr et al. 2018), as well as the ability to degrade a wide range of organic contaminants. Previous research has demonstrated that due to their huge surface area, suspended TiO₂ particles used in photoreactors create a high degree of activity (Carabin et al. 2015; Patchaiyappan et al. 2016). Titanium dioxide absorbs UV rays from the sun or any other ultraviolet-emitting light source. Under normal pressure and temperature, the energy of UV light is sufficient to free a negative electron and a positive hole. When titanium dioxide absorbs UV light, the electron in the valence band becomes active, and the e⁻ electron moves to the conduction band, leaving a positive gap in the valence band h⁺. The e-electron combines with the oxygen molecule and produces a highly powerful oxidizing anion, a process that continues as long as there is light available.

Review papers focusing on various aspects of photocatalysis have been published by Castilla-Caballero et al. (2022), Liu et al. (2022a), Wang et al. (2022), and Kajitvichyanukul et al. (2022). The authors’ goals of the review papers were concentrated on waste plastic mitigation using solid-state photocatalysis (Castilla-Caballero et al. 2022), sewage treatment by coupling photocatalysis with biological processes (Liu et al. 2022a), modification strategies for heterogeneous photocatalysis used for environmental remediation (Wang et al. 2022), and constraints in the applications of photocatalysis for the treatment of pesticides-contaminated wastewater (Kajitvichyanukul et al. 2022). The present study aims to further contribute to the existing review papers by analysing the various application of photocatalysis processes for the removal of organic pollutants from wastewater using TiO₂-based photocatalysts. Furthermore, the article concentrated on the mechanics of the adsorption of developing organic pollutants. usage, the photocatalyst process’s most recent industrial uses.

**An overview of photocatalytic mechanism for wastewater treatment**

The mechanism of a photocatalyst is dependent on the electrical structure of a semiconductor, which is a critical step. As seen in Fig. 1, the semiconductor is made up of a valence band and a conduction band. The bandgap energy is defined as the distance between the valence and conduction bands. When light is present, the high energy of photons stimulates the ions in the valence band to move on to the conduction band (Berenice and Garcia 2021; Sujatha et al. 2020).
| Table 1 | Advantages and disadvantages of pollution treatment methods (Liu et al. 2022a) |
|---------|---------------------------------------------------------------------------|
| **No**  |
| **Physical methods** | **Advantages** | **Disadvantages** | **References** |
| Sedimentation | 1. There is no requirement for energy  
2. High level of repeatability | 1. A selective process  
2. Isn't precise | Gottfried et al. (2008) |
| Degasification | Reduces the number of chemicals needed for the next step in the process | Pollutant removal capacity is limited | Saravanan et al. (2021) |
| Filtration | In some circumstances, autoclaving is possible | 1. Process that takes a long time  
2. Filters may become clogged | Medeiros et al. (2020) |
| **Chemical methods** | **Advantages** | **Disadvantages** | **References** |
| Flocculation and Coagulation | 1. It is used to remove tiny particles  
2. Metals, colour, and turbidity are all removed | 1. There are multiple steps in the procedure  
2. Toxic if used incorrectly  
3. Produces a lot of sludge  
4. High operational costs | Sun et al. (2020) |
| Ozonation | 1. There is no need for chemicals  
2. Removal of a wide range of microorganisms, organic and inorganic chemicals  
3. There's no need to change the pH or the temperature  
4. Increased germicidal efficacy | 1. Ozone's low solubility necessitates unique mixing techniques  
2. Ozone generation is more expensive than other methods  
3. Ozone generation might result in toxicity and fire hazards | Guo et al. (2019) |
| Chemical Precipitation | 1. Process control is simple  
2. Low-cost operations  
3. It works in a wide temperature range  
4. A pH that can be adjusted | 1. Sludge production in big quantities  
2. Difficulties with sludge disposal | Son et al. (2020) |
| Adsorption | 1. Low operating expenses  
2. relatively high Efficiencies  
3. Design simplicity  
4. Non-toxic technique  
5. The process of regeneration | 1. Adsorbent selectivity is low  
2. Disposal issues | Manikandan et al. (2018) |
| Ion exchange | 1. Resin regeneration is possible  
2. It is possible to obtain zero hardness  
3. Process of rapid separation  
4. The need for a small footprint | 1. In most effluents, pre-treatment is required  
2. Ionic competition is number two  
3. Matrix contamination | Liu et al. (2020) |
| **Biological methods** | **Advantages** | **Disadvantages** | **References** |
| Bioremediation | 1. A natural occurrence  
2. Treatment on-site  
3. Process that is cost-effective  
4. Total annihilation | 1. Take your time  
2. Heavy metals are not allowed to be ejected  
3. The bioremediation site must have high penetrability soil  
4. There are significant gaps in our understanding of the microbial ecosystem | Pavithra et al. (2019) |
| Aerobic Treatment | 1. Activity simplicity  
2. Reduces smell production  
3. Reduces pathogens and lipids in the body  
4. A greater variety of microbe kinds can be used for processing | 1. Expensive price  
2. Issues with upkeep | Pejman et al. (2009) |
| Anaerobic Treatment | 1. It generates renewable energy  
2. Less pollutants in the environment | 1. Expensive capital  
2. Unpleasant odour | Kong et al. (2019) |
| Oxidation ponds | 1. A high level of concentration  
2. There is a symbiotic relationship | 1. An issue with odor  
2. Requires more room | Haq et al. (2021) |
| Activated sludge | 1. Providing a reasonable profit for a new endeavour  
2. Doesn't take up a lot of room  
3. Is simple to use  
4. Effective in a moderate way | 1. Exorbitant operating costs  
2. The issue of sludge disposal | Bayan et al. (2021) |
The photocatalytic mechanism of TiO$_2$ photocatalyst is depicted in Fig. 1, and Eq. 1 explains how it works. The absorption of a photon from an energy source causes the active electron to shift to the conduction band, resulting in an apposite hole (hVB) in the valence band.

As electrons and holes recombine, the absorbed light energy is lost as heat, culminating in the process’s end. To avoid recombination, electrons and holes must be confined during the process (Kong et al. 2019). The positive hole in the valence band of the TiO$_2$ particle can react directly with the adsorbed material impurities (Caviggli et al. 2009). As seen in EQs, the hole oxidizes water or hydroxide ions (OH) to generate hydroxyl radicals (·OH) Eqs. (2) and (3)

\[
\text{TiO}_2 (h^+_\text{vb}) + \text{H}_2\text{O}_{\text{ads}} \rightarrow (\text{TiO}_2) + \text{HO} + H^+ \tag{2}
\]

\[
\text{TiO}_2 (h^+_\text{vb}) + \text{OH}^-_{\text{ads}} \rightarrow \text{TiO}_2 + \text{HO}_{\text{ads}} \tag{3}
\]

The photocatalysis mechanism is extremely oxygen-dependent. Superoxide (O$_2^-$) is produced during the oxygen reduction (O$_2$) in the conduction band. (Konstantinou and Albanis 2004) This phase results in the formation of oxygen radicals, which can aid in the elimination of pollutants by preventing electrons from recombining with holes (Pejman et al. 2009).

\[
\text{TiO}_2 (e^-_{\text{cb}}) + \text{O}_{\text{2ads}} + 2H^+ \rightarrow \text{TiO}_2 + \text{HO}_2 \rightarrow O_2^+H^+ \tag{4}
\]

The mechanism that generates superoxide ions in the conduction band can be further protonated to form the medium hydroperoxyl radical (HO$_2$), which is then coupled with hydrogen ions (H+) to produce hydrogen peroxide (H$_2$O$_2$) (Berenice and Garcia 2021).

\[
\text{TiO}_2 (e^-_{\text{cb}}) + \text{HO}_2 + H^+ \rightarrow H_2\text{O}_2 \tag{5}
\]

when H$_2$O$_2$ is used as an oxidizing agent in the photocatalytic process, it generates more hydroxyl radicals (Pejman et al. 2009). As a result of the increased hydroxyl radical yield, greater pollutant degradation rates may be attained, resulting in significant cost savings and decreased treatment complexity:

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{HO} \tag{6}
\]

\[
\text{H}_2\text{O}_2 + O_2 \rightarrow \text{HO} + O_2 \text{HO}^- \tag{7}
\]

\[
\text{H}_2\text{O}_2 + \text{TiO}_2 (e^-_{\text{cb}}) \rightarrow \text{HO} + \text{HO}^- + \text{TiO}_2 \tag{8}
\]

Hydrogen radicals and superoxide ions have a high rate of assault on impurities on the surface of TiO$_2$ particles. As a result, these two molecules (OH and O$_2$) are the major byproducts of TiO$_2$ photocatalysis. Because the contaminated molecules are continually broken down throughout this process, no trace of the original chemical remains, and no sludge is produced to be disposed of in landfills. There is no consumption of the catalyst utilized, and its concentration does not change. (Pejman et al. 2009; Kong et al. 2019) Formalized paraphrase.

**Application of TiO$_2$-based nanoparticles for wastewater treatment**

Semiconductor catalysts such as TiO$_2$, SrTiO$_3$, ZnS, ZnO, CdS, Ni/KTaO$_3$, and CuCrO$_2$ have been used to remove
pollutants from water. TiO₂ has attracted a lot of interest in the field of photocatalysis because of its high catalytic efficiency, stability, and non-toxicity. However, various TiO₂ modifications have been developed and tested (Chong et al. 2010a; Goodeve 1937; Lan et al. 2013), to overcome its poor photocatalytic reduction efficacy. Titanium is the ninth most prevalent element in the Earth's crust, and it is a very appealing compound (Zhao et al. 2020). Since 1916, pigment white, also known as titanium white, has been used in paint studios (food colouring, it is a natural white colouring agent for food and beverages). For the first time, white pigments with titanium dioxide photoactivity were produced in 1929 (Zhao et al. 2020). TiO₂'s photoactivity was first noticed between 1932 and 1934 (Hashimoto et al. 2005), and in 1938 TiO₂ was utilized as a photo-bleaching agent for dyes (Fujishima and Honda 1972), which was then referred to as a photosensitizer. TiO₂ photocatalysis was first used in 1956 after it was invented in 1969 (O'regan and Grätzel 1991; Ni et al. 2007). According to recent statistical research, there has been an exponential increase in the number of papers on TiO₂ photocatalysis since 2000, owing to its excellent properties. Particularly because of its larger surface-to-volume ratio than bulk (Linsebigler et al. 1995; Hashimoto et al. 2005; Fujishima and Honda 1972). TiO₂'s application has already been described (O'regan and Grätzel 1991; Ni et al. 2007; Wold 1993). Because it is non-toxic and chemically robust, it is employed as a dye in printing inks, plastics, cosmetics, soap, toothpaste, food (Murphy and Strongin 2009; Blake et al. 1992). It's also used to make sunscreen and foundation (Laschewsky 2003; Grätzel 2004). Because of its excellent optical and electrical properties, such as bandgap, acceptable band-edge, non-toxicity, thermal stability, and high chemical strength, broad titanium dioxide is now widely used to address current energy and environmental issues. It is also corrosion resistant, low-cost, long-term, and environmentally friendly. (Goodeve 1937; Fujishima and Honda 1972; Awati et al. 2003; Othman et al. 2014) and organic pollutant photodegradation TiO₂ has been widely used in solar cells and solar harvesting (Lan et al. 2013; Wold 1993; Bordes et al. 2021; Hoffmann et al. 1995) and is seen as a potential candidate (Chong et al. 2010a; Goodeve 1937; Othman et al. 2014; Roy et al. 2011).

Titanium dioxide (TiO₂) is often accessible in two forms: rutile and anatase, as seen in Fig. 2. Both forms may be obtained by two distinct procedures; the sulphate and chloride methods are only accessible for TiO₂ anatase, but they are more modern and less hazardous to the environment (Duan and Progress 2013). The structural differences between rutile and anatase titanium dioxide affect their physicochemical qualities significantly. Rutile-TiO₂ (r-TiO₂) is a more stable and less photoactive form of titanium dioxide. It possesses lower electron mobility, a higher dielectric constant, and a larger density (a-TiO₂) than anatase-TiO₂. The concentration of rutile in the sample lowers the point of zero charges of TiO₂ (Duan and Progress 2013; Linsebigler et al. 1995). Charge recombination rates are lower in r-TiO₂ materials (Fröschl et al. 2012). Anatase is less thermally stable than rutile (Han et al. 2009; Carp et al. 2004). However, anatase frequently reaches higher specific surface areas than rutile, which is important for (photo)catalytic applications (Han et al. 2009). In terms of photocatalytic activity, anatase outperforms rutile (Carp et al. 2004; Kinsinger et al. 2013). TiO₂ has a bandgap of more than 3 eV (3.2 for anatase and 3.0 for rutile), making it especially reactive to UV light. (Wang et al. 2015).

When compared to pure phases, phase mixes of diverse polymorphs should be aware of heightened photocatalytic
activity and synergistic effects (Hanaor and Sorrell 2011). However, for pure phases, anatase is usually considered to have better photocatalytic activity than rutile TiO₂ (Hanaor and Sorrell 2011; Chen and Mao 2007). Furthermore, the two polymorphs not only exhibit distinct photoactivity, but also different crystallographic orientations of the same material (Luttrell et al. 2015; Ohno et al. 2001). Despite substantial TiO₂ studies, there is no agreement on why different polymorphs or surface orientations have different photocatalytic activity. Some probable theories are as follows:

- Because anatase has a larger bandgap than Rutile TiO₂, the amount of light that may be absorbed is reduced. In comparison to the redox potentials of adsorbed molecules, it may raise the valence band maximum to higher energy levels. This increases the 'power' of electron oxidation and facilitates electron transport from TiO₂ to adsorbed molecules (Scanlon 2013). This idea has also been expanded to explain surface orientation-dependent activities by claiming that different surfaces have variable band gaps (Liu et al. 2012).
- Surface properties may impact molecule adsorption and subsequent charge transfer to the molecule. Surface properties may not only be polymorph dependant, but they may also change dramatically for the same material for different surface orientations or reconstructions (Kislov 2009; Yamamoto et al. 2005), which may explain why photocatalytic activities exhibit large surface effects.

Surface characteristics are classified into the following groups: (i) chemical effects such as surface coordination structure, which controls molecule adsorption (Batzill 2011); (ii) electronic structure of the clean surface or defects and adsorbate (e.g. hydroxyl)-induced states, which may be important for charge trapping and separation at the (Pan et al. 2003; Wilson and Idriss 2003); molecule (iii) Anatase’s indirect bandgap is smaller than its direct bandgap. Rutile, on the other hand, has either a direct bandgap or an indirect bandgap that is quite similar to the direct bandgap. Indirect bandgap semiconductors have longer charge carrier lifetimes than direct gap materials. Surface reactions would be more frequent with charge carriers, and rutile has a longer electron–hole pair life. Transient photoconductivity investigations on single crystalline samples show that anatase has higher charge carrier lifetimes than rutile (Wilson and Idriss 2002).

**An overview of organic pollutants and microorganisms in wastewater**

Organic pollutants in water can take different forms such as phenolic compounds, surfactants, organohalides, hydrocarbons, plasticizers, and other contaminants (Diebold 2003; Tao and Batzill 2010). Chemically stable, toxic, even carcinogenic, and resistant to breakdown in water (Tao et al. 2011; Xu 2011). The removal of organic pollutants such as cyanide and sulfite from simulated wastewater using photolysis had earlier been reported by Ali et al. (2012). Carey and co-workers also investigated the removal of polychlorobiphenyls using TiO₂-based photocatalysts under UV light (Ren et al. 2004). Also, it was discovered that halogenated organic molecules like trichloroethylene and trichloromethane can cause photocatalyzed oxidative breakdown (TiO₂) in a titanium dioxide-sensitive system, and formally proposed the oxidative decomposition function of semiconductor catalytic materials for organic pollutants (Wang et al. 2014; Li et al. 2019).

**Dyes**

Over 100,000 dyes are commercially available and employed in a variety of industrial applications (Tao et al. 2011). According to a World Bank estimate, textile dyeing generates 17–20% of industrial water pollution. With greater environmental concern comes the need for environmentally friendly technologies to remove colours from industrial and municipal wastewater (Frank and Bard 1977). The vast majority of dyes are water-soluble, non-biodegradable, and environmentally hazardous. Methyl Orange (MO), Rhodamine B (RhB), and Methylene Blue are a few examples (MB). Some of the hues utilized are Victoria blue, Rose Bengal, Indigo Red, Carmine, Red 120, Eriochrome, Methylene Blue (MB), Black-T (EBT), and Thymol blue. (John et al. 1976) Nguyen investigated the influence of TiO₂/ZnO/rGO composites on the UV-induced degradation of MB, RhB, and MO and presented degradation mechanisms and pathways. According to their findings, the heterojunction of TiO₂/ZnO/rGO materials can outperform a single material in terms of photocatalytic practical applicability, stability, and recyclability. This is attributable to the carrier's excellent separation efficiency, large surface area, narrow bandgap, and high dye adsorption capacity (Pruden and Ollis 1983a) on the other sides. Smith concentrated on the morphology of ZnO immobilization on PALFs as well as the photocatalytic activity of ZnO/PALFs in the removal of Congo red-containing wastewater. The catalyst displayed excellent performance (> 95%) and reusability for Congo red degradation under UV/vis irradiation settings (Pruden and Ollis 1983b). Mkhaiul investigated how a mesoporous Ag/Ag₂O–TiO₂ p–n heterojunction photocatalyzed the breakdown of dimethenamid-P herbicide under visible light. The photocactivity results demonstrated that imazapyr had been eliminated within 180 min (Rafiqa et al. 2021).
Pesticides

Pesticides are used as growth regulators, defoliants, desiccants, fruit thinning agents, ripening regulators, and to keep fruits and vegetables fresh throughout storage and transportation. Pesticides, on the other hand, are a significant source of water pollution. Pesticides are carcinogenic and have several negative side effects (Lu et al. 2020). Pesticides have two properties: toxicity and biological resistance. Pesticides, even tiny amounts, can remain in the environment and have a substantial impact on human health. Pesticide decomposition has also profited from semiconductor photocatalysis technology, which is chemically stable and non-biodegradable. (Nguyen et al. 2020) Liu examined the photocatalytic breakdown of triazophos residues in Chinese cabbage using Ce-doped TiO₂. (Senthil et al. 2019) Their findings revealed that the degradation efficiency of profenofos and triazophos after one day was 53.3% and 32.1%, respectively. Shawky investigated the photocatalytic degradation of atrazine herbicide using an Ag/LaTiO₃ nanowire (Liu et al. 2020). The results shown that using 2.5 wt. % Ag loading resulted in complete photodegradation of herbicide with photocatalyst after 40 min under visible light.

Microorganisms

Among the most common wastewater bacteria are enteroviruses, which cause a variety of gastrointestinal ailments, Adenoviruses, which cause respiratory illnesses, coronaviruses, which cause diarrhoea, tracheitis, and pneumonia, and Salmonella, which causes colitis, dysentery, and meningitis. Matsunaga et al. found in 1985 that utilizing TiO₂ as a photocatalyst may kill bacteria in water, so opening up a new route for photocatalytic inactivation of microorganisms. (AbuKhadra et al. 2020) Aside from the breakdown of various organic and inorganic molecules, additional studies have revealed that ROS oxidized the cell membrane, resulting in the release of nucleic acids, proteins, and specific cations, eventually leading to bacterial cell death (Mkhalid et al. 2020). Kim et al. used a Co-doped BiVO₄ technique to pretreat wastewater. E. coli (81.3% in 5 h) and Chlamydomonas pulsatilla (65.6 per cent in 1 h) are both killed by this method (Liu et al. 2019). Jamal Sisi et al. (2020) found photocatalytic inactivation of E. coli by g-C₃N₄@CoTiO₃ nanofibrous under visible light irradiation. The inactivation of E. coli resulted in a 6-log decline in bacterial cells after 90 min. Wong et al. (Wu et al. 2010) investigated the effects of photocatalyst concentration, solution pH, temperature, and inorganic ions of magnetic Fe₂O₃–AgBr under LED light on Gram-negative (E. coli) and Gram-positive (Staphylococcus aureus) bacteria inactivation. Further analysis of the mechanism (as illustrated in Fig. 3) demonstrated that bacterial inactivation can still be helped by the oxidation of H₂O₂ produced by the CB of Fe₂O₃ and the direct oxidation of h⁺ of AgBr.

Heavy metals

Heavy metal ions are required for metabolism, but excessive amounts can be hazardous. As metallurgy, mining, nuclear energy, and chemical manufacturing expand, large volumes of dangerous heavy metal ions are produced, posing a threat to surface and subsurface water supplies. Heavy metal ions have the unique capacity to connect to nucleic acids, proteins, and small metabolites in living animals, causing organic cells to be damaged and causing severe health problems. Heavy metal ions are not biodegradable; thus, they accumulate in the bodies of humans and animals via the food chain and drinking water. (Wang et al. 2012) As a result, harmful heavy metals such as Cr, Hg, Cd, Ni, Zn, and Mn ions must be removed from wastewater before it is dumped into the environment.
Photocatalytic removal of heavy metal ions in water can be accomplished by transforming dangerous high-valence heavy metal ions into low-valence ions or zero-valence metals.

**Chromium (Cr)** Chromium ions and compounds are released into the environment as carcinogens through oxygen anions (CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$, or HCrO$_4^-$) and cations (Cr$^{3+}$), where they directly harm human skin and internal organs (Regmi et al. 2017). The net reaction for Cr (VI) reduction in acid aqueous solutions is (Eqs. (9) and (10):

$$2\text{CrO}_4^{2-} + 16\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 8\text{H}_2\text{O} + 3\text{O}_2$$  

Heavy metal ions were eliminated by photocatalysis utilizing TiO$_2$-ZrO$_2$, which has great chemical stability and excellent sorption characteristics. According to studies, this material can easily degrade Cu (II) and Cr(VI) in one step and has high clearance rates of Cr(VI) (100%) and Cu(II) (91%) after four cycles (Song et al. 2020). The organic–inorganic hybrid PW12/CN@g-C$_3$N$_4$ composite increased photon absorbance and facilitated charge transfer, resulting in a Cr(VI) removal rate of 98.7 percent (Ng et al. 2016). The new Mn$_3$O$_4$ ZnO/Mn$_3$O$_4$ heterojunction was used to reduce Chrome VI and studying the removal mechanism revealed that Cr (VI) was reduced to Cr (III) by photocatalysis, and Cr (III) was further removed by adsorption, with a Cr (VI) reduction efficiency of 94.0% within 70 min under simulated sunlight irradiation (Khan et al. 2015).

**Lead (Pb)** Urban sewage, mining, and the chemical industry are the principal causes of lead (II) pollution. Lead has been related to several toxicological effects on human health and behaviour, and lead poisoning is potentially fatal. An example of a photocatalytic reaction (Eq. 10) is as follows:

$$2\text{Pb}^{2+} + 2\text{H}_2\text{O}_2 \rightarrow 2\text{Pb}^{2+} + 4\text{H}^+ + \text{O}_2$$  

Using heterogeneous photocatalysis, Pb (II) may be readily removed from aqueous solutions (Wang et al. 2020a). It exhibited a clearance rate of 98% and 97% against Pb$^{2+}$ and Cd$^{2+}$ ions, respectively, when utilizing superparamagnetic NiFe$_2$O$_4$-Pd, demonstrating greater photocatalytic activity than bare NiFe$_2$O$_4$ (Yan et al. 2020a). Kanakaraju et al. (2019) found that catalytic multifunctional TiO$_2$/Alg/FeNPs magnetic beads had a high removal rate for a range of heavy metal ions, and that removal of mixed heavy metals, notably Cr(III), Cu(II), and Pb(II) ions, was virtually complete (>98.4%) for all three ions within 72 min.

**Mercury (Hg)** Mercury (II) is a frequent constituent of industrial effluent, deriving mostly from Chlor-alkali, plastics, batteries, electronics, and obsolete medical equipment. The most severe injury to human health is caused by inhaling mercury vapour or organic mercury absorption through aquatic organisms, known as Minamata illness (Li et al. 2017). The following equation shows the process of metallic mercury deposition (11):

$$\text{Hg (II)} + \text{H}_2\text{O} \rightarrow \text{2H}^+ + 1/2\text{O}_2 + \text{Hg (0)}$$  

The use of mesoporous -Fe$_2$O$_3$/g-C$_3$N$_4$ nanocomposites, which displayed 4.6 and 6.8 times greater photocatalysis activity than pure -Fe$_2$O$_3$ NPs and g-C$_3$N$_4$ nanosheets (Murruni et al. 2008), is an exciting application of Hg (II) photocatalysis.

**Arsenic (As)** Heavy metal ions, such as arsenic (As), are difficult to biodegrade, rapidly accumulate in organisms and the environment, and are extremely dangerous despite their low concentrations (Thomas and Alexander 2020; Kanakaraju et al. 2019) Ebrahimi et al. A hydrothermal technique was used to create a BiVO$_4$/TiO$_2$/LED system. They discovered that under ideal conditions, more than 99.97% of arsenic at pH 4.5 could be eliminated in 120 min. Recently, nano-Fe$_2$O$_3$ enclosed in a carbon sphere as a photocatalytic nanocomposite has shown a greater capacity for oxidizing As (III) at pH 3.0, with a removal efficiency of around 70% of As (III) obtained in 120 min at a concentration of 400 µM.

**Pharmaceutical**

New pollutants, such as pharmaceutical compounds (PCs), have caused substantial concern in recent years due to their harmful impacts on the ecosystem (Tao et al. 2011). Traditional treatment methods, like as flocculation, air stripping, reverse osmosis, and others, are limited in their capacity to manage such pollutants. Heterogeneous photocatalysis is one of the most effective methods for decomposing hazardous compounds such as antibiotics (Hadi et al. 2015).

**Antibiotics**

Antibiotics have garnered considerable attention from PCs because they have an impact on aquatic ecosystems and are dangerous to human health (Kadi et al. 2020a). Antibiotics and their by-products are highly toxic, have good stability, and have a great potential to disrupt the environment and ecology. Antibiotics are discharged in large quantities into the aquatic environment via sewage and animal waste, causing major water pollution issues. As a result, it is vital to investigate effective methods for eliminating toxic compounds from wastewater. Moradi et al. (Yang et al. 2020b) used the MgO/ZnO/Graphene (MZG) ternary nanocomposite to test binary and single processes against refractory...
sulfamethoxazole antibiotics in simulated wastewater. After 120 min of sono-photocatalytic treatment at MZG: 0.8 g/L, pH: 9.0, LED power: 90 W, and US power: 250 W, 100 percent breakdown of sulfamethoxazole antibiotic (55 mg/L) is possible. The deteriorating effects of the nanocomposite decreased by up to 9.8% after six consecutive reuse cycles. Tetracycline (TC) is one of the most important antibiotics used in medicine. Tetracycline can be found in soil, groundwater, surface water, and even drinking water, where it contributes to antibiotic resistance and ecotoxicity (Wang et al. 2020b). It is seen as a potential risk to human health and aquatic ecosystems (Wu et al. 2019). Isari et al. (2020) produced N-Cu Co-doped TiO2@CNTs and employed them as a heterogeneous catalyst for sewage treatment using visible light and ultrasonic radiography. Under ideal conditions, sulfamethoxazole, (COD), and the (TOC) all exhibited removal efficiencies of 100%, 93%, and 89%, respectively. Adhikari et al. (Meng et al. 2017) observed that in visible light, Adhikari et al. The MoS2/Ag2Mo2O7 photocatalyst was created to oxidize the medicinal drug levofloxacin under visible light. There was improved catalytic activity (% efficiency) and remarkable stability with 30wt% MoS2/Ag2Mo2O7. This is because the heterojunction structure has the potential to dramatically enhance electron–hole separation, light absorption, and interfacial charge transfer efficiency to the adsorbed substrate.

Anti-inflammatories

Anti-inflammatory drugs have a high polarity and strong hydrophilicity, but their soil absorption coefficient is low, allowing them to persist in subsurface, surface, and even drinking water resources, causing major pollution. In the raw water supply of drinking water treatment plants, anti-inflammatory drugs such as ibuprofen, naproxen, diclofenac, ketoprofen, and others are routinely used. Humans excrete it into the aquatic environment, where it has a substantial impact on several marine animals such as freshwater algae, daphnia, and fish (Moradi et al. 2020). Khalaf et al. (2020) examined the removal of ibuprofen from water using titanium dioxide and photocatalysis. They confirmed that the TiO2 active thin layer immobilized on the glass substrate might be a feasible environmental protection method against emerging pollutants such as ibuprofen and its derivatives (Isari et al. 2020).

Petroleum hydrocarbons

Persistent priority pollutants include petroleum hydrocarbon pollutants such as alkanes, olefins, and polycyclic aromatic hydrocarbons (Adhikari et al. 2019; Yang et al. 2020a; Günal et al. 2019) reported that photocatalytic removal of organic pollutants from petroleum refinery effluent using nano-TiO2/Fe-ZSM-5 was effective. After 4 h of UV irradiation, the maximum chemical oxygen demand (COD) removal efficiency was 80% at a photocatalyst concentration of 2.1 g/L, pH of 4, and temperature of 45 °C. Two-dimensional ultrathin g-C3N4 nanosheets with high specific surface areas, short carrier migration lengths, and regulated electronic topologies exhibit significant photocatalytic oxidation removal capability for petroleum hydrocarbons in an aqueous solution. Khalaf et al. (2020) proposed a new visible-NIR-light-responsive decatungstate charge-transfer salt hybrid material that exhibited excellent charge-carrier separation through local surface plasmon resonance. As a consequence, it possessed significant photocatalytic activity and could be reused for the removal of petroleum hydrocarbons. Figure 4 depicts the mechanism of the RCD-CTS photocatalyst.

The effect of operational conditions on photocatalytic degradation efficiency

Several factors, such as catalyst dose, starting pollutant concentrations, pH, catalyst dosage, reaction temperature, and so on, impact the efficacy of photocatalytic degradation of organic pollutants. Aside from these optimization requirements, the catalyst’s qualities influence the overall efficiency of a process. As a result, to design an optimal photocatalytic process, a thorough understanding of these features is necessary (Fathinia and Khataee 2013; Liu et al. 2020).

Fig. 4 Under Vis–NIR light stimulation, the mechanism of the RCD-CTS photocatalyst (Li et al. 2017). 2020 Elsevier Inc. Copyright
Effect of pH solution

The initial pH of the aqueous solution influences the photocatalytic degradation rates. This is related to the pH of the solution, which may impact the adsorption of pollutants on the surface of the photocatalyst (Douglas et al. 2012). The pH is important because it allows the surface charge of the photocatalyst, TiO₂, to be measured. The photocatalyst’s isoelectric point (ZPC) is significant because when the pH of the solution is at the ZPC of the catalyst, the adsorption of pollutants (such as dyes) is at its lowest value (Ghasemi et al. 2016; Zare et al. 2021). In general, especially when TiO₂ is used as a photocatalyst, the interaction between the catalyst particles and the water contaminant(s) would be negligible at the TiO₂ ZPC. This is due to the lack of an electrostatic force. However, when operated at pH PZC(TiO₂), the photocatalyst’s surface charges become positively charged, resulting in an electrostatic attraction force towards negatively charged molecules. If the existing organic molecule contains an anionic charge, the adsorption of the organic contaminant(s) onto the surface of the activated TiO₂ is enhanced (Zare et al. 2021). When the pH of the photocatalyst exceeds PZC(TiO₂), the photocatalyst surface becomes negatively charged, rejecting anionic molecules in water (Jallouli et al. 2017).

Effect of pollutant concentration

The initial reactant concentration is regarded to be a critical element in the photocatalytic degradation of pollutants. The adsorption of material on the photocatalyst surface is utilized to investigate the relationship between titania’s photocatalytic activity and initial pollutant concentration. TiO₂’s photocatalytic activity normally decreases as the initial reactant concentration increases. This is explained by the limited number of activities accessible on the surface of photocatalyst nanoparticles (Wu et al. 2019). High ACT concentrations, for example, result in competition for active reaction sites and photons on the photocatalyst’s surface. Simply put, if the initial reactant concentration is high, the pollutant will occupy a greater number of titania active sites, preventing oxidant production and slowing breakdown rates. Furthermore, higher initial ACT concentrations might result in a greater quantity of photon absorption. As a result, there are fewer photons available to activate TiO₂, resulting in decreased photocatalytic activity owing to the inactivated catalyst surface (Jallouli et al. 2017).

Effect of irradiation intensity and time

Light intensity and irradiation duration are critical in the heterogeneous photocatalysis process. This is due to the activation of the photocatalyst and the generation of hydroxyl and oxide radicals, which can only occur in the presence of sufficient light energy and wavelength. As a result, several studies have investigated the effect of light irradiation on photocatalyst activity and pollutant degrading capacity (Kumar and Pandey 2017). The increased emphasis on using solar energy to degrade pollutants provides a sustainable, ecological, and cost-effective option for the heterogeneous photocatalysis process (Gogniat et al. 2006). Sharma et al. effectively created TiO₂–Fe₂O₃ nanocomposites with varying molar ratios using an ex-situ technique. They employed the manufactured catalyst to inactivate the dangerous pathogenic bacteria Escherichia coli under natural sun radiations (E. coli). The breakdown of E. coli was determined to be 99.28% in 120 min under direct sun irradiation (600–900 W/m²). The deterioration process can also be controlled by the irradiation period (Chong et al. 2010b). Davari et al. studied the effect of irradiation time on DHP photodegradation using a Fe₂O₃-TiO₂-Zeolite nanocomposite photocatalyst. The degradation of DHP was discovered to be time-dependent. For example, the DHP breakdown rate increased from around 60% after 60 min of irradiation to 90% after 180 min. This is because some medications, such as DHP, have a convoluted structure that needs a longer irradiation duration to achieve maximum breakdown (Khaki et al. 2017).

The effect of oxygen hydroxide

The presence of H₂O₂ accelerates photocatalysis dissociation for a variety of reasons, including an increase in the concentration of hydroxide radicals, the formation of additional oxidizing species, a weakening of electron recombination with positive holes, and thus an increase in the concentration of positive holes (Wu et al. 2019). The major cause of Photocatalyst for TiO₂ weakening is electron recombination with positive holes. The reactions shown below demonstrate the importance of (TiO₂) in improving the photocatalytic dissociation process. Equations (12), (13), and (14)

\[
\text{H}_2\text{O}_2 + e^- \to \text{OH}^- + \cdot\text{OH} \quad (12)
\]

\[
\text{H}_2\text{O}_2 + \cdot\text{O}_2^- \to \text{OH}^- + \cdot\text{OH}^+ + \text{O}_2 \quad (13)
\]

\[
\text{H}_2\text{O}_2 \to \cdot\text{OH}^- + \cdot\text{OH}^+ \quad (14)
\]

Catalytic dosage

The concentration of catalysts influences both the performance and practical implementation of a photocatalytic process. Maximum efficiency with the least quantity of catalytic dose is chosen for the economic feasibility of a process. Because reactive species are formed at the surface reaction centers of the catalyst, the rates of photocatalytic
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reactions are frequently low in the absence of a photocatalyst. As a result, there is a positive relationship between the rate and the catalytic dosage until an optimal catalytic dose is attained (Borges et al. 2016). However, there is a negative impact on the optimal limit, which varies based on the system in question. Excessive catalyst dosages can result in turbidity and a blocking effect, reducing light transmission through the bulk solution. According to Yakout (Sharma et al. 2018), low sunlight penetration into the system with a high concentration of Mn-doped -Bi₂O₃ resulted in a decreased breakdown of MB. Sun et al. discovered that UV light over 0.5 mg of BiVO₄ prevented phenol decomposition (Davari et al. 2017). Furthermore, at higher concentrations, the catalysts have an excellent agglomeration propensity due to their increased surface energy. These agglomerated structures result in a longer diffusion path and a lower surface area, which are both key factors associated with active sites. Achilleos et al. (2009) showed the effect of agglomerated structures and prolonged route length on the performance of sepiolite-TiO₂ nanocomposites towards OG degradation. As a result, the optimal catalyst dose should be maintained for better photocatalytic efficacy Achilleos et al. (2009).

Light energy

The intensity and wavelength of the light source, as well as the duration of light irradiation, can all affect the quantum efficiency and kinetics of a photocatalytic degradation process. Light irradiation provides the energy necessary for electron excitation from the VB to the CB of the catalyst. Because the intensity of the light source determines the overall energy available for a photocatalytic system, and the energy of each photon is dictated by the wavelength, both the intensity and wavelength of the light source are crucial. Malik et al. (2016) to get the most out of photocatalytic degradation of organic pollutants, the catalyst must be active over the whole spectrum of sunlight. However, the most widely used photocatalysts, such as TiO₂, ZnO, and SnO₂, are only active when exposed to UV light, which accounts for just 5% of the solar spectrum, or 388 nm (Yakout 2020). Due to their huge bandgap (E_g > 3.0 eV), most photocatalysts are unable to exploit visible and infrared light, which accounts for 43 and 52 percent of solar energy, respectively (Zare et al. 2021). Recent photocatalyst research has focused on the harvesting of visible light.

Temperature

Although temperatures over 80 °C encourage charge carrier recombination and prevent organic compound adsorption on the Titanium surface, they typically increase photocatalytic activity. (Chong et al. 2010a) Adsorption is favoured when the reaction temperature is less than 80 °C, although reducing the reaction temperature to 0 °C increases the apparent activation energy (Sun et al. 2011) As a consequence, the temperature range necessary for effective photo-mineralization of organic material has been determined to be 20–80 °C.

Mixing process

A good catalyst-water combination increases dissolved oxygen in the water and therefore the effective (O₂) in the photocatalytic process, emphasizing that oxygen is required as an electron acceptor in order to maintain the periodicity of the photocatalytic process (Zhou et al. 2018). It can be seen that the photocatalytic degradation of organic pollutants in wastewater is influenced by several factors discussed above which include pH of the wastewater, the concentration of the organic pollutants in the wastewater, the irradiation intensity and time, catalytic dosage, temperature, and the mixing process. The effectiveness of the photocatalytic wastewater treatment method is dependent on the optimization of these parameters. It is expedient that research efforts are concentrated on the optimum conditions of the various operating conditions in order to obtain an effective wastewater treatment process.

An overview of photocatalyst applications in wastewater treatment

In recent years, several researchers have investigated the use of photocatalytic processes in wastewater treatment. Sheikholeslami’s (Dong et al. 2015) employed c-Fe₂O₃ nanoparticles to evaluate the photocatalytic degradation of BTEX in generated wastewater, with BTEX serving as a produced water indicator. The essential factors affecting the photocatalytic degradation of BTEX were determined using the OFAT (one-factor-at-a-time approach) technique (pH (3–7), catalyst concentration (0–250 mg/l), UV light intensity (0–100 W), and visible light intensity (0–225 W). The COD test was employed as an indication to investigate the performance of the variables in the photocatalytic operation of BTEX breakdown by maghemite nanoparticles. According to their findings, the best removal efficacy of maghemite nanoparticles under visible and UV light was 95% in 5 days and 97% in 90 min. Indeed, maghemite nanoparticles are effective in removing BTEX.
Olga Sacco (Kumar and Devi 2011) investigated the removal of various water pollutants using visible light-emitting diodes in a packed-bed photo reactor with a simple cylinder architecture and an external light source utilizing a flexible LED strip. The structured visible light active photocatalyst is composed of N-doped supported TiO₂ particles (the N-TiO₂/PS photocatalyst) on polystyrene spheres. Methylene blue was nearly eliminated after 120 min of photoradiation. After 180 min of visible light irradiation, ceftriaxone, paracetamol, and caffeine were effectively eliminated from the photoreactor.

Tahir Hanee (Peral et al. 1997) investigated Euphrates (VI) oxidation, which eliminates aromatic polycyclic hydrocarbons from water. For the first time in this study, Euphrates (VI) oxidation was employed to treat 15 polycyclic hydrocarbons (PAHs) in the produced water sample, with a total content of 1249.11 mg/L. Operational factors such as Ferrate dosage (VI), contact, and pH duration were tuned for maximal PAH disposal and chemical oxygen demand. A central compound design (CCD) based on response surface methodology (RSM) was utilized to establish the best values of operating parameters. The percentages of PAHs and COD excluded were chosen as dependent variables. PAHs accounted for 89.73% of the total under optimal circumstances of independent factors such as iron (VI) content (19.35 mg/L), pH (7.1), and contact length, whereas COD accounted for 73.41%. The high values of the code client for identification (R) of PAHs (96.50%) and COD demonstrate the models’ accuracy and applicability (98.05%). Ferrate (VI) oxidation is an effective treatment method for removing pathways and COD from PW. RSM has also been demonstrated to be a good tool for optimizing operational factors, which has the potential to considerably cut testing time and costs.

The assessment of continuous flow in a packed bed (Pang et al. 2019) investigated the use of a TiO₂ reactor to remove microcystin from a waste stabilization lake. The photocatalytic efficacy of titanium dioxide in a complex matrix was investigated in this work (waste stabilization lake water). Four naturally occurring microcystin analogues were catalytically eliminated utilizing a flowing photocatalysis reactor (MC-LA, MC-RR, MC-YR, and MC-LR). In waste lake water, the removal of single MC isotopes has been proven to reach up to 51%. The treatment of MC-containing micro-gem cells did not result in a decrease in cell quantity or survival with the reactor structure and present treatment technology, but the catalytic treatment improved the overall quality of the waste lake water. The photocatalysis elimination process occurred in a continuous flow state. At the bench, this design enabled a reactor with a substantially longer route length to be modelled. To extend the results to a bigger system (one with a longer route), each sample point may be thought of as the consequence of a 900 mm path length increase. Because the test solution was insulated from UV light when not inside the reactor, no microcystin removal would occur between passes through the reactor. The reactor architecture suggested in this research lends itself to a larger application by raising the route length and catalyst load. The packed bed construction removes the requirement for post-treatment catalyst separation. Despite the existence of natural organic chemicals, this study shows that microcystin may be successfully eliminated in a complex environmental matrix.

Reyhaneh Nekooie (Sheikholeslami et al. 2018) created and employed a nanocomposite of copper oxide, titanium dioxide, and polyaniline (CuO/TiO₂/PANI) for the breakdown of chlorpyrifos in water under visible light irradiation. Fourier transform infrared (FT-IR) and diffuse reflection spectroscopy were used to investigate the nanocomposite (DRS). The light characteristics demonstrated that the nanocomposite could be powered by visible light irradiation, and the structural properties of the nanocomposite proved that it had been effectively produced. The resultant nanocomposite was utilized as a photocatalyst for the breakdown of chlorpyrifos in water, removing 95% of the pesticide after 90 min of light exposure. As parameters influencing the photocatalytic process, the initial pesticide concentration, pH, irradiation period, and photocatalyst dosage were all modified. Under the same circumstances, the photocatalytic activity of the CuO/TiO₂/PANI nanocomposite was greater than that of TiO₂/PANI and CuO/TiO₂. According to their findings, the nanoscale bandgap was narrowed, and the rate of photo-induced charge recombination was slowed. As a consequence, nanocatalyst catalytic efficiency has already been enhanced.

Cabangani Donga (Sacco et al. 2019) investigated the success made in eliminating organic pollutants, pharmaceuticals, and heavy metals from industrial effluent by utilizing magnetic graphene nanoparticles and graphene/TiO₂ nanoparticles. The nanocomposites revealed magnetic materials with effective graphene adsorption potential, as well as good photocatalytic capabilities based on graphene/TiO₂ in decontaminating industrial effluent including hazardous organic pollutants and heavy metals. Magnetic Characteristics Once impurities have been adsorbed, graphene-based magnetic materials allow for straightforward separation via magnetism. TiO₂ semiconductors’ great photocatalytic capacity assists in the quick elimination of organic pollutants, whereas graphene materials increase the surface area accessible for pollutant adsorption. In the literature, numerous nanocomposite materials with magnetic and photocatalytic activity capabilities to remove organic and inorganic pollutants from water and wastewater, such as GO/TiO₂, rGO/TiO₂, and Fe₃O₄/GO, have been created using a combination of synthetic approaches. The photocatalytic efficacy of graphene derivatives (such as GO) is proportional to their...
high surface area, and when an external magnetic field is applied to TiO$_2$, electron–hole recombination is reduced. Magnetic nanoparticles (such as Fe$_3$O$_4$) included in heavy metal adsorbents aid in magnetic separation.

Whereas Hanee et al. (2020) sterilized pesticide-contaminated water using photochemical reactions aided by visible light/nanobubbles, advanced photocatalysis has proven to be a successful method for inactivating bacterial spores due to its ability to convert solar energy efficiently while producing fewer byproducts. Through the intimate connection of micro/nanobubbles, a new technology for optically visible light water disinfection has been developed (MNBs). Bacillus subtilis inhibited at a steady rate of 1.28 h, which was 5.6 times faster than in the absence of MNBs. The remarkable order of gradation was confirmed using transmission electron microscopy (TEM) and emission-excitation matrix (EEM). Germ cells are destroyed during therapy. Experiments using ROS scavengers revealed that H$_2$O$_2$ and ·OH were the primary species actively engaged in microbial inactivation. The photocatalyst (Ag/TiO$_2$) oxidizes the efficient oxygen supply given by the H$_2$O$_2$-assisted Air-MNBs. Furthermore, it was discovered that the interfacial photoelectric effect of MNBs plays a role in spore inactivation. MNB, in particular, induced substantial light scattering, resulting in a 54.8% extension in the optical path length of the photocatalytic medium at 700 nm, which boosted photocatalyst light absorption. Because of the dielectric irregularity, the electric field was quite heterogeneous. In research, micro/nanobubbles (MNBs) have been employed to increase the disinfection capabilities of the classic visible light photocatalysis approach without the use of chemicals. Bacillus subtilis inhibitory effectiveness was much higher in the presence of MNBs than in the absence of MNBs. H$_2$O$_2$ and ·OH were the primary ROSs that contributed to the purges. By collecting photoelectrons and causing substantial light scattering, the MNBs offered a continual source of oxygen to commence hole oxidation, therefore extending the optical path in the solution.

To extract and recover lead (Pb) from the aqueous phase, a hybrid photocatalysis and crystallization reduction method was applied. The greatest removal of lead ions (Pb$^{2+}$) by photocatalysis was 79.6% under ideal circumstances (UV light intensity 35 W cm$^{-2}$, pH 5.3, and 2 g L$^{-1}$ TiO$_2$), according to a novel technique that combines crystallization reduction (RC) with photocatalysis (PC). (Pestana et al. 2020) Vivek Kumar However, when reducing agents such as hydrazine hydrate were used, the removal efficiency of lead ions improved to 90% under ideal circumstances (temperature 80 $^\circ$C and pH 10). Photocatalysis and crystallization reduction are two CO reduction processes that have been combined to remove 98.2% of lead (Pb$^{2+}$) ions from the aqueous phase, allowing for maximal lead removal and recovery. To evaluate the recovered sediments and photovoltaic catalysts, scanning electron microscope energy dispersive X-ray spectroscopy (SEM–EDS), X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) methods were utilized (TiO$_2$). The element lead was found in the collected sediments and TiO$_2$ based on EDS spectrum analysis (Pb). According to the XRD peak analysis, the deposits included lead with crystal diameters of roughly 90 nm. Indeed, the extracted titanium dioxide’s XRD spectrum exhibited additional peaks at specified angles, confirming the presence of lead on the surface of TiO$_2$. The photocatalysis rate for the elimination of lead (Pb$^{2+}$) ions was calculated using the first-order Langmuir–Hinshelwood equation.

Rong Zhang (Nekooie et al. 2020) employed ultrasound-assisted TiO$_2$/graphene oxide electrospray on polyacrylonitrile, where nanofibrous membranes increased the catalytic breakdown of organic dyes. Nanofibril films consisting of composites were created using electrospinning and ultrasonic-assisted electrospinning. Nanoscale titanium dioxide (TiO$_2$) and graphene oxide stabilised polyacrylonitrile (PAN)/cyclodextrin (-CD) (GO). SEM, EDS, TEM, and X-ray diffraction all show that GO and TiO$_2$ are uniformly distributed on the shell and inside the nanofibers after 45 min of ultrasonic treatment. The fibre diameter was lowered by the addition of TiO$_2$ and GO; when the TiO$_2$ to-GO mass ratio was 8:2, the fibre diameter was 84.66 40.58 nm (PAN/CD 191.10 nanofiber sheets were 45.66 nm). To investigate the photocatalytic activity of nanofibril membranes in natural sunlight, both anionic dye (Methyl orange (MO)) and cationic dye (methylene blue (MB)) were utilized as pollution simulators. The dye degradation efficiency of the composite PAN/-CD/TiO$_2$/GO nanofibrous membrane with an 8:2 TiO$_2$-to-GO mass ratio was found to be the highest. Degradation efficiencies for MB and MO were 93.52% and 90.92%, respectively. Meanwhile, the antibacterial properties of the PAN/-CD/TiO$_2$/GO composite nanofibrous membrane were good, and the degradation efficiency of MB and MO was maintained at more than 80% after three cycles, according to researcher Azar Fattahi (Donga et al. 2020). P25 supplemented with Ag nanoparticles was used for photodecomposition in the presence of natural organic matter. Advanced oxidation processes (AOPs) have received a lot of attention in water treatment research for removing PPCPs (Pharmaceuticals and personal care products) The capacity of commercially available titanium dioxide nanoparticles (P25) and P25 modified with silver nanoparticles (Ag-P25) to kill 23 specific PPCPs (2 g L$^{-1}$) (Suwanee River NOM, 6.12 mg L$^{-1}$) in actual water matrices containing natural organic matter was investigated in this work. UV-LED (ultraviolet light-emitting diode) lighting at wavelengths of 405 and 365 nm was used in the testing, with a final simulated visible light exposure. The results revealed that when both (P25) and (Ag-P25) were used, 99% of the PPCPs were eliminated.
after 180 min of treatment with UV-LED at 365 nm. The percentage of PPCPs destroyed by 405 nm UV-LED irradiation was 57% for P25 and 53% for Ag-P25, respectively. UV absorbance at 254 nm and DOC) dissolved organic carbon (UV254) measurements revealed that the aromatic component of NOM (natural organic matter) was preferentially eliminated from the aqueous matrix following the experiment. Furthermore, Ag-P25 was more effective in removing DOC from P25.

To eliminate medications, two researchers, Emine Baştürk (Fan et al. 2021a), employed modern therapy procedures. Their research sought to determine how effective the ozone, Nano TiO₂, and UV systems are at removing EDCs. Under varied working settings, the performance of Nano TiO₂ in breaking down endocrine-disrupting compounds targeted by catalytic and optical ozone was examined. With an ozone concentration of 10 mg/L, a pH of 6.8, a catalyst dosage of 0.050 g/L, and a photocatalytic performance duration of 10 min, the maximum pollutant removal was attained. The mechanism of the endocrine-disrupting drug's surface reaction, as well as ozone removal by stimulatory and photo-stimulation ways, were also studied. According to the findings, the catalyst can greatly enhance the composition of the targeted chemical disposal. Removal rates for catalytic ozone, catalytic partitioning, and single ozone were 99.0%, 88.3%, and 51.8%, respectively. These findings suggest that ozone/TiO₂/UV technology can be employed in engineering applications to eliminate endocrine disruptors such as steroid hormones and other micropollutants.

An intimately linked photocatalysis and biodegradation (ICPB) system comprised of Fe⁴⁺/g-C₃N₄ and biofilm were developed for the treatment of synthetic household wastewater containing SMX. Qidi Liu Jun Hou (Kumar et al. 2020) was the researcher in this study. The results showed that this ICPB system could remove 96.27% of SMX and 86.57% of COD simultaneously, which was superior to photocatalysis alone (SMX 100%, COD 4.2%) and solo biodegradation (SMX 42.21%, COD 95.1%). LED photocatalysis, biodegradation, LED photolysis, and the adsorption action of the carrier all contribute to SMX removal in the ICPB system, but biodegradation is primarily responsible for COD removal. Increasing the initial SMX concentration decreases the rate of SMX removal while increasing the photocatalyst dosage enhances the rate of SMX removal while not affecting COD removal. Our study of biofilm activity found that microorganisms in this ICPB system had a high survival rate and metabolic activity, and the microbial community structure of the biofilm remained constant, with Nakamurella and Raoultella as the two dominating taxa. This paper presents a unique method for treating antibiotic-polluted home wastewater effectively.

Alsarayreh (Zhang et al. 2021a) investigated the feasibility of exploiting the generated PW, which has the potential to be a beneficial supply of water. While there are a variety of approaches for treating PW for reuse, biological treatments provide a feasible, long-term option. Microalgae in particular is a low-cost, long-term alternative for eliminating organic toxins from PW throughout the bioremediation process. PW’s microalgae grow without interference, eliminate pollutants, and generate clean water that can be recycled and reused for a variety of treatment techniques. As a result, atmospheric CO₂ levels are reduced while biofuels, other valuable chemicals, and value-added goods are produced. As a result, the focus of this analysis is on the creation of PW in the oil and gas sector, the characteristics of PW, and various approaches to treating PW, with a particular emphasis on algae-based technology. Several aspects of algae formation and growth in PW were also reviewed, as well as the impact of growth conditions, water quality parameters, and treatment efficacy. Finally, as a long-term solution, this study looks into bioremediation using algae and PW, as well as how to catch algae that can be processed to make value-added commercial biofuels.

**Significant design and scale-up considerations in wastewater treatment**

**Photocatalytic solar reactor**

The artificial generation of photons required for the detoxification of filthy water is the major source of expenditures during the operation of photocatalytic treatment of wastewater plants. This demonstrates that the sun may be employed as a low-cost and ecologically beneficial light source (Fattahi et al. 2021). These photons are mostly employed in photocatalytic reactors to remove pollutants from water. Several Solar Photocatalytic Water Treatments Reactors have been created and tested during the previous 15 years (Enesco 2021). The following are the four most prevalent reactor designs (Baştürk and Karataş 2021; Liu et al. 2022b; Alsarayreh et al. 2022).

**Parabolic trough reactor (PTR)**

It is a plug flow reactor composed of 30–50 parallel (direct) rays of the sun spectrum’s active ultra-violet region. (Fattahi et al. 2021) Solar detoxification loops were initially developed in Albuquerque, New Mexico (by Sandia National Laboratories), Lawrence Livermore, California (by Lawrence Livermore Laboratories), and Almeria, Spain (by Lawrence Livermore Laboratories) (by the Platformer Solar de Almeria, PSA) (Alsarayreh et al. 2022). As illustrated in (Fig. 5) (Bahmann 2004b), it includes a parabolic trough collector (PTC), an SO₂ gas tank, a carrier gas tank (N₂),...
a gas mixing tank, a mass flow controller (MFC), and a flue gas analyzer. PTC is made composed of a single stainless steel parabolic mirror, one receiver tube, and collector support. PTC’s design was created using the parabola (Braham and Harris 2009). By concentrating, the sun is focused on the focal point of the parabola through the reactor (PTR). It is routed via a Dewar pipe, which is analogous to a parabola traveling through a solar-focusing pipe. The PTR was examined by different research organizations from several European nations (Kong et al. 2019).

**Thin film fixed bed reactor (TFFBR)**

It is one of the most essential varieties that may be utilized without concentrating equipment. TFFBR photocatalysis therefore employs both diffuse and direct UV-A radiation from the sun. A slanted plate with a photocatalyst such as Degussa P25 and a very thin coating (*100 m) washed with dirty water is a crucial parameter in the TFFBR process. It was critical to test the TFFBR to ensure that it worked properly. TFFBR was proven to be more effective than PTR in eliminating the same pollutants dissolved in pure water and genuine wastewater received from a variety of industrial units. (Kong et al. 2019; Braham and Harris 2009) Formalized paraphrase as illustrated in, a pilot-scale solar photocatalytic reactor of this sort has been created (Fig. 6). The entire procedure was designed to be a single-pass flow-through. As previously stated, (Kanmani and Sundar 2019), the reactor tilt was preserved at 20 degrees to the horizontal, and it was kept North-facing to offer the most potent effect from natural sunlight. During the whole operation, a Pyranometer (model SP1110, Skye Instruments, UK) was used to measure solar irradiance in W/m² at the same angle as the refractor, producing results in the range of 980–1100 W/m² (full sun-light conditions). The light surface area was 1.17 M in-depth and 0.4 min broad (0.47 m²), as in earlier studies (Alpert et al. 1991), and the irradiation size of the volume...
was 200 mL with a residence time (2.5 min) and a flow rate of (4.8 Lh⁻¹). The photocatalyst layer was not coated during the experiment, and the density of the TiO₂ photocatalyst was 20.50 g m⁻².

**Compound parabolic collecting reactor (CPCR)**

The solar CPC (10 L) was made up of an intake tank that was constantly aerated and stirred, a peristaltic pump, and a solar collector unit area (0.24 m²) (Alpert et al. 1991). As shown in the illustration, a reactor is made up of six Borosilicate pipes coupled to an Aluminium framing positioned on a panel at 30 degrees according to Patiala (India) locations (Fig. 7). To connect the glass tubes, which were evenly packed with catalyst-coated beads, plastic couplings and pipes were employed. A pyranometer was used to measure the intensity of light (Apogee: MP-100). The light intensity ranged from 800 to 900 Wm². Before the irradiation procedure, the wastewater is swirled for 30 min at a steady mixing rate to homogenize the reaction. The reaction was then started in the CPC containing composite beads using sun energy. The curvature of the reflecting mirrors on the PTR and CPCR is noticeably different. The reflector of a PTR has a parabolic shape, and the pipe runs parallel to the focal line. As a result, only parallel light entering the parabolic trough may be focused on the pipe. While the CPC's reflector is often made of two half-circle profiles arranged next to each other, focusing the light on a line directly above the two circles' linkages. (Miller 2017). Compound parabolic concentrators may collect radiation at various angles depending on the angle at which the sun's rays fall upon the surface. The absorber surface at the collector's bottom will absorb a light beam that enters the aperture at the permitted angle. The low reflectivity of the surface might result in significant optical losses (Anderson 1983).

**Double skin sheet reactor (DSSR)**

It is a flat and transparent structural box made of PLEXIGLAS® (Malato et al. 2009) PLEXIGLAS® is a trademark for a commercially available transparent thermoplastic known as Poly (methyl methacrylate) (PMMA). PLEXIGLAS® transmission begins below 400 nm, which is the wavelength of the UV-A part of the solar spectrum. Figure 8 displays the DSSR’s internal construction. These channels allow the model pollutant and photocatalyst suspension to flow. The DSSR can benefit from both diffuse and direct sunshine (Malato et al. 2009).

As discussed above, each of the reactor designs has proven to have a significant potential effect on scale-up considerations in wastewater treatment. However, there is a greater prospect of utilizing the TFFBR which has proven to be more effective than PTR in eliminating the same pollutants dissolved in pure water and genuine wastewater received from a variety of industrial units. However, advances in research and development to improve the design of the CPCR could revolutionize the scale-up of the photocatalytic wastewater treatment process.

**Photocatalytic reactors design**

Figure 9 depicts the basic components of photoreactor setup technology, including photocatalysts, light irradiations, auxiliaries, additives, and so on. Composition and morphology are the two most important elements to consider when it comes to semiconductor photocatalysts. The composition influences the mobility of charge carriers during photocatalytic activity (Khan et al. 2012; Talwara et al. 2020). The fundamental composition includes a mono-component photocatalyst such as TiO₂ (Chee et al. 2012), WO₃ (Kalogirou 2016), ZnO (Chen et al. 2021), and Cu₂S (Yang et al. 2020c). Even when doped or surface photosensitized,
these materials exhibit charge recombination issues, a limited absorption range, and low chemical stability (Zhang et al. 2021b; Fan et al. 2021b; Qiao et al. 2020). The heterostructures, which are multi-component photocatalysts, benefit from a broad light spectrum, allowing them to use UV, visible, or near-infrared photoexcitation depending on their energy band gaps and capacity to produce oxidative radicals for organic pollutants removal. Several processes may be used to create the heterostructure: type I junctions (Baneto et al. 2015), type II junctions (Teixeira et al. 2019), Schottky junctions (Wang et al. 2019), Z-scheme mechanisms (Abdullah et al. 2019), or S-scheme mechanisms (Albornoz et al. 2021). Except for the Schottky junction, which may have one semiconductor connected with metal, these heterostructures contain at least two semiconductors with the appropriate location of energy bands. The heterostructure photocatalysts perform better than their components due to their variable band energy configurations and effective charge carrier separation. Because photocatalysis is a surface-dependent process, photocatalyst form is critical. Nanoparticle semiconductors and immobilized thin films are frequently mentioned in articles discussing the evolution of the photoreactor. Increased active surface area is essential for high photocatalytic effectiveness because it facilitates the formation of high-energy active sites that contribute to the formation of oxidative radicals (Das et al. 2021; Feng et al. 2021).

The photocatalyst morphology is influenced by the production process, chemical composition, and technical parameters (Li et al. 2021). The light source is an important consideration when designing a photoreactor. The overall pollutant removal efficiency is controlled by the photocatalytic setup’s light intensity, spectral range, and radiation source position (Wageh et al. 2021; Kadi et al. 2020b).

Except when sunlight is used directly to excite photocatalysts, all artificial light sources must be designed to ensure uniform photon dispersion and long-term process energy sustainability. The penetration index required to overcome dispersion produced by the working environment must be incorporated into the intensity of the light source. Furthermore, the photocatalyst qualities required to overcome the bandgap energy should be linked with the spectrum range of the light sources (Kaur et al. 2018; Yan et al. 2020b). The operating regime (static or dynamic), photocatalyst morphology (powders or bulk), and liquid volume all have an impact on photoreactor design and concepts (Pu et al. 2019; Bagyalakshmi et al. 2018). Suspension photocatalyst photoreactors have the advantage of being simple to build and having a large specific photocatalyst surface area. The disadvantage is the difficulty in retrieving and reusing the catalyst, as well as the shadow effect, which may limit light penetration during photocatalytic activity.

Fibers (Tao et al. 2018), fixed bed reactors (Enesca et al. 2015), packed beds, and monolith (Qin et al. 2020) photoreactors with immobilized photocatalysts have the advantage of easy operation and catalyst recovery. However, homogeneous dispersion of the photocatalyst in the wastewater volume remains a challenge. Experiment-derived mass transport and reaction kinetic data may be integrated with the computational fluid dynamics approach to optimize important photoreactor setup factors like reactor chamber design or operational parameters (flow rate, irradiation duration, etc.) (Supplis et al. 2018; Sawicka et al. 2019). As a consequence, experimental and numerical techniques may be utilized to provide input data for the development of sustainable and cost-effective photoreactors tailored to a certain pollutant and volume (Li 2015).

Cylindrical photoreactors

Cylindrical reactors are frequently irradiated by a central lamp or lamps positioned in a circular pattern (Fig. 10) (Neolaka et al. 2019). The photocatalyst can be dispersed in the liquid or fixed on various surfaces (including the lamp cover). A storage tank (with aeration and mixer), pumps, valves, a flowmeter, and a control system capable of managing the entire system are all standard components of the arrangement. The storage tank must be aerated in order to maintain oxygen saturation levels during the formation of oxidative radicals. The cylindrical reactors benefit from radial flow distribution, which increases the diffusion homogeneity of the mobile photocatalysts. The most common organic pollutants that may be eliminated by this sort of Photocatalytic utilizing cylindrical reactors (phenols, pharmaceutically active chemicals, colours, and so on) are listed below. By optimizing the geometrical arrangement with the irradiation scenario, pollutant characteristics, and
technological aspects, cylindrical photoreactors may be entirely integrated into large-scale wastewater treatment systems. Energy consumption must be considered while proposing a cost-effective plan for expanding reactor capacity.
A key issue is a difficulty to anticipate changes in photocatalytic performance based on pollutant type and catalyst interface chemistry (Neolaka et al. 2019; Manjunath et al. 2020).

Rectangular photoreactors

Irradiation sources in this sort of reactor can be placed on the interior lateral sides, as indicated in Fig. 11 (Neolaka et al. 2019), in the middle, horizontally, or vertically in the corners, or on the interior lateral sides. Immobilized photocatalysts can be placed on reactor walls, lamp covers, or even individual substrates (e.g. glass, textiles, and composites). When using mobile photocatalysts, the flow rate must be tuned to the shape of the reactor to provide equal diffusion across the volume. As a consequence, the photoreactor setup components are chosen to maximize the formation of oxidative species, which is required to eliminate organic pollutants. The rectangular reactors, which are based on a modular design, may be readily upcaled, allowing for an increase in the volume of treated solution in each cycle. Rectangular reactors, because of their form simplicity and geometrical variety, may be employed for both small indoor and big outdoor applications. The main problems are to minimize excessive velocities and provide homogenous photocatalyst irradiation by managing the flow rate and irradiation settings (Azam et al. 2019).

Conclusion

Photocatalytic processes have made significant progress in the treatment of highly contaminated industrial wastewater, according to this review. The review of the published articles revealed that TiO₂-based photocatalysts outperform alternative wastewater treatment photocatalytic systems in degrading organic contaminants. The synthesis technique, chemical composition, and technical qualities all have an impact on the photocatalyst's physicochemical properties. Organic contaminants in wastewater can be considerably reduced if photoreactors are increased in size. Using the photocatalysts, the pollutants are transformed into CO₂ and H₂O. TiO₂ is one of the most commonly utilized catalysts in the process, even though there are many other types of catalysts. The photoreactor setup must be optimized to enhance the photocatalytic performance with the added components to achieve a proper balance between the treated solution volume and the pollutant quantity removed at the end of the cycle. Furthermore, testing conditions should be constant to decrease testing errors across several works. The use of solar light-driven photocatalysis for environmental remediation should be broadened to encompass newer areas such as CO₂ reduction and N₂ fixation. Overall, photocatalysis powered by solar light is one of the most promising technologies for tackling global energy shortages and pollution. Future research should focus on the creation of pilot-plant studies that use actual wastewater under actual conditions to evaluate the treatment system's efficacy in terms of pollutant degradation rate as well as economic aspects.

The solutions for improving photocatalytic performance were outlined by the synergistic impact of various operating conditions. The degradation efficiency and re-utilization are still low and cannot be implemented in reality, despite recent significant gains. The research trends in this study show that photocatalytic efficiency is strongly influenced by various operational factors and reactor designs. In addition to the effectiveness of the catalyst itself, factors such as degradation concentration, pH, temperature, the charged nature of the pollutant, the reactor, and the light source lamp are all critical to achieving optimal efficiency in a photocatalytic reactor. As a result, the design and manufacture of photocatalysts for the photocatalytic treatment of organic contaminants require careful consideration of all relevant parameters.

The photocatalytic water treatment studies take numerous elements into account, although they generally employ laboratory sites of simulated single pollutant wastewater, which nevertheless entails a high degree of complexity in comparison to genuine industrial or natural waste. Reactor design to enhance separation efficiency, photocatalyst optimization, and immobilization for recycling are all important aspects of furthering rational photocatalytic system development.

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Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

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