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Photocatalysis and photodegradation of water: A review of processes and advancements

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Abstract

In recent decades, photocatalysis has drawn in a great deal of consideration as a low-cost and environment friendly technology that has shown to have a substantial potential for cleaning up water contamination. The photocatalyst is the crucial component; numerous photocatalysts have been created. The potential for photocatalytic processes to aid in the deprivation of impurities in the aquatic environment and wastewater treatment is significant. It has been demonstrated that humic compounds exposed to sunlight in natural waters produce several reactive species, including hydroxyl radicals, hydrogen peroxide, singlet oxygen, and superoxide. These species can cause the oxidation and/or dichlorination of organic contaminants by interacting with them. A considerable portion of some contaminants can be found in biologically based elements of natural waterways like algae, and research has shown that algae can photo catalyze the breakdown of several persistent organic pollutants. Numerous organic and inorganic contaminants have been proven to be broken down by heterogeneous photocatalysis employing semiconductors like titanium dioxide (anatase).

Keywords: degradation, photocatalysis, water pollution, emerging photocatalyst

Full length review article **Corresponding Author*, e-mail: aqsabaig098765@gmail.com

1. Introduction

Water, air, and soil—three of nature's most valuable gift—are essential to our survival on this planet. Water is the most vital component because it is the basic medium in which life began [1]. But this precious gift is now getting contaminated due to many natural reasons (global changes) and human activities. Agricultural, industrial, domestic activities, accidental oil leakage, fossil fuels, radioactive substances, river dumping are the main causes of water contamination because it adds many microorganism (including bacteria and viruses), organic pollutants (dye, lubricants, surfactants), inorganic compounds (heavy metals) and other hazardous substances in the water. Therefore, there is a great necessity to increase the superiority of the water. The need of water quality depends upon the purpose of its use in drinking, agriculture, domestic, and industries [2]. The class of synthetic organic compounds known as dyes plays an important role in a variety of industries. In a recent world, textile industry effluents have been increasing which caused water contamination. There are various dyes for textiles which are carcinogenic in nature and the occurrence of these dyes in the liquid wastes has a undesirable effect on the aquatic environment's equilibrium, necessitating their prior treatment [3]. If the dyes remain untreated, it may cause the coloration of water bodies as it obstructs the sunlight to reach the photic zone and have cancer-causing, teratogenic and mutagenic properties that poisonously affect aquatic animals and plants [4]. Moreover, in human beings, in addition to cancer(especially of kidney, bladder and liver), these dyes may be responsible for causing skin allergic reactions [5]. Water pollution leads to a process called eutrophication (algae and plant growth increases on the surface of water) that may increase the death percentage of aquatic organisms especially fish. In humans, drinking polluted water may spread many diseases for instance; cholera, polio, typhoid, kidney damage, hepatitis and many others. Every year, about 485000 deaths are caused due to diarrhea by drinking contaminated water [6]. Many water-dwelling animals may get suffocated due to contaminated water. Many herbivorous animals which depend upon the irrigation water, may get infected by intaking the polluted irrigated water. Contaminated water has also adverse effects on the plants as it damages the root hairs, and bark of the leaves. Moreover, it may also inhibit the photosynthetic process in many aquatic plants. Many marine animals and seabirds have been killed because of ocean wastes [7]. Detection of the dyes and other pollutants in the water is easy but many hydrologists face difficulty in eliminating the dyes and some other pollutants from the water as a result of their high solubility in water, small amount and aromatic chemical structure [8-11]. The procedure of making water appropriate and suitable for a particular end-use, with the removal and reduction of the concentrations of pollutants in the water, is referred as water treatment. Coagulation, extraction, chemical oxidation, reduction, membrane separation, reverse osmosis, electrochemical oxidation, biological degradation and ozonation are some old methods for removal of pollutants from the water. But these methods are not significantly favorable for removal of contaminants, in a recent era, because of their high cost, less efficiency, and poor dye separation ability. So, there should be cost friendly method for the elimination of impurities from the water. [12]. Photocatalytic degradation technique is considered as more significantly favorable for the removal of contaminants from the water. These techniques have an excellent approach in removing the pollutants and metal ions from the water, because of its cost friendliness and greater effectiveness which makes it more appealing [13].

One of the biggest problems affecting the world nowadays is the purification of water sources. 844 million people are facing the shortage of clean water for drinking purposes, with 159 million reliant on surface water, according to the World Health Organization (WHO) [14]. The rapid rise in inhabitants and industrial expansion has made water contamination one of the most urgent problems. Water dirtied with lipids, dyes, dissolved particles, inorganic ions, suspended solids, organic ions, and radioactive chemicals is often purified via separation. Modern methods for treating water include reverse osmosis, nanofiltration, thermal distillation, ion exchange, and membrane filtration. These treatment techniques help to remove the majority of inorganic and organic pollutants, as well as dispersed particles [15]. To clean water of dangerous contaminants, a variety of wastewater treatment technologies have been employed. Biological therapy removes organic pollutants. For instance, water treatment processes that use both biological and chemical methods might discharge toxic byproducts into the environment. However, some contaminants like benzene, toluene, and ethylbenzene xylene were not completely eradicated [16] In current decades, photocatalysis has drawn in a great deal of consideration as a low-cost, environmentally benign technique that has revealed to have a substantial potential for cleaning up water contamination. During the photocatalytic process, impurities are transformed into CO_2 and H_2O_2 using nano catalysts [17]. Technologies based on photocatalysis are crucial in tackling key natural shift problems like environmental cleanup and renewable energy conversion. In water splitting, photocatalysts are frequently employed. The photocatalytic scheme is built on the chemical use that hastens the reaction without disturbing the reactants' quantity or composition. The term "catalyst" refers to this chemical. Because of the less energy difference between the valence and conduction bands, semiconductors are used as photocatalysts. As electrons move from the valence band to the conduction band so, there is an electron in the conduction band and a positive gap in the valence band. The positive gap is a powerful oxidant that can oxidize countless substances. The energy is comparable to that of an UV photon, or one with a wavelength of 388 nm. TiO_2 is regarded as the best material for usage as a photocatalyst due to its advantages, i.e., resistant towards corrosion, chemically inactive properties, necessitating less dealing out and preparation as compared to other semiconductors, less harmfulness, minimal expense, commercial accessibility, photochemical steadiness, and the capacity to separate numerous organic impurities. Studies have exposed that the deferred TiO_2 particles employed in photoreactors produce a elevated degree of activity as a consequence of their enormous surface area [18]. Any UV light source, including the sun, is absorbed by titanium dioxide. A negative electron and a positive hole can be liberated by UV radiation under conditions of normal pressure and temperature. The valence band electron in TiO_2 becomes active because of UV light assimilation, and the electron transfers from the valence band to the conduction band, creating a positive gap in the valence band h^+. As long as there is light available, the electron interacts with the oxygen molecule to create a very potent oxidizing anion [19].

2. Historical background

This article highlights the key developments in photocatalytic technology from the 1960s to 1993, as well as the mechanisms by which photocatalysts remove contaminants from water.

2.1.1960s-1993

Muller noted that Zinc Oxide could separate isopropanol on exposure to UV light, in 1969. This discovery disclosed that photocatalysts can separate organic compounds in water. Using a TiO_2 electrode and UV light treatment, Fujishima and Honda made a noteworthy finding in 1972: hydrogen development from the water. Many scientists spent their time and energy in the process of transforming solar energy into chemical energy [20].

2.2. 1994-2000

Research on photocatalytic water treatment technology advanced quickly after “The 1st International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air" in 1993. With the advancement of semiconductor band theory and sophisticated characterization methods (SEM, TEM, XPS, ESR, EIS, etc.) between 1994 and 2000, understanding of the photocatalysis phenomena and mechanism gradually expanded. [21]

2.3. 2001-2010

Different nanoscale photocatalysts have been created for water decontamination since 2000 as a result of the increased attention that nanotechnology has received. A new era in the study of photocatalysts began with this. The advantages of larger charge transport rates, bigger definite surface areas, and more exposed active sites contribute to the improved photocatalytic performance of nano-sized photocatalysts [22].

3. An overview of photocatalysis along its major types

Photocatalyst utilizes the energy that light gives to impel reactions that are testing, frequently even unimaginable, to complete in darkness. Photocatalysis has potential as a drawn out answer for huge scope sun based energy capacity when used for thermodynamically tough responses like photosynthesis [23].

3.1. Homogeneous photocatalysis

A procedure known as homogeneous photocatalysis uses soluble molecular catalysts that are all present in a single form (solution), including a light-retaining framework (photosensitizer), catalytic positions for oxidation, and reduction methods. The reactants and the photocatalysts are present in same phase during homogeneous photocatalysis. Ozone and photo-Fenton systems (Fe + and Fe + /H_2 O_2)$_2$ are the most often utilized homogeneous photocatalysts. •OH is the reactive substance, and it serves a variety of functions [24].

3.2. Heterogeneous photocatalysis

In heterogeneous photocatalysis, the photocatalyst is a solid, and the reactions happen at the solid-liquid or solid-gas interface between the two phases. A wide range of chemical processes, including minor or total oxidations, dehydrogenation, hydrogen transfer, 18 O_2 - 16O_2 and deuterium-alkane isotopic conversion, metal deposition, decontamination of water, and gaseous impurity eradication, are all included in heterogeneous photocatalysis. Over the past forty years, the discipline of heterogeneous photocatalysis has significantly grown, particularly regarding energy and the environment [25].

4. Recent advancements of photocatalysts for light-initiated water splitting

Semiconductors are utilized as photocatalysts on the grounds that there is little energy contrast between the valence and conduction band. Since electrons travel from the valence band to the conduction band, there is an electron in the conduction band and a positive hole in the valence band. A strong oxidant that may oxidize a variety of compounds is the positive gap.

4.1. Graphene based semiconductors as photocatalyst

In the realm of creating novel nanohybrid materials, the combination of TiO_2 and graphene has as of late drawn in a great deal of consideration due to its advantages in efficient partition of photoexcited electron-opening charge transporters, which works on the photocatalytic action of these composites. In contrast with other carbon consolidated TiO_2 nanomaterials, graphene has unique features that make it very appealing. Graphene nanoparticles are also well recognized as antifouling agents, sodium cation sorbents in the detoxification procedure, and improved materials that allow the particular entry of all things either anions or cations. The special electrical, mechanical, optical, and thermal capabilities of graphene make it superior to conventional materials. However, the kind of graphene material utilized in the research procedure determines the characteristics of the TiO_2 and graphene-based nanocomposites [26].

4.2. Cu_2O based semiconductors as photocatalyst

Cu_2O is an emerging semiconductor for the photocatalytic degradation of water. Cu_2O is a Fenton-like catalyst as well as a conventional p-type semiconductor. Due to its narrow bandgap (2.0 eV), low cost, non-toxicity, and abundance, it has gained significant scientific interest as a photocatalyst for the deprivation process of impurities existing in the water [27]

4.3. Semiconductor based on Heterojunction.

By creating semiconductors created on heterojunctions, which reduces their band stretch and creates the internal electrical field, semiconductors based on g-C_3N_4 may improve their capacity for photocatalysis. As a result, it can significantly improve structural charge separation, which maximizes the redox potential and reaction efficiency. Even the activity of water oxidation can benefit from the heterojunction semiconductors. CdS, NiS, and TiO_2 are the semiconductors that are typically employed with g-C_3N_4. Nanoparticles of NiS_2 impregnated on the surface of g-C_3N_4 reasonably boosted the capacity of g-C_3N_4 to release hydrogen in the presence of visible light. So, development of heterojunctions of g-C_3N_4 might raise photocatalytic capacity as it enacts the twisting of band went with the arrangement of inside electrical field and result in a strong underlying charge partition [28].

4.4. Mxene based semiconductors as photocatalyst

MXenes typically have an intermediate bandgap, which can vary depending on the chemical make-up from 0.05 to 2.87 eV. This property makes it possible to modify the MXene structure and achieve potent photocatalytic activity. MXenes can therefore be successful with other nanocomposites for photocatalytic activity, including pollutant degradation, water splitting, etc. They have demonstrated excellent potential for removing pollutants by photocatalytic degradation, catalytic removal, and interfacial chemical change in addition to sorption. MXenes (Ti_3C_2) are efficient adsorbents for the elimination of organic dyes and hazardous contaminants from water because of their layered and porous architectures, which also aid in their capacity for adsorption and storage.[29]

4.5. Non-metal loading

The photoactivity of a semiconductor may also be significantly improved by doping with non-metals. When non-metals including Nitrogen, Boron, Oxygen, Sulphur, and Phosphorus are added to g-C_3N_4, there is a significant influence on both the electronic and the optical properties. As a result of the better optical absorption and increased charge mobility, the photocatalytic performance is improved. As non-metal loading controls a catalyst's erection, lowering band gap, limiting the degree of charge recombination, and increasing the stability of the catalyst, the production of hydrogen may increase.

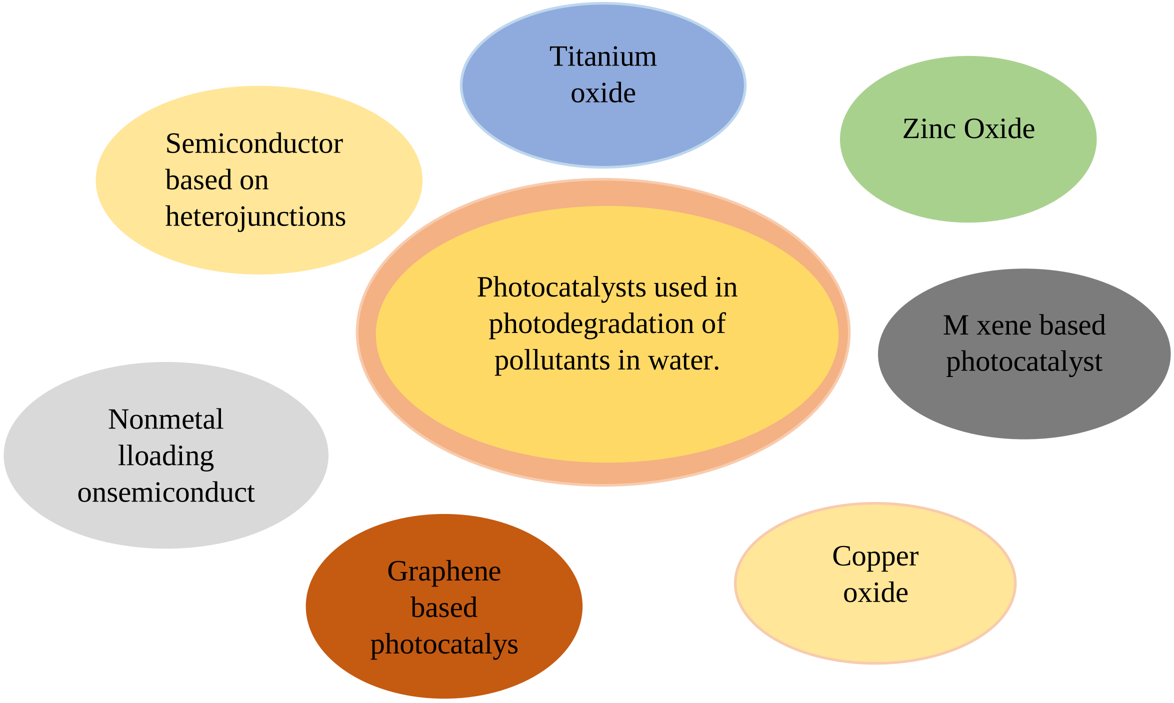

Figure 1. Photocatalysts used in photodegradation of pollutants in water.

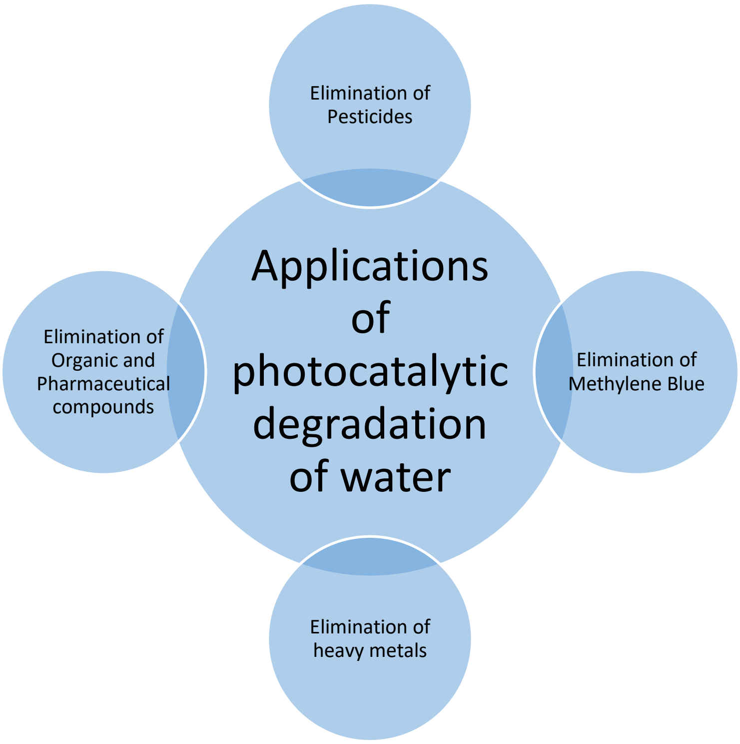

Figure 2. Applications of photocatalytic degradation of water

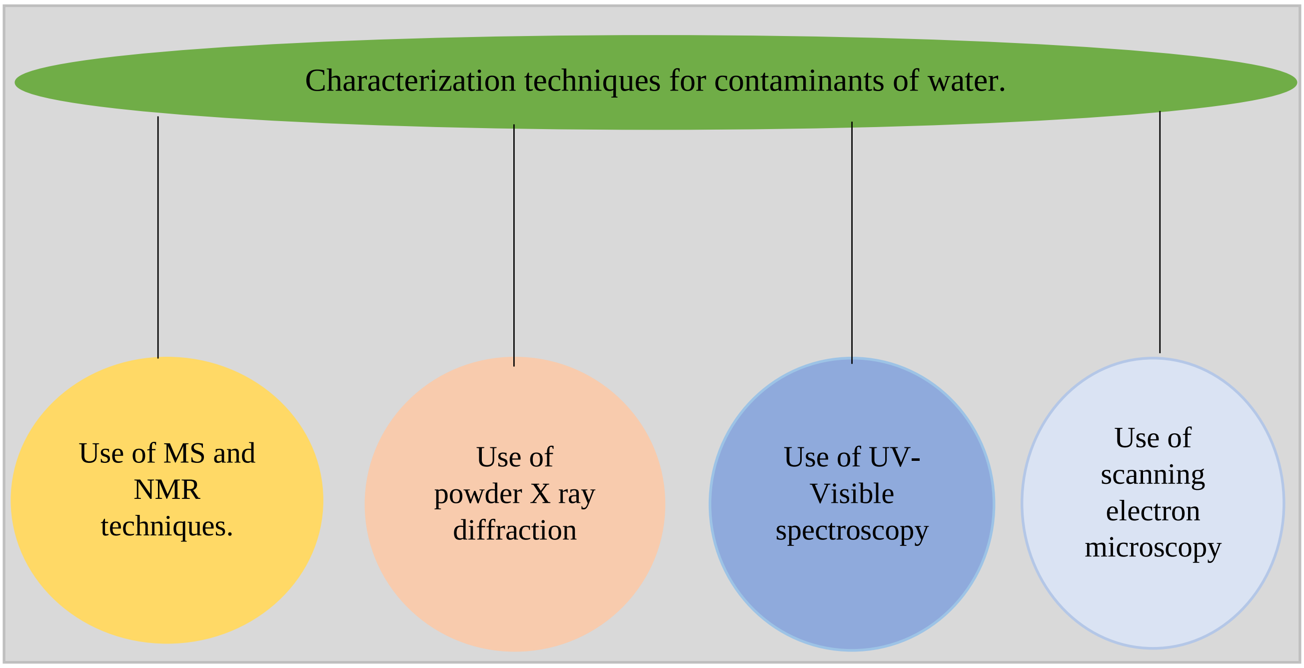

Figure 3. Characterization techniques for contaminants of water.

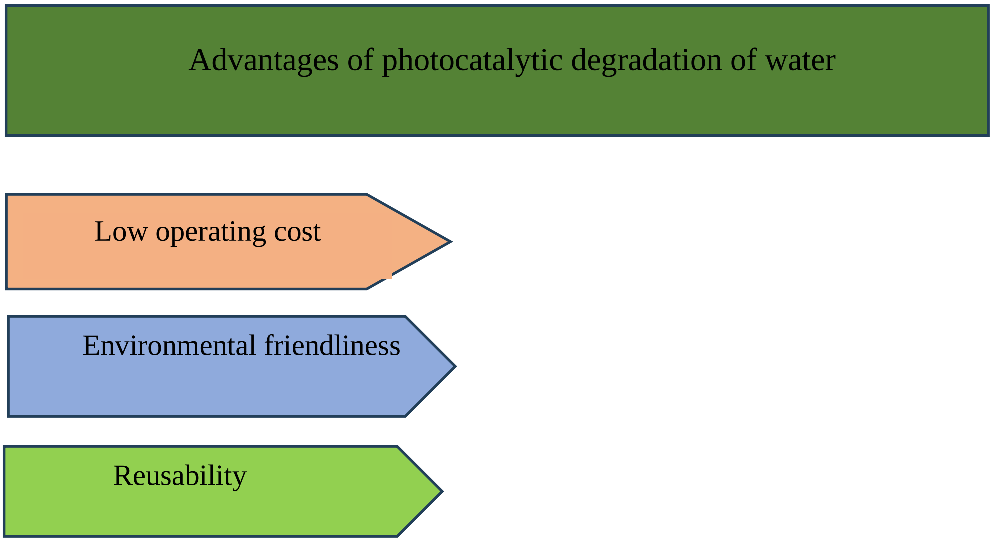

Figure 4. Advantages of photocatalytic degradation of water

It has been noted that sulfur incapacitating leads to an intensification in the surface's dynamic cross-sectional region and the creation of nitrogen vacant positions, which limit photo-produced charge recombination and enhance the catalyst's response to visible light. g-C_3N_4 that has been doped with various non-metals typically has increased stability, a trivial band gap, and improved light fascination along with reduced potential and charge carrier motility. Along with restricted recoupling of charge over g-C_3N_4, another convenience of re-establishing the photocatalyst structure to raise optical absorptivity also occurs, which enhances the pursuit of photocatalysis. [30].

5. General Mechanism of photocatalytic degradation of water

The electrical erection of a semiconductor is quite difficult. The space between the valence and the conduction bands is used to define bandgap energy. The high energy of photons advances the ions in the valence band to the conduction band when light is available. The dynamic electron movements to the conduction band because of the retention of a photon from an energy source, making positive opening (h_{vb}) in the valence band [31].

$$TiO2 \rightarrow (TiO2) + hvb^{+} + TiO2$$

The process comes to an end as the light energy is wasted by means of heat and electrons and holes join once more. Electrons and holes should be constrained throughout the procedure in order to prevent recombination [32].

The impurities in the adsorbed material might directly react with the positive hole in the valence band of the TiO_2 particle. The hole produces hydroxyl radicals (OH) by oxidizing water or hydroxide ions (OH) [33].

$$TiO_2\,(hvb^{+}) + H_2O_{ads} \rightarrow (TiO_2) + HO + H^{+}$$
$$TiO_2\,(hvb^{+}) + OH^{-}_{ads} \rightarrow TiO_2 + HO_{ads}$$

The photocatalysis method depends heavily on oxygen. The oxygen reduction (O_2) in the conduction band prompt the production of superoxide (O_2). By averting electrons from rejoining with holes, oxygen radicals produced during this phase can help in the removal of impurities [34]

$$TiO_2\,(e^{-}_{cb}) + O_{2ads} + 2H^{+} \rightarrow TiO_2 + HO_2^{+} \rightarrow O_2^{+}H^{+}$$

It is possible to further protonate the process that produces superoxide ions in conduction band to create the medium hydroperoxyl radical (HO_2), which is then joined with hydrogen ions (H +) to create hydrogen peroxide (H_2O_2). More hydroxyl radicals are produced when H_2O_2 is utilized as an oxidizing agent in the photocatalytic procedure [35].

$$TiO_2\,(e^{-}_{cb}) + HO_2 + H^{+} \rightarrow H_2O_2$$
$$H_2O_2 + hv \rightarrow 2HO$$
$$H_2O_2 + O_2 \rightarrow HO + O_2HO^{-}$$
$$H_2O_2 + TiO_2\,(e^{-}_{cb}) \rightarrow HO + HO^{-} + TiO_2$$

The assault of hydrogen revolutionaries and superoxide particles on toxins on the outer layer of TiO_2 particles is fast. On account of this, OH and O_2 are the two key byproducts of TiO_2 photocatalysis. No traces of the original chemical are remained overdue because contaminated molecules are nonstop broken down throughout this procedure, and no sludge is made that should be unloaded in landfills. The catalyst that is used is not consumed, and its concentration remains unaffected [36].

6. Applications of photocatalytic degradation in water treatment

Many organic constituents, organic acids, estrogens, pesticides, inorganic acids, dyes, crude oil, microbes (with viruses and chlorine-resilient organisms), inorganic molecules such as nitrous oxides (NO_x), and metals (such as mercury) can all be stopped using photocatalysis when united with precipitation or filtration. Photocatalysis using nanoparticles as catalysts is employed for water purification because of its universal application. [37].

6.1. Elimination of organic contaminants in water

Photocatalysis is regarded as a promising and environmentally acceptable process for the removal and deprivation of organic contaminants. The exceptional photocatalytic action of semiconducting oxide nanoparticles, for instance metal oxides, is used to eradicate organic impurities from wastewater. Researchers' interest in the creation of Fe_2O_3-TiO_2 based nanocomposite photocatalysts has grown recently because of how well they remove POPs from water [38].

6.2. Elimination of pharmaceutical compounds from water

Due to their toxicity and possible risk to ecosystems and people, pharmaceuticals and endocrine troublesome substances, sometimes known as developing toxins, have drawn increasing attention. These pollutants cannot be successfully eliminated by the biological processes-based conventional treatment procedures. The exclusive properties of the ZnO catalyst, for instance the fascination of a greater percentage of the solar spectrum, wide band gap, biocompatibility, non-toxicity, and reasonable price, make photocatalytic removal of developing pollutants easier. A lot of work has recently been put into enhancing the photocatalytic performance of ZnO through elemental incapacitating, fabrication method optimization, and the use of nano-ZnO [39].

6.3. Elimination of pesticides from water

Pesticides are useful for eradicating pests. However, pesticides' persistence in the environment, chiefly in water, may have undesirable consequences. Pesticides have huge wellbeing influences by polluting groundwater and surface water, which is a chief issue in several areas. These pesticides have an influence on ecosystems and human health at the point when they are available in water [40].

The photocatalytic treatment gives the idea to be the most effective, auspicious, and ecologically acceptable technique utilized for the removal of such pests, and it has drawn the interest of many researchers in recent years. Doped TiO_2 nanomaterials are the most common photocatalysts used for the removal of such hazardous chemicals [41].

6.4. Elimination of Methylene Blue in water

Perhaps of the most widely recognized compound that renders water hazardous for drinking is industrial colors (dyes). Methylene blue, one of these dyes, poses the extreme hazard to human health and ecological safety since it is lethal, oncogenic, and not-decomposable [42]. Photocatalytic deprivation of methylene blue from water is possible by using multilayer photocatalytic TiO_2 coated on a High Density Polyethylene disk [43].

6.5. Elimination of heavy metals from water

Discharges of heavy metals into aquatic environments have a undesirable influence on the environment, human health, and other organisms [44]. As a sustainable, economical, and ecologically benign method of eliminating heavy metals (including chromium, nickel, cadmium, mercury, arsenic etc.) from wastewater, photocatalysis technology is a good choice. By converting harmful high-valence heavy metal ions into low-valence ions or zero-valence metals, it is possible to eradicate heavy metal ions from water by photocatalysis. For this purpose, mostly TiO_2 photocatalyst is used [45].

7. Factors influencing performance of photocatalyst.

7.1 Temperature

It subsidizes in improving product desorption from the catalyst surface with the intention of intensification the photocatalytic action. As a result, the rate of reaction is accelerated. Applied temperatures differ depending on the catalyst. Therefore, it is easily controllable to increase the photocatalytic activity. Because product desorption is gentler than reactant adsorption, lowering the temperature has a detrimental impact on hydrogen production because it stops reactions. A high temperature allows for greater transport of electrons from the valence band to energy levels above it. It now makes it possible and easier for electrons to develop relative to holes, which can be used to start reduction and oxidation events, correspondingly, and help reactions work more efficiently by reuniting charge carriers [46].

7.2 Band separation energy

Because of the alteration in energy between the valence band and conductance band, the energy of the band gap is frequently employed to describe the electrical configuration of semiconductors. The acceptor's latent level often needs to be powerfully lower than the semiconductor's conductance band. TiO_2 doped with g-C_3N_4 makes it suitable for the irradiation of visible light.

By adjusting the surface, which may be done even by changing the quality of the surface, the band gap of the catalyst may be lowered [47].

7.3. Intensity of Light

By increasing the light intensity and using energies over the threshold needed for activation, the photocatalytic effectiveness of splitting water may be improved [48]. Photocatalytic generation of hydrogen using Zinc Sulphide displayed 20% improved photo-performance by magnifying light concentration has been discovered [49].

7.4. pH

Since protons are condensed by photogenerated electrons during the process of water splitting, the production of hydrogen from splitting water depends on the concentration of protons, or, more specifically, on the pH of the solution. Since any organic sacrificial substance must be present, this notion is only relevant to photo reforming. While variations in pH have an impact on the energy shift of the band gap, weakly basic solutions are more effective at producing H_2 than acidic or strongly basic solutions. The catalyst band gap may change as a result of pH adaptation [50].

7.5. Initial concentration of sample pollutant

According to many scientists, the amount of degraded organic species increased with an increase in initial concentration, but production of reactive species, photocatalyst concentration, intensity, and illumination period remained unchanged, resulting in a decrease in degradation efficiency. [51]

7.6. Photo reactors

The layout and arrangement of the photocatalyst used in the photoreactor also significantly affect photocatalytic action. Basically, the photoreactor is the vessel where the combination of reactants and photocatalysts, in order to produce products, takes place while being exposed to light. An ideal photoreactor must have even light distribution all over the total apparatus. Mostly rectangular and cylindrical shaped photoreactors are used [52].

8. Advanced characterization strategies for photocatalytic water treatment.

8.1. use of mass spectrometry and NMR techniques

Survey of the types and quantities of active substances generated during catalyst dilapidation has been increasingly important in recent years for unraveling the reaction process. For instance, combining mass spectrometry and NMR methods to further explore chemical intermediates is a useful strategy for understanding how pollutant molecules are transformed and removed from the surface of the material. Furthermore, phenol's decomposition is highly complex, and its intermediates, including o-diphenol, m-diphenol, quinones, and aldehydes, are more harmful as compared to phenols. Consequently, for disclosing the reaction procedure, obtaining insight into the effects of many elements, managing the reaction process successfully, and choosing the best circumstances, a thorough study of the intercedes of the deprivation procedure is necessary [53].

8.2. Use of powder x-ray diffraction

With the help of new hybrid MO/F polymer composites, powder X-ray diffraction was executed for the removal of various dyes from water [54].

8.3. Use of UV-Visible spectroscopy

UV-Visible spectroscopy can be carried out for measurement of many pollutants present in water and wastewater [55].

8.4. Use of SEM

Scanning Electron Microscope coupled with FTIR and EDX used for the qualitative and quantitative determination of biomass content present in the water [56].

9. Advantages of photocatalytic degradation in water treatment

The key benefits of photocatalytic deprivation in water treatment consist of its low operating expense, high degree of specific impurity mineralization, and lack of high pressure requirements in the treatment [57].

10. Challenges

A potential approach for producing H_2 is photocatalytic water degradation. However, its performance is still a long way off from being suitable for production at large scale. Theoretically and practically, photocatalytic water degradation is challenging to accomplish. Unfavorable thermodynamics, sluggish kinetics, dissolved oxygen, and quick reverse reaction are some of the limiting factors [58].

Only UV light can trigger pure nano-TiO_2. Therefore, it is crucial to generate a catalyst that can fascinate visible wavelengths for indoor applications. To ensure supreme longevity, competence, and working of the photocatalyst, it is also necessary to establish the best system setup and substrate materials for countless usages in private and public facilities [59].

One of the main serious issues faced during the photocatalytic degradation of water is that some semiconductors suddenly corroded in the dark. So, there should be an appropriate set-up to overcome this concern [60].

11. Conclusions

Photocatalysts uses the light for the degradation of harmful impurities present in the water. In short, photocatalytic degradation is a high-level oxidation process, which can be utilized to debase contaminations with high fixation, intricacy and low biodegradability. Future examination lines need to explore photodegradation and photocatalysis medicines to decrease the likely wellbeing and ecological dangers from the release of treated wastewater containing drugs; support wastewater reuse, thinking about the pace of filtration; and exploit the reusability of photocatalytic layers by remembering them for the cycle.

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