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Review

The application of titanium dioxide for deactivation of bioparticulates: An overview

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ABSTRACT

This paper reviews the studies published worldwide on killing bacteria, fungi, prions and cancer cells using photocatalytic reaction with titanium dioxide. There are many circumstances, where removing or killing microorganisms in water, air and on surfaces is necessary or desirable. For example, water disinfection requires deactivation of pathogenic organisms. Literature on the potential use of titanium dioxide nanoparticles in daily life and in development of new self-cleaning and antimicrobial surfaces and paints along with toxicological data are also included in this review.

Contents

1. Introduction

Titanium dioxide, also known as titanium (IV) oxide or titania is naturally occurring oxide of titanium, which exist in three forms, namely: rutile, anatase and brookite. All these forms are associated with well-known minerals such as: quartz, tourmaline, barite, hematite, silicates, feldspar, chalcopyrite, hematite and sphene [1]. There are some differences in physical (e.g. crystal structure, stability, hardness, density) and optical (e.g. color, luster, brightness, refractive index) properties between them [2,3]. Crude titanium dioxide, called titanium white, Pigment White 6, or CI 77891 is obtained by chemical reactions viz. chloride, sulfur or Becher Processes. From the beginning of the 20th century titanium dioxide has steadily replaced toxic oxides uses as pigments for white paint. At the present the annual production of TiO_2 exceeds 5,480,000 million tons, what accounts 70% of the total production volume of pigments [4]. It is widely used to provide whiteness in products such as paints, lacquers, plastic and paper and is also a permitted color in foodstuffs as E171 [5]. Nanoparticles of titanium dioxide are also used as an opacifier in textiles, leather, glass and porcelain enamels, pharmaceuticals, cosmetics and skin care products [4–6]. Furthermore, titanium dioxide has excellent photocatalytic properties and effectively transforms the light energy into the chemical energy [7]. It has been most commonly believed that the first description of this process was given by Fujishima and Honda [8] in 1972. However, according to Ohtani [9] it is scientifically incorrect. Based on recent review by Herrmann [10] photocatalysis originated

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from Germany and the first article including the term "photocatalysis" has been published in 1964 by Doerffler and Hauffe. Disregarding the photocatalysis beginning date, scientific interest towards the photocatalytic properties of TiO_2, has been greatly increasing. There is thus a vast amount of data on understanding the fundamental processes and on enhancing the photocatalytic efficiency of titanium dioxide [6,7,11–31]. The high photoactivity of titania evokes the destruction of polymer matrix, loss of luster, decolorization or chalking in pigmentary applications. Therefore, the majority of currently published studies have been focused on finding new TiO_2-based catalysts [32–37] and on application of TiO_2 photocatalysis in industry (e.g. for water splitting, cell production, etc.), water treatment and daily life [25,29,38–42]. Numerous studies on photocatalysis disinfection have also been conducted [30,43–53]. The studies have demonstrated that titanium dioxide deactivates a wide range of pathogenic microorganisms. The main advantages of photocatalytic method are operation under ambient temperature and pressure, high stability and the low cost of TiO_2 catalyst, completed mineralization without crating secondary pollution and possibility of using solar light. So far, the applications of photocatalysis based on titanium dioxide for deactivation of bioparticulates is still not regarded. This can be explained by several causes. "Bioparticulates" is the term used not only for bacteria, including cyanobacteria, and microscopic fungi but also for viruses, prions and cancer cells. Although, all these forms exist close together, they are completely different in structure and functions. Only a small group of model organisms has been extensively studied in a majority of works on TiO_2 photokilling mechanisms [6,41,43–47,51]. Since experiments have been carried out in unique conditions (different photocatalysts, pH, temperature, light source, microbial strains), a comparison of data obtained by various research groups seems to be problematic. It has been indicated, however, that TiO_2 catalysis is still presenting a series of scientific challenges. One of them, essential in order to apply new technologies, is in-depth understanding of the photokilling mechanism in various groups of organisms.

This review delivers data on different photokilling mechanisms and some useful information for chemistry engineers and researchers, who work in the field of photocatalytic products.

2. Antibacterial effect of titanium dioxide

Bacteria are prokaryotic microorganisms, which do not contain the nucleus characteristic for eukaryotic cells. It is long since known that bacteria may colonize all environments in the biosphere and play a key role in ecosystems. Pathogenic properties of bacteria against plants, animals and humans are widely known. For many illnesses, modern medicine has found the treatment or developed effective prevention ranging from vaccines to antibiotic products. Nowadays, the major scientific challenge is the dissemination of increasingly virulent and antibiotic resistant pathogens such as vanomycin-resistant enterococci (VRE) and methicillin-resistant *Staphylococcus aureus* [53–55]. For this reason, special attention should be paid to the development of more effective antibacterial strategies.

The antimicrobial effect of titanium dioxide photocatalysis was reported for the first time by Matsunga et al. in 1985 [56]. They observed that when TiO_2–Pt catalyst in contact with microbial cells was exposed to near ultraviolet light for 60–120 min, the cells in water could be killed. Although, there are at least three hypotheses of the killing effect of TiO_2-photocatalytic reaction, that mechanism is still to be proved [58–61].

The titanium dioxide in anatase and rutile crystal forms is a semiconductor with a band gap 3.2 eV and 3.02 eV, respectively. Upon excitation by light, whose wavelength is less than 385 nm

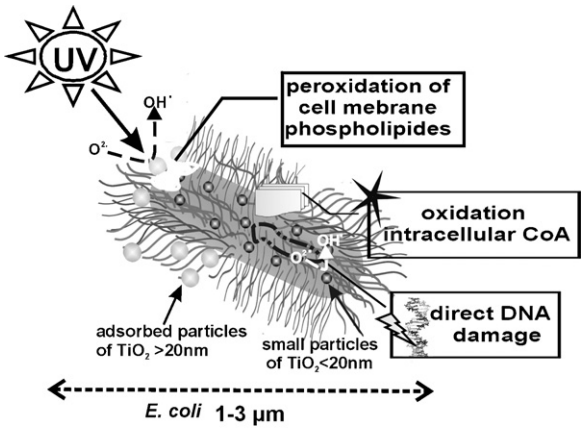

Fig. 1. The photodegradation of bacterial cell.

(about 3% of the solar light spectrum), the photon energy generates an electron hole pair on the TiO_2 surface. These highly unstable state has strong oxidation/reduction power and converts water and oxygen into reactive oxygen species (ROS) such as hydroxyl radicals ($^{\bullet}OH$), superoxide ion ($O_2^{\bullet -}$) and hydrogen peroxide H_2O_2. This phenomenon has been well documented by many authorities in photocatalysis based on titanium dioxide [14,16,20,24–25]. Among the above-mentioned ROS species, the hydroxyl radicals have been theorized to be the root of titanium dioxide's bactericidal effect [57,61–62]. The hydroxyl radicals are short-lived and only produced on the surface of the titanium dioxide molecule in contact with water [15]. In turn, superoxide $^{\bullet}O_2^-$ ions are long-lived but, due to the negative charge, they cannot penetrate the cell membrane. This penetration is possible by hydrogen peroxide H_2O_2 [58]. Ireland et al. [63] reported that $^{\bullet}OH$ might act as a biocide due to its high oxidation potential and nonselective reactivity. In conjunction with oxygen, hydroxyl radicals may harm cellular macromolecules (e.g. lipids, proteins and nucleic acids) and promote other deleterious changes in bacterial cells (e.g. phospholipids peroxidation). Since phospholipid membrane contains essential components of the respiratory chain, it is one of the most sensitive cell structure during direct oxidative attack. It has been documented that irradiated TiO_2 surface reacts with the intermediate hydroperoxide and initiate cascades of autoxidation reactions [58,64]. Kiwi and Nadtochenko [65] demonstrated the formation of peroxidation products such as aldehydes, ketones, and carboxylic acids in parallel to the disappearance of cell wall membrane constituents. All these products exhibited potentially carcinogenic, toxic and mutagenic properties. Sunada et al. [66] confirmed this finding. Kiwi and Nadtochenko [67] also demonstrated that different components of the *Escherichia coli* cell wall had various resistance towards peroxidation during photocatalytic process with titanium dioxide. They found that the lipopolysaccharide (LPS) layer (its lipid portion acts as an endotoxin in gram-negative bacteria) was easily photodegraded [67]. Some of the experiments were verified by scanning electron microscopy (SEM) that showed morphological lesions of cell structures in the presence of TiO_2 [58,60,62,68–70]. Fig. 1 schematically illustrates the process of photodegradation of bacterial cells.

The second killing mechanism assumes the oxidation/reduction of the intracellular Coenzyme A (CoA). This process causes the loss of bacterial respiratory activity and leads to cell death [56,71,72]. If the titanium dioxide particles are sufficiently small, they can penetrate in the cell giving rise to the photocatalytic process inside. This has been theorized to be the third mechanism of bacterial death during photocatalytic processes [21,72]. Free TiO_2 particles

may also attack intracellular components directly. It is known that UV irradiation induces DNA and RNA physical and chemical damage. Pyrimidine and purine bases are converted to carbon dioxide and ammonia and nitrate ions [59,73–75]. Both ultrafine and normal size TiO_2 particles can cause bacterial plasmid DNA breakage [41,76]. Desai and Kowshik [77] reported the destruction of bacteria occurring in two distinct phases. The microorganisms were not much affected within the first 10 min of the process. In the initial phase, the oxidative damage of the cell wall took place, but bacterial cells were still visible. As far as the photocatalysis progressed, the titanium dioxide particles caused deleterious oxidation processes and cell death. The kinetic data showed that the cell wall damage took place in less than 20 min, followed by the progressive damage of cytoplasmic membrane and intracellular components [72].

As mentioned earlier, anatase and rutile phases are commonly used as photocatalysts. It has been demonstrated that the anatase phase has greater photocatalytic activity than the rutile phase [15,78–82]. There are also reports, however, that the rutile phase has the photocatalytic activity greater or comparable to the anatase phase activity [12,16,32,83]. Finally, some experiments have proven that a mixture of anatase and rutile with an approximate composition of 70–75% anatase and 30–25% rutile is more active than a pure phase [79,84,85]. Such a composition has P-25, produced by Degussa Chemical Company (now Evonic, Germany), most widely applied in the research of antibacterial effect [6,21,64,78–81]. This catalyst is used as a standard reference for comparison of photoactivity under different conditions. As has been shown, there is no consensus in the literature as to the photocatalytic activity among these two phases. The discrepancy of the data could have been caused by many photocatalyst properties, i.e. crystal size, surface area, crystal defects, pore size distribution, oxygen adsorption capacity, size and mobility of electrons, degree of hydroxylation (number of hydroxyl groups on the surface), and by the presence of indirect or direct band gaps [58,78,80–83]. Among the photocatalyst properties some are believed to be significant for antibacterial activity. Rincon and Pulgarin [83] documented that in water disinfection the TiO_2 surface area appeared a prime importance. In another work, however, the antimicrobial effect of TiO_2-coated film was independent of the TiO_2 particle size on the surface of plastic film [86]. Generally, nano-sized titania exhibits greater photocatalytic bactericidal properties than bulk material [83]. If an average diameter of nano-TiO_2 particles was 20 nm, it touched and slicked to the surface of the cell wall and destroy the cell membrane [70], whereas the smaller particles (<20 nm) could penetrate the interior of bacterial cells [77,84].

Almost all studies have reported the mechanism of TiO_2 antibacterial activity under UVA light. Although, the titanium dioxide photocatalysis shows a great potential to kill bacteria, the use of this process is limited to the environments with sufficient UV light [21,51,84,87–88]. For this reason, the development of new catalysts by inclusion of specific dopants, so that visible light may also be used to stimulate the photocatalytic activity, represents an important target [34,39,48,52,62,83,88]. Noble metals (Ag, Ni, Pt, Au, Ag, Cu, Rh, Pd) and oxides (ZnO, WO_3, SiO_2, CrO_3) or non-metals (C, N, S, P) have been shown to broaden and enhance the TiO_2 photocatalytic activity [89–92]. For instance, Hu et al. [68] and Hu et al. [69] demonstrated that AgI/TiO_2 and NiO/$SrBi_2O_4$ catalysts were highly effective at killing *E. coli* and *S. aureus* cells under visible light. Additionally, the TiO_2-based photocatalyst could significantly decrease bacterial viability and pathogenicity [78,87,93]. Based on the results, it can be concluded that the bactericidal mechanism of doped catalysts in visible light is comparable to that of TiO_2 in UV illumination.

Photocatalytic processes are conducted in photoreactors, which configurations depend on potential applications. Various types of photoreactors with suspended photocatalyst particles, or immobilized photocatalyst have been used in water disinfection. In most studies, operating parameters affecting experimental outcome have been given [29,43,94–96]. Under similar operating conditions, the antibacterial activity of TiO_2-based photocatalysts has been found to be dependent on bacterial strains, light source, irradiation time, photocatalyst type, concentrations of water contaminants, etc. The TiO_2 loading is postulated to be one of the most important operating parameters [57,95]. Shang et al. [89] demonstrated that the TiO_2 concentrations from 1 to 10 mg $\times$ L^{-1} were most effective in bacteria killing due to higher light absorption and higher quantities of oxidants. On the contrary, Rincon and Pulgarin [83] reported that the bacteria killing process did not depend on the titanium dioxide concentration. Subsequently, Manes et al. [64] and Cho et al. [57] found that the satisfied effect of killing *E. coli* at different initial concentrations of bacteria (from 10^2 to 10^8 CFU $\times$ mL^{-1}) were obtained when the load of titanium dioxide P-25 was 1 g $\times$ L^{-1}. It has recently been accepted that when the TiO_2 concentration exceeds 1g $\times$ L^{-1} UV light can be blocked by the catalyst itself [81].

It has been evidenced that the solution composition is essential for the antimicrobial effect of the photocatalysis process [15,68,83]. The presence of the 0.9% NaCl solution increased bacterial adsorption on titanium dioxide particles and fostered the photocatalytic action [95]. The presence of organic impurities decreased the bacteria killing rate by even 40% [97]. Wong et al. [93] demonstrated that if the protein BSA or dye contaminant was present in the solution, the antibacterial ability was exhibited.

The effects of temperature and pH on experimental outcome have been examined by many authors [62,68,69,83,90,91,94]. Robertson et al. [94] postulated that the temperature rise increased the bacteria killing reaction rate, what is consistent with the van Hoff–Arrhenius law. Herrera Melián et al. [98] demonstrated that the bacterial deactivation rate was enhanced in low pH (pH 5.0). On the other hand, Rincon and Pulgarin [83] did not observe any differences in the *E. coli* deactivation rate, when the initial pH varied between 4.0 and 9.0. Generally, the viability of bacteria to the titanium dioxide photoactivity action in dependent of incubation conditions, bacterial resistance to temperature and pH [29,69].

The initial bacterial concentration also displays direct effect on experiment outcomes [45,50,91,93]. In the bacterial concentration up to about 10^3 CFU $\times$ mL^{-1}, the killing rate was found to be usually independent of the initial concentration [45]. However, very high (over 10^8 CFU $\times$ mL^{-1}) bacterial concentrations may decrease the catalysis effect [63,64]. The explanation is that co-agglomerization of numerous bacterial cells with TiO_2 particles takes place.

The removal of pathogenic bacteria from drinking water and wastewater has been studied for many occasions [44,46,48,70, 88,89,91,92,96,98–109]. *E. coli* is extensively used as a biological indicator of the efficiency for drinking water treatments, so it is an easy target to destroy by photocatalysis [45,47,50,56,57,59,62–64,66–70,72,75,77,78,81,83,86–88,90,92,94–97,99–101,106–121]. However, the titanium dioxide antibacterial activity has been examined on a wide spectrum of bacteria, including gram-negative bacteria: coliforms [48,89,98,99,102], *Pseudomonas aeruginosa* [77,78,91,94,101,106,112], *Pseudomonas stutzeri* [122], *Pseudomonas putida* [121], *Klebsiella pneumoniae* [77], *Shigella flexnerii* [60,93,109], *S. dysenteriae* [44], *Acinetobacter baumannii* [60,93], *A. calcoaceticus* [121], *Salmonella typhimurium* [109,119], *S. choleraesuis* [80], *S. enterica* [94], *Vibrio parahaemolyticus* [80,93], *V. cholerae* [109], *Enterobacter cloacae* [119], *Serratia marcescens* [122], Bacteroides fragilis [112], *Legionella pnemophila* [123]; and gram-positive bacteria: Lactobacillus acidophilus [56], *Deinococcus radiophilus* [56], *Streptoccocus faecalis* [98], *S. mutans* [124], *S. aureus* [60,68,69,77,90,92,93,106,112,114,117], *S. pyogenes* [93] *Enterococcus faecalis* [90,98], E. hirae [112], *E. faecium* [114] *Listeria monocytogenes* [80,93], *Lactobacillus helveticus* [120], *Bacillus anthracis* [73,84], *B. subtilis* [78,104,115], *B. cereus* [104], *B. pumilus*

Table 1
The TiO_2 anti-bacterial action in exemplary applications.

Bacteria	TiO_2	Source power	Time irradiation	Loss of bacteria [%]	Applications	Ref.
UV light						
E. coli	TiO_2	UVA: 2 × 15 W	1 h	91.6	Surface disinfection	[114]
S. aureus	(P-25, Degussa)			53.8		
E. faecium				44.4		
E. coli	TiO_2	Black light lamp	24 h	79.7	Textile applications	[117]
M. luteus		UVA: 0.6mW/cm^2		15.0		
S. aureus MRSA				62.0		
E. coli K12	TiO_2	UVA: 5.5 W/cm^2	40 min	100.0	Water disinfection	[119]
S. typhimurium	(P-25, Degussa)			100.0		
E. cloacae				100.0		
P. putida	TiO_2 (Sigma Aldrich)	SVD-120A UV lamp:1.89 W/cm^2	4 h (daily) for 4 days	99.8	Membrane modification	[121]
Simulated solar light/visible light						
E. coli AN 387	Ag_2O/TiON	metal halogen desk lamp with a filter (>400 nm): >1.6 mW/cm^2	30 min	99.5	Water disinfection	[88]
S. flexneri	TiO_2	Classictone	25 min	~1.0	Medical usages	[93]
S. aureus	TiO_2 (N)	incandescent lamp		~58.0		
	TiO_2	60 W Philips:		~1.0		
	TiO_2 (N)	3×10^4lux		~30.0		
P. aeruginosa	TiO_2	870 W/m^2 in the	8 h	~99.0	Water disinfection	[101]
E. coli		300 nm–10 microm. range, 200 W/m^2 in the 300–400 nm UV range		~99.0		
E. coli	TiO_2	Sodium lamp	40 min	~100.0	Water disinfection	[106]
S. aureus		400 W	120 min	~100.0		

[105] *Micrococcus luteus* [115,117], *Micrococcus lylae* [125], and *Clostridium perfringens* [126].

According to some authors [72,116], the bacteria deactivation rates under photocatalytic action show the following sequence: *E. coli* > gram-negative bacteria (other than *E. coli*) > coliforms (other than *E. coli*) > *Enterococcus* species > gram-positive bacteria [71,114]. This precedence order is compliant with the complexity and density of the bacterial cell wall. Gram-positive bacteria possess a thick cell wall; containing many layers of peptidoglycan and teichoic acids, whereas gram-negative bacteria have a relatively thin cell wall; consisting of a few layers of peptidoglycan surrounded by a second lipid membrane containing lipopolysaccharides and lipoproteins. However, other studies have not confirmed this finding. Wolfrum et al. [115] shown that there were no significant differences between the rates of oxidation of gram-positive and gram-negative bacteria. The recent contribution of Gogniat and Dukan [59] indicated that the bacteria resistance to TiO_2 photocatalysis was produced largely by genes involved in reactive oxygen species resistance [59].

TiO_2 has also been proved to be highly efficient in killing antibiotic resistant bacteria, i.e. methicillin-resistant *S. aureus* (MRSA), and highly resistant to UV light bacteria such as *Enterobacter cloacae* [43,60,77,93,117,119,127]. Most of these bacteria occur in water, sewage, soil, meat, hospital facilities as well as on the skin and in the mouth. Due to its high killing efficiency, TiO_2 has been used to destroy bacterial spores (endospores) of *B. anthracis* and *B. cereus* [73,84,104,128], remove toxins secreted to water by cyanobacteria and to neutralization of algae present in water [129]. It was found that the bacterial spore destruction was attributed to the highly oxidizing radicals generated by TiO_2 [127].

Photocatalyst does not only kill cells but also decompose the cell itself [21,117]. Jacoby et al. [116] demonstrated that bacterial cell death could occur within 30 min, and the cells were completely oxidized to CO_2 after 75 h.

The titanium dioxide photocatalyst are considered more effective than any other antibacterial agent. It does not deteriorate technical material surfaces and shows a long-term antibacterial effect [21,29,116]. The TiO_2 photocatalyst has been found to be stable under ambient conditions and maintained its bactericidal activity for 1 year [96]. It was suggested that the disinfection with titanium oxide was more effective than the disinfection with chlorine or ozone [6].

Killing of pathogenic organisms with TiO_2 catalyst is not always sufficient. For instance, it concerns the endospore killing efficiency, which is not sufficient compared with vegetative cell killing [73]. Besides, aerobic bacteria, e.g. some gram-positive bacteria and, less commonly, gram-negative bacteria produce a superoxide dismutase enzyme (SOD) and catalase enzyme. The dismutase catalyzes the conversion of $O_2^{\cdot-}$ to H_2O_2 and O_2, and the catalase converts H_2O_2 to H_2O and additional O_2 as innocuous end products. *E. coli* has evolved to produce three different SOD forms strategically distributed within a cell to shield the cells from any oxidative damage resulting from their normal metabolism [72]. Evidences have shown that *E. coli* is capable of DNA damage recovery and dark repair of defective DNA segments [89,118]. It has also been observed that the addition of H_2O_2 and combined photocatalysis (photo-dark-Fenton reaction) resulted in the repression of microbial re-growth and dark repair [29,96].

A choice of experimental conditions is dependent of the specified TiO_2-based photocatalyst application. The examples of some experiments are presented in Table 1.

3. Titanium dioxide vs. viruses and prions

In comparison with bacteria, viruses are much smaller in size (from 0.01 to 0.3 μm) and can pass through filters that retard most of bacteria. Viruses are unique in that they have no independent metabolic activities and have to rely solely on infecting living hosts to reproduce themselves. Viruses infect all types of organisms, from bacteria and archea to animals and plants.

Titanium dioxide in aqueous environments, or absorbed on films, possesses antiviral properties caused by photocatalytic reactions [103,130–144]. Some studies were performed under UV irradiation, where TiO_2 was destructive to most viruses,

including bacteriophage T4 used as a model for deactivation of viruses [132,134,144]. Titanium dioxide under visible light irradiation also deactivated many viruses, namely: Herpes simplex virus HSV-1 [61], Hepatitis B [139], poliovirus [141], MS2 phage [133,138], rotavirus, astrovirus, feline calicivirus [142], influenza virus A/H5N2 [108] and influenza virus [143]. The viral deactivation rates could be very high [133]. In some studies, viral deactivation rates were found to be even higher than those for bacteria [141,145]. Li et al. [138] demonstrated that the use of visible-light photocatalysis with TiON/PdO fibers allowed to reach the final virus MS2 phage removal rates of 99.75–99.94%. Subsequently, Mazurkowa et al. [143] proved that the titanium dioxide nanoparticles destroyed the influenza virus hardly after 30 min of incubation.

However, the mechanism of virus destruction by photocatalysis is poorly understood [139]. It has been demonstrated that viruses respond differently from bacteria, when come into contact with TiO_2. It is well documented that the MS2 phage is inactivated by free surface-bound hydroxyl radicals as a major path and by ROS as a minor path [133]. Kashige at al. [135] suggested that the mechanism of *Lactobacillus casei* phage (Pl-1) deactivation by TiO_2 under UVA irradiation was primarily caused by the damage to the capsid protein by active oxygen species such as superoxide anions ($\bullet O_2^-$) and hydroxyl radicals (•OH). In the next stage of the virus destruction, the genome DNA or RNA inside the viral particles was considerably fragmented as observed electrophoretically [134,135,143].

It is believed that among bioparticles viruses are the most photocatalysis-sensitive. Several studies revealed the deactivation of viruses by TiO_2 depending on different factors such as the concentration of nanoparticles, incubation period, solution composition, light source, etc. Sang et al. [142] documented that the addition of bovine serum albumin could protect the FCV virus against deactivation by TiO_2 in a dose-dependent manner.

In the presence of UVA light titanium dioxide oxidizes and destroys organic substances, including infectious agents such as prions (proteinaceous infectious particle). After treatment with $4\,g \times L^{-1}$ TiO_2 (P-25) $\times$ H_2O_2 and 4 g H_2O_2 diluted in distilled water and irradiated with UVA lights for 12 h, completed degradation of proteins PrP^{Sc} was achieved [140].

4. Antifungal effect of titanium dioxide

Fungi (filamentous forms and yeasts) are very diverse in their morphology. There are almost 200,000 fungal species described all over the world. About 500 species are presently known to be pathogenic or potentially pathogenic to animals, including humans, and plants. Fungi have been identified as a primary contributor to the problem of indoor air quality. In fact, the term "sick building syndrome" is used to describe buildings, in which various physical, chemical and biological factors, including fungi (their spores and mycotoxins), considerably decrease the indoor air quality and, consequently, lead to discomfort or illness of the occupants. Allergies, asthma, infections, and the long-term repercussions of mycotoxins are just a few of the many real health effects associated with fungal contamination of indoor environments. Outdoor environments can also be negatively affected by these organisms. Fungi can destroy wood, fibbers and other materials; causing severe damage to buildings and technical materials. Most antifungal chemicals are non-specific to the organism affected and can be detrimental to the environment, including toxicity to plants and animals [145]. Due to that fungal cells share many similarities with the cells of higher organisms, it is difficult to find fungi-specific agents. Photocatalysis has been discussed to be a solution to this problem. However, the available literature contains little data on the deactivation of fungi and/or fungal spores by TiO_2-mediated photocatalysis [56,90,100,101,106,115,146–152].

The first research on the photocatalytic destruction of fungi, specifically the yeast *Saccharomyces cerevisiae*, was carried out by Matsunga et al. in 1985 [56]. In their study *titanium dioxide* (P-25) enhanced the killing of the yeast from 80% to 100% over 120 min of the reaction time. The antifungal activity of titanium dioxide has been examined intensively on other fungal species, namely: *Candida albicans* [90,101,106,114,148], *S. cerevisiae* [56,100,106], *Penicillium expansum* [146], *Daporthe actinidiae* [149], *Aspergillus niger* [90,106,150], *Fusarium. solani* [49,51,101,151], *F. anthophilum* [151], *F. equiseti* [49], *F. oxysporum* [49], *F. verticillioides* [49] and *Penicillium chrysogenum* [152].

Chen et al. [150] found the photocatalytic sensitivity of fungi to be considerably weaker than that of bacteria. Titanium dioxide irradiated with UV and visible light rarely induced photoreaction for fungal inhibition [101,106,151]. This probably resulted from different chemical composition, structure and thickness of cell walls in these organisms. One major difference is that fungal cells have cell walls that contain chitin, unlike the cell walls of bacteria, which contain peptidoglycan. Furthermore, due to the structural differences between fungal groups (e.g. filamentous and yeast species) and also between fungal spores (conidia) and filaments (hyphae), these organisms display differentiated reactions to the photocatalysis. Seven et al. [106] demonstrated that the photocatalytic water disinfection could not completely inactivate the *Aspergillus niger* spores, while this process killed the *Candida albicans* cells. Akiba et al. [148] proved that the photocatalytic antifungal effect resulted from the denaturation of the Candida cell. In addition, a SEM examination revealed that the surfaces of the cell were grainy, dissolved, furrowed and dilapidated [114]. However, the penetration of the catalyst through the fungal spore wall was impossible. The reason was that these spores were larger (a few order of magnitudes) than the TiO_2 catalyst particles and multicellular [148].

Sichel et al. [49] demonstrated that from 1 to 6 h were necessary to inactivate *Fusarium* sp. spores in water solution (from 10^3 CFU $\times$ mL^{-1} to almost zero) by solar photocatalysis. Subsequently, Chen et al. [150] documented that the *A. niger* mycelium, which grown on the wood surface with TiO_2 coated film, was completely inhibited after 20 days under UVA irradiation. However, after that time the spores of *A. niger* were still viable and the fungal re-growth was observed [150]. Similar findings were reported by Wolfrum et al. [115] and Mitoraj et al. [90]. The photocatalysis was found to be ineffective in controlling latent infections of *Daporthe actinidiae* in kiwifruit [149].

Maneerat and Hayata [146] reported that TiO_2 alone did not affect the growth of *Penicillium expansum*. This finding is consistent with previous data, which showed that TiO_2 itself did not act as germicide or fungicide in the dark. When UVA was combined with TiO_2, the viable number of this fungus apparently decreased [83].

5. Toxicity of titanium dioxide for cell and cancer cell

Cancer treatment is one of the most important topics associated with photocatalysis [6,20,21,153–156]. The cancer cells are eukaryotic cell (containing the nucleus) and their structure is complex. Based on this knowledge is thought that killing cancer cells might be more difficult than killing microorganisms by the photocatalytic reaction with TiO_2 nanoparticles. In all probability, in the presence of UV light titanium dioxide induces the apoptosis of cancer cells. However, the mechanism of this process is still unknown. Cancer cells die, if their membranes are damaged or if the oxidation/reduction compounds needed for adenosinotriphosphate (ATP) production in the cell are depleted or exhausted. Human U937 monocytic leukaemia cells were treated with 1 mg $\times$ mL^{-1} of colloidal TiO_2 for 2 h at 37 °C followed by irradiation with UV light (300–400 nm). About 80% of cells were killed after 10 min of illumination and complete destruction of leukaemia cells were obtained

after 30 min [18]. Titanium dioxide showed the evidence of membrane damage and DNA fragmentation, especially the formation of DNA ladder. All these effects are characteristics for apoptosis. It has been suggested that reactive oxygen species are responsible for this process [74]. Zhang and Sun [154] found that photoexcited TiO_2 induced series of oxidized chain reactions, which damaged cancer cells. The human carcinoma cell damages occurred in two stages. The initial oxidative damage took place on the cell membranes, where the TiO_2 nanoparticles had its first contact with intact cells. At this stage, the cells did not lose their viability but the membranes became somewhat permeable. Subsequently, the nanoparticles diffused into the damaged cells and directly attacked intracellular components. These findings are in agreement with those of Fujishima et al. [156] and other authors [157–160]. Specifically, Lagopati et al. [157] reported that nanoparticles of titanium dioxide exerted cell-dependent effects on cellular functions such as proliferation and viability.

The antitumor activity of titanium dioxide has been investigated with human skin fibroblasts and alveolar macrophages [153,20], Ls-174-t human colon carcinoma cells [154], human colon carcinoma LoVo [155], HeLa (also Hela or hela cell) implanted in nude mice [156], breast epithelial cancer cells cancer cells line MCF-7 and MDA-MB-468 [157], Bel 7402 human hepatoma [158], and with brain cancer cell [159]. The limitation of cancer treatment by photocatalysis generally consists of the weak penetration of UV and visible light through the skin. Despite, the cerium element-doped titanium dioxide nanoparticles induced the apoptosis of Bel 7402 human hepatoma cells in the presence of visible light [158]. Xu et al. [155] showed that the deposition of gold on TiO_2 nanoparticles greatly increased the photocatalytic deactivation effect of TiO_2 on tumor cells. The optimum Au content in the Au/TiO_2 nanocomposites was about 2 wt.%.

Recently, scientists from Illinois reported the development of the first nanoparticles that seek out and destroy brain cancer cells without damaging nearby healthy cells [159]. The authors utilized the TiO_2 nanoparticles covalently conjugated with antihuman-IL13α2R via DOPAC (3,4-dihydroxyphenlacetic acid) linker. After a 5-min exposure to polychromatic visible light, titanium dioxide initiated the production of reactive oxygen species, which damaged the cancer cells and induced their programmed death. Moreover, even after 48 h after light exposure, the TiO_2 toxicity to cancer cells was still high.

6. Titanium dioxide toxicity

Generally, titanium dioxide has been proved to be non-toxic [8,11,20,21]. Although photocatalysis provides many benefits for industry and medicine, there is an increasing concern that titanium dioxide may indeed become toxic in nanoparticulate state. It has been found that nanoparticles may be more toxic than larger particles of the same substance [160–162]. One of the main differences between nano and ultra size titanium dioxide is the much greater surface area. Such property affords a greater potential for catalytic activity and light absorption. In this context, normal size (>100 nm) TiO_2 has been considered to be biologically inert [4,153,163–166]. Nevertheless, titanium dioxide dust, when inhaled, has recently been classified by the International Agency for Research on Cancer (IARC) as an IARC Group 2B carcinogen possibly carcinogenic to humans. The IARC classification was based on the discovery that high concentrations of pigment-grade (powdered) and ultrafine titanium dioxide dust caused respiratory tract cancer in rat and humans exposed by inhalation and intratracheal instillation [167].

Titanium dioxide nanoparticles (~20-nm diam.) exhibit cytotoxicity and potential genotoxicity to protozoa such as *Giardia lamblia* [168] *Cryptosporidium parvum* oocysts [169] and also to higher animals, e.g. fish *in vitro* conditions [170]. Fortunately, this effect occurs during combined expose of titanium dioxide and UVA. On the other hand, some studies have shown that TiO_2 particles (10–20 nm diam) simulated ROS production in the absence of UV [171]. The exposure to different nano-sized particles causes negative health effects such as chronic pulmonary inflammation in rat and mice [172,173], allergic sensitization and lung inflammation in mice [174], damages neurons *in vitro* [171], and also oxidative DNA damage, lipid peroxidation in human bronchial epithelial cells [161]. Another harmful effect of TiO_2 nanoparticles was presented by Dunford et al. [174]. The authors showed that titanium dioxide particles from sunscreen constitute to the formation of ROS in skin cells. This can result in DNA damage, mutations and cancer development. Not all researches agree with this finding [175–178]. Based on DNA microarray analysis, Fujita et al. [177] showed that the innate TiO_2 (without illumination) cytotoxicity was weak. The differences in size and shape did not affect the mechanical toxicity of nano-TiO_2 particles [176]. It was also found that the anatase phase was more cytotoxic than the rutile phase [177].

Poor data on TiO_2 concentrations in the environment have been found in the available literature. It is believed that titanium dioxide concentrations are higher in water sediments and organisms than in water. According to Zang et al. [179] TiO_2 accumulates in fish but the uptake mechanism is still discussed. Muller and Nowack [180] first performed the quantitative risk assessment of TiO_2 nanoparticles in water environment. Nano-TiO_2 might pose a risk to aqueous organisms in concentrations from 0.7- to 16-times higher than the Predicted No Effect Concentration (PNEC). The PNEC for nano-TiO_2 in water was found to be <0.001 $mg \times L^{-1}$. Based on the data, it could be assumed that the risk to aqueous organisms from nano-TiO_2 was low.

Although the present use of nano-TiO_2 in water treatment facilities is limited to pilot testing, the potential exposure and risk to the general population can be very high. A number of TiO_2 nanoproducts and nanomaterials available to the consumer has rapidly increased within the last couple of years [20,39,42,153,163–165]. The nature of the products is diverse and so is the nature of the consumer exposure. According to EPA rapport [164], beside such titanium dioxide sources as topical sunscreens, cosmeceuticals (traditional cosmetics such as moisturizers and color cosmetics that incorporate active sunscreen ingredients with nano-TiO_2), sun-protective clothing, cleaning agents, air purifiers, coatings, and food packaging, TiO_2 nanoparticles are run off from both new and naturally aged building facades painted with paint containing nano-TiO_2 and are emitted to air by nano-TiO_2 powder-coated materials (wood, polymer, and tiles). Of course, the presence of nano-TiO_2 in a product does not mean that exposure will occur. Unfortunately, very few producers/distributors provide information about the content of nanoparticles in their products. However, the calculation made by Hansen [163] estimated the consumer exposure for a facial lotion, fluid and spray containing nanoparticles is about 26, 15 and 44 $\mu g \times kg^{-1}$ body weight/year, respectively. From a survey on the industrial production and application of nanotechnology in the Danish industry, it is known that producers of sun lotions use 10–20 nm TiO_2 nanoparticles as UV absorber and that the nanoparticles are present in concentration up to 10%. Possible exposure percentage are equally high ranging, between 20 and 30% except for food and beverages, and electronics and computers, for which about 10% fall into the category of possible exposure [163].

7. Titanium dioxide applications

The antibacterial, antiviral and antifungal properties of photocatalysis with TiO_2 have been increasingly exploited in a number of experimental and commercial applications [39,42,163–165,181–182]. Some applications are as follows:

- Antibacterial textile fibers containing TiO_2 photocatalyst (Kurare, Inc.);
- The anti-flu suit (Haruyama Trading Co.);
- Architectural material e.g. aluminum coatings (YKK, Inc.), nano glass (Pilkington);
- Cement containing TiO_2 photocatalysts and other coating materials for architectural walls (Taiheiyou Cement, Inc., TX Active®, ItalCement Group, TioCem Górażdże; National, Inc., Tomorrow Nano Science and Technology Co., Ltd);
- Photocatalytic paints e.g.: C1 (contains about 3% wt of TiO_2), T2 (contains about 10% wt of TiO_2) obtained from Millennium Chemicals Co, Titanium FA (PIGMENT Building Chemistry Producer Szczecin); StoPhotosan Color (Sto-ispo);
- AirCide filters (KES Science and Technology, Daikin);
- Fresh^2 light bulbs (Topbulb, Victoria Supply Company, USA);
- Antimicrobial nanoemulsion (NanoBio Corporation) and cleaners (Nanotec);
- Photocatalysis Mosquito & Fly Trap, Kongfu Dude (Foshan Edalight Photon Technology Co, Ltd.).

8. Concluding remarks

In recent years the photocatalysis methods based on titanium dioxide have gained considerable attention by industry. With the assistance of ultraviolet or visible light the methods posses unique properties associated with strong oxidation power.

The methods offer the great potential for TiO_2 use in a variety of settings to reduce the transmission of pathogens in the environment. The emergence of increasingly virulent and multi-resistant pathogens in hospital and human settings provides another motivation for development of alternative, new approaches. Photocatalysis with titanium dioxide is toxic to all forms of bioparticulates and kills many pathogenic organisms. The diverse sensitivity of bioparticulates towards photocatalysis follows the order: viruses > gram-negative bacteria > gram-positive bacteria > endospores > yeasts > filamentous fungi.

When TiO_2-based coatings are applied to exterior surfaces, such coatings allow to wash away microorganisms by rainfalls. The use of the low-cost photocatalyst and the possibility of its activating with solar light offer economically reasonable and environmentally friendly solutions to the disinfection process, development of self-cleaning materials, biofouling resistant filtration membranes and the protection of technical materials from biodeteriorating microorganisms. It is also noteworthy that the photocatalysis process was suggested to be attractive as a defense tool against bioterrorism [128]. However, nanotechnology engineers should keep in mind that using TiO_2 nanoparticles poses the potential risk to the environment and human health.

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