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Review

Disinfection of Water using Supported Titanium Dioxide Photocatalysts

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Abstract: TiO_2 based photocatalyst has potential material for disinfection of harmful pathogens as well as removal of organic compounds. The formation of reactive oxygen species is a key part for overall process but aggregation and band gap constraint explore a new dimension to use of support for propounding its physicochemical properties. Therefore, the modification of TiO_2 using various support alters photocatalytic action and promising ways of the mechanism based on nature of substrates and environments. In addition, the immobilization of nano dimension photocatalyst may reduce overall cost of operation and recovery of photocatalytic materials. In this perspective, extensive range of support materials as carbonaceous matters, clay, polymers, metal oxides have been studied by various researchers; that have been compiled in this review article. The properties of support were the key features for the assortment of appropriate supports for increase its efficiency as photocatalyst. In brief, overall TiO_2 based photocatalyst supported on various substrates pave the ways toward new strategies for water disinfection.

Keywords: Photocatalyst, Water Disinfection, TiO_2

Introduction

The world is continuously shifting into a new arena due to fast economic growth, industrial development and increasing population, but necessity of clean and pure water is excessive demand. On an average 1.2 billion people still shortage of pure water and diseases are spread due to contaminated water, which led to infant and child deaths (Catley-Carlson, 2017). Worldwide, around 502,000 people are died because of waterborne pathogenic bacteria and viruses (WHO, 2017).

The contamination of the water was increasing continuously due to industrial processes and urbanization in the natural water cycle. Therefore, there is need to reuse and recycle of water for the human being. In this regard, the various practices have been used for purification of water (Qu and Fan, 2010, Deshmukh *et al*., 2013). In this perception, biological approaches were employed to remove the desired contaminates in the wastewater in the less time but formation of other pollutant was major constraint. Therefore, ecofriendly and viable methodologies are the key aspect for antimicrobial disinfection and water treatment with more prominent route (Deshmukh *et al*., 2019a-b).

Nowadays, as environmental viewpoint the photocatalysis and antimicrobial photoinactivation was grasping enormous consideration in the scientific world. In addition, it is increasing awareness due to poor quality of water that leads to various types' infections among the human being. The water treatment methods such as chlorination, ozonation have been used from the last few decades. These conventional treatment methods have a limitation as carcinogenic nature; formation of by-product with mutation and non-economical process. Hence, there is need to develop new techniques, the advanced oxidation process is one of the ecofriendly method for the water treatment purpose; it has an ability to degrade water pollutants, heavy chemicals and generating environmental benign by-product (Saleh *et al*., 2020). Therefore, photocatalyst is the emerging area for the water disinfection as compared to the conventional water disinfection methods (Magalhaes *et al*., 2017). Photocatalyst is the process in which formation of reactive oxygen species and free radicals in the presence of light radiations; that could be useful for water disinfection. It has a capability to kill the microorganism without other chemicals and remove the pollutant in the water by photocatalytic process. Furthermore, cost of the process is lower and use of renewable energy sources as solar spectrum for photocatalysis process. Currently, various semiconducting materials as ZrO_2, Fe_2O_3, WO_3, ZnO, CdSe used for the same but among these TiO_2 is the foremost advantages as cost effective, chemically stable, non-toxic with higher quantum efficiency (Patil *et al*., 2017; 2019).

The antimicrobial activity of TiO_2 was reported (Matsunaga *et al*., 1985) by for inactivation of bacteria. TiO_2 shows the three phases as anatase, rutile and brookite. In which, rutile phase is more stable but anatase phase is extensively used during photocatalysis process because of ease to prepare and better activity. Brookite is compared to least stability and less used in photocatalysis. In addition, the various types of photocatalytic materials have used for wide range of antimicrobial events against the viruses, bacteria, fungi and algae (You *et al*., 2019). The photocatalytic activity was depend on the process of photo-excitation by visible, UV or near infra-red light radiation based on band gaps. The band gaps of TiO_2 are relying upon the preparation methods, formation of defects and phases. The band gap of TiO_2 is 3.2 and 3.0 eV for anatase and rutile phases respectively (Mills and Le Hunte, 1997).

The role of TiO_2 as photocatalyst is effective in the UV region, so there is need to tune their band gap in the visible region. The visible light active material is effective for the bacterial inactivation. The various strategies have been used for effective antimicrobial purpose (You *et al*., 2019). Among these strategies the TiO_2 supported catalyst are effective path for the water disinfection. The different methodology have efficiently employed to immobilize catalyst on various supporting materials as a glass material, metals, zeolites, Chitosan, Cellulose, etc. (Srikanth *et al*., 2017, Chen *et al*., 2010). The wide dimensions of support were useful for the photocatalyst. In addition, photocatalytic activity was executed by using the proper wavelength of light. This review compiles the titanium dioxide supported photocatalyst for the water disinfection.

Mechanism of Photocatalytic Antimicrobial Inactivation

An environment is surrounded by wide range of the pathogenic microorganism; this is major reason of diseases for typhoid, cholera and illness as the flu and cold, etc. These diseases transfer via aerosol particles, surfaces, agriculture product and water. Last few decades, we are facing a problem of water purification so that TiO_2 based photocatalyst is effective strategy for the bacterial inactivation. Besides disinfection of water, it is a very effective process that can be used to diminish water contaminate, odour of water. Photocatalyst is the process in which formation of electron-hole pairs in the presence of light radiation. Sufficient amount of light radiation is irradiated on the photocatalytic material and it is higher energy as compared to the band gap of TiO_2 materials. The electron is excited from Valence Band (VB) to Conduction Band (CB) that lead to hole formation at VB of photocatalyst. These electrons- hole pair's reaches to surface of the catalyst and carrying out redox reactions. These charged particles are responsible for the formation of reactive oxygen species.

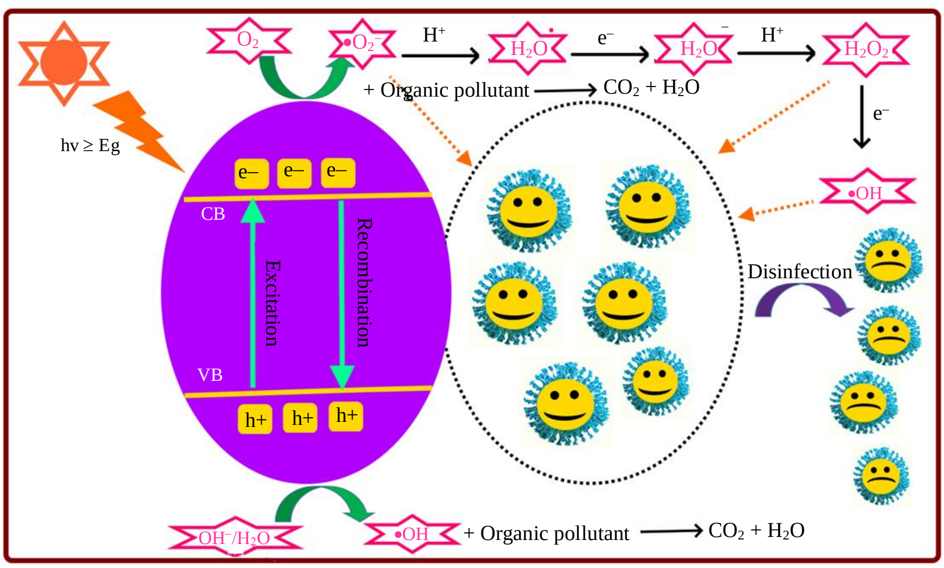

Fig. 1: Photocatalytic disinfection and pollutant degradation mechanism

The redox process leads to formation of reactive oxygen species which can reduces oxygen molecules and generating O_2^-, $^{\bullet}OH$ and H_2O_2. These species damage the cell wall of the microbes, viruses and changes permeability of cell and increase stress on the cell. It also inhibited proteins actions that are useful for the biological process of the cell (Koli *et al*., 2020). Photocatalytic inactivation process of viruses and organic pollutant by the different reactive oxygen process is shown in the Fig. 1. The oxidative stress is another cause to generate pyrimidine dimers in the DNA. Such changes in the structure of DNA pave the ways towards improper working of the cell and finally cell death. Furthermore, RNA is also more sensitive to photocatalyst than DNA in vivo and vitro circumstances (Pigeot-Rémy *et al*., 2011).

Necessity of Supported Titanium Dioxide

In the water treatment process the Degussa P-25 TiO_2 was normally used as photocatalyst. It is very efficient semiconducting material as compared to other reported photocatalytic materials. Degussa P-25 TiO_2 was the in the form of fine particles having ability to form reactive oxygen species as relative to surface particles in the dispersed phase. On the other hand, when it was incorporated on the inert surfaces, it would diminish dynamic spots and mass transfer drawbacks. It has also problems with formation of reactive oxygen species leads to decrease in photocatalytic activity (Pozzo *et al*., 1997). The post-treatment path is important part of separation of the catalyst, in which decreasing amount of the catalyst and introducing of a new pollutant during the process water treatment using TiO_2 is the crucial challenges (Yang and Cheng, 2007). The major problem was retrieval of catalyst from the solution, controlling pH of the solution and other membrane obstruction and fouling. To improve catalytic properties there is need to use supporting materials to overcome this limitation as reusability of the catalyst, increasing active hotspot of catalyst to increase their activity.

As the solar energy is abundant in the nature but only 3-4% of UV light radiation has been used for the photocatalytic process for the bare TiO_2. The average 43% of visible light radiations are useful for the photocatalytic activity. The major limitation of TiO_2 is unable use visible light spectrum for photocatalytic activity, therefore tuning or optimizing TiO_2 into the visible light radiation is better route for increasing efficiency for the disinfection (Deshmukh *et al.*, 2019a). In the literature, various routes have been used such as doping, metallization, sensitization and supporting material. Among them supported metal nanoparticles have more efficient for bacterial inactivation that other; therefore herein we reported TiO_2 supported metal nanoparticles (Chen *et al*., 2010, Mohite *et al*., 2015). Therefore, carbonaceous matters, clay and ceramics, polymers, metal oxides are used as supporting material for the TiO_2.

Polymers

The efficiency of the catalyst is depends on its nature and type of support and at ease between TiO_2 and support for appropriate combination for better catalytic activity. In all other support polymer is used because of their some remarkable advantages. Thermoplastic nature of the polymer has thermoplastic properties which are useful for the simple coating on TiO_2 using simple way (Singh *et al*., 2013). Polymers are stable and inert in nature with the long life spans. The adsorption ability of TiO_2 was improved due to polymer support with hydrophobic nature. Such nature of the polymer exhibits the effective support material for the photocatalysis process (Reddy *et al*., 2020). The incorporation of metal oxides with polymers led to formation of composites with improved thermal, electrical and rheological properties. The polymer support is playing important role for recovery of catalyst and multiple use of photocatalyst. Among the various conducting polymers as polyaniline, polypyrrole and polythiophene and their by-products were effective to shift of UV light to visible light spectrum to improve quantum efficiency of TiO_2 photocatalyst. Polyaniline is photosensitizer and economical, stable and better electrical conducting ability (Tamboli *et al*., 2013). The polyaniline/titanium dioxide nanocomposites reduces bacterial growth of *E. coli* pathogenic organism and effective for the dye degradation also (Jeong *et al*., 2014). PANI/TiO_2 is auspicious adsorbent and ability to remove more than 70% of biopolymer from secondary effluent. It also having very less antifouling activity analogous with less quantity of foulants. Furthermore, setup cost was less and majorly effective for advances on water quality (Li *et al*., 2020b). Porous Polymethyl Methacrylate (PMMA) substrates was employed to immobilize TiO_2 nanoparticles in the fiber forms and efficiently used for degradation of methylene blue. The photocatalytic performances were analyzed by optimizing fiber porosity and its architecture with higher surface area (Kanth *et al*., 2020). The poly (acrylonitrile) supported carbon doped titanium dioxide nanocomposite was developed by sol-gel method and immobilize by phase inversion route. Thereafter, methyl orange and golden yellow textile dyes was degraded using this nanocomposites (Mpelane *et al*., 2020).

Carbonaceous Materials

Carbonaceous materials are another class of the materials useful for supporting purpose due to their admirable properties. Basically, carbonaceous materials are better chemical stability, optimized structural and optical properties and increased surface to volume ratio, better mobility of charges particles. Carbonaceous materials are consisting of carbon nanotubes, activated carbon, graphene and graphitic carbon nitride. The carbon based materials are efficient for adsorption of the pollutants or other contaminated chemicals in the water; it is also enhances the active surface of the catalyst and act as effective photocatalyst (Sakthivel and Kisch, 2003). Several researchers are reported that quantum efficiency of TiO_2 may be increased using carbonaceous materials in the visible spectrum as associated to pure TiO_2, it is because of chemical linkage between them (Silva *et al*., 2020). TiO_2 was coated on the carbon foam act as effective treatment for degradation of dye present in the wastewater under the solar spectrum. The 3 D outline of foam was upgraded for increasing thermal stability and avoids particles agglomeration. Photocatalytic capacity of the catalyst was increased due to light absorption of nitrogen based foam and better charge carrier separation (Lu *et al*., 2020). Mesones *et al*. (2020) reported the photo-electrocatalytic activity of TiO_2 supported on activated carbon for water disinfection using 3 D bipolar electrodes. The electrocatalytic activity can generates the chlorine and hydroxyl radicals lead to synergic effect for water disinfection process. Polymer binder is used as produce char which is act as structural support of TiO_2 to conquer mechanical stability and diminish aggregation. The carbonaceous char was co-exist with TiO_2 and enhanced physicochemical properties lead to higher photocatalytic activity for acid orange 7 dyes under ultraviolet light. (Wang *et al*., 2016). Carbon-supported TiO_2 was prepared using hydrothermal route to study its adsorption ability and photocatalytic activity against phenol, naphthol blue black and reactive black in the presence of UV radiation (Nguyen *et al*., 2020).

Clays

Clays are an enclosed phyllosilicate mineral that arises naturally in the earth's crust and significant ingredients of the soils. Clay have astonishing properties as surface activity, better adsorption ability, cation exchange, swelling and biocompatibility which provides them as alternative material for wide-range of applications. Clay minerals are rich in environment and ease to modify to increase efficiency for water disinfection (Mishra *et al*., 2018). The proper mixing of clay and photocatalytic materials as TiO_2 may improve efficiency pave the way towards the better material for removal of toxic chemicals and pathogens from the water and act as active water disinfectant. Fig. 2. represent the water disinfection process using TiO_2 as photocatalyst. In which, the representative type of dyes were degraded as well as killing of pathogenic microbes was presented. Water disinfection was carried out using physical, chemical and biological process; while each process has some advantages and disadvantages. Therefore, use of photocatalytic material with clays as support for nano-size semiconducting materials may useful to improve their catalytic activity as analogous to bare materials. In this context, wide range of clay such as kaolinite, bentonite and montmorillonite were used as excellent support (Mustapha *et al*., 2020). Dalai *et al*. (2014) reported chemical interaction between adsorbent TiO_2 with bacteria using XPS techniques and it also reveals that formation of charge carries were responsible for the damage of the cell wall.

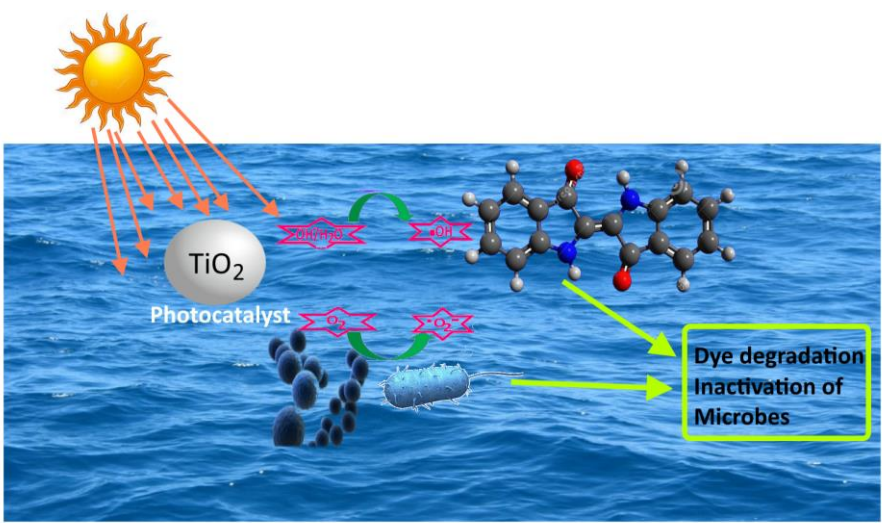

Fig. 2: The water disinfection process

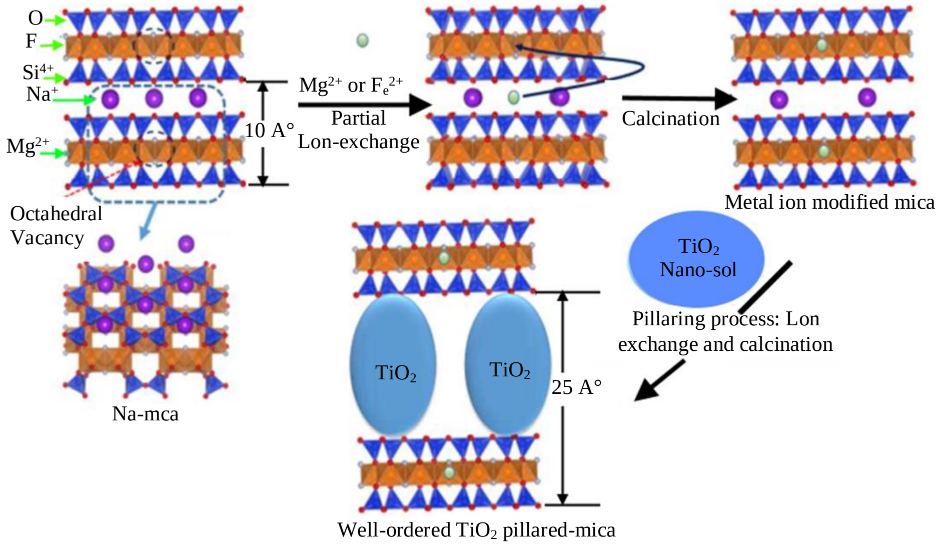

Fig. 3: Synthesis of well-ordered TiO_2_pillared clay

TiO_2_pillared clays with spongy structure were prepared through combining TiO_2 nano-sol elements into the clays. It exhibits better photocatalytic activity against the methyl orange in the presence of UV radiation (Yang *et al*., 2015). Figure 3 shows the well-ordered TiO_2 pillar clay.

Micro-fibrous palygorskite and halloysite clay inorganic incorporate with TiO_2 and coated on the glass surfaces to avoid aggregation of TiO_2. These composites were better efficacy as photocatalyst for the water disinfection (Panagiotaras *et al*., 2014). Clay-TiO_2 nanocomposites were synthesis using biomass supported the process for the removal of antibiotics such as ampicillin, sulfamethoxazole and artemether consisting in the water. Surface active oxygen vacancies and charge particles and defect present in the crystal lattice playing crucial role of photocatalytic activity for water disinfection (Alfred *et al*., 2020).

Metal Oxides

Improved TiO_2 can increase their photocatalytic action using the various mechanisms, consisting of decreasing band gap of such materials; it also reduces recombination of the electron-hole combination. Contemporary year's metal and metal oxides have been used as support for the TiO_2 to increase photocatalytic efficiency and water disinfection ability. Metal supported TiO_2 with antibacterial activity in the presence of UV/Visible and dark condition were analyzed with higher antibacterial activity due to strong interconnectivity between Ti-O-Ag bonds (Deshmukh *et al*., 2018). Li *et al*. (2020a) reported the modification of TiO_2 using various routes for water treatment. In addition, the various materials such as glass, clay, metal oxides act as support for the TiO_2 useful for water treatment. While some metal contaminates are also major reason for reduction in the photocatalytic activity. WO_3/TiO_2 based heterostructure has been used for removal of Rhodamine B and Reactive red dye from the wastewater in the presence of sunlight radiation. The crystalline nature, better optical properties and without mixed phases were the key properties for competent photocatalytic activity in the visible light ratiation (Hunge *et al*., 2018a-b). Mahlambi *et al*. (2015) reported the recent development in TiO_2 nanocatalysts were playing major role for environmental remediation as removal of the pollutant from the water bodies. Furthermore, the roles of TiO_2 nanoparticles act as accompanying and analogous to water processing technologies in which, the conversion of toxic chemicals into the oxides of carbon and water molecules. Shi *et al*. (2018) reported recyclable light and heat assisted route for removal of the pollutant from the wastewater system. The TiO_2 supported on Fe_3O_4 nanoparticles was revealed the enhanced proficiency for Rhodamine B dye degradation in the wastewater treatment. In addition, the magnetic properties of the materials was also astonishing properties; hence it can be easily separable and reuse consistently. Jia *et al*. (2016) reported TiO_2-Bi_2WO_6 binanosheet prepared using hydrothermal route and used as capable material for visible light active photocatalyst for inactivation of *E. coli* pathogenic bacteria. The electron and hole were playing major roles in photocatalytic disinfection. In which, leakage of the cell as DNA and protein lead to damage of the cell membrane was observed. The better separation of the charge carrier is useful for the disinfection process. Table 1 represents the various types of substrate used as support and synthesis protocol and water disinfection as pollutants or microbes.

Table 1: A comparative overview of TiO_2 and its support for disinfection process

Catalyst	substrate	Method of synthesis	Microbes/pollutants	References
TiO_2	PANI	chemical polymerization	Secondary effluent	Li *et al*. (2020a)
TiO_2	PANI	chemical polymerization	methylene blue, *E. coli*	Jeong *et al*. (2014)
TiO_2	PMMA	wet phase inversion	Methylene blue	Kanth *et al.* (2020)
TiO_2	Poly acrylonitrile	sol-gel method	methyl orange and golden yellow	Mpelane *et al*. (2020)
TiO_2	Activated Carbon	impregnation method	*E. coli*	Mesones *et al*. (2020)
TiO_2	Carbonaceous char	spinning-pyrolysis	Acid orange 7	Wang *et al*. (2016)
TiO_2	Activated carbon	hydrothermal process	phenol, Naphthol Blue Black (NBB) and Reactive Black 5 (RB5)	Nguyen *et al*. (2020)
TiO_2	Microfibrous palygorskite and tubular halloysite	sol-gel method	Basic blue 41 azo dye	Panagiotaras *et al*. (2014)
TiO_2	kaolinite clay	biomass assisted synthesis	ampicillin, sulfamethoxazole and artemether	Alfred *et al*. (2020)
TiO_2	cationic clays	ion-exchange reaction	methyl orange	Yang *et al*. (2015)
TiO_2	Fe_3O_4	Chemical reduction method	Rhodamine B	Shi *et al*. (2018)
TiO_2	Bi_2WO_6	hydrothermal method	*E. coli*	Jia *et al*. (2016)

Conclusions

This review highlights the properties and different types TiO_2 supported materials used as photocatalyst for the water disinfection process. The photocatalytic activity based TiO_2 supported materials new approaches for the water disinfection. In addition, the metal supported materials were optimized by tuning the structural and optical properties to use a wide range of the solar spectrum. The various supports such as carbonaceous materials, polymers, clay and metal oxide were used to improve its physicochemical properties of TiO_2. Moreover, there is more scope for enhancement of this technology as a photocatalytic material design, overall operation process and so on. The key factor is using of not only UV but also visible range, i.e., wide range of the solar spectrum. In addition, in waste water containing a wide range of the pathogenic microorganism, numbers of dyes which are degrading completely and remove the pathogenic microorganism are the key challenge of human being yet to resolve.

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Author's Contributions

Shamkumar Pandurang Deshmukh: Lead role of writing and completing the paper.

Dattatray Krishna Dalavi: Revising data of review article.

Yuvaraj Mohan Hunge: Supporting and rewriting.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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