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Journal Pre-proof

Titanium-based photocatalytic coatings for bacterial disinfection: The shift from suspended powders to catalytic interfaces

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Abstract:

Accessibility to a clean indoor environment is still an important problem in the world. Photocatalysis based on semiconductor materials was proposed as a green solution for contaminated surfaces and domestic areas. This treatment has been considered by many researchers using diverse preparation methods. Titanium dioxide (TiO_2) was extensively investigated to treat dyes and microorganisms in wastewater, indoor air and even in wild environments. TiO_2 showed divergent efficacy against Gram+ and Gram- bacteria, viruses (DNA-viruses, RNA-viruses, and/or reverse transcribing viruses), algae (unicellular, microalgae…) and free-floating genomic DNA. Today, photocatalysis mediating TiO_2 for pollutants removal in real settings is attracting a lot of attention. TiO_2 absorbs in the UV spectral region and many techniques were adopted to red shift its absorption to the visible region such as doping, coupling with other semi-conductors or decorating it with plasmonic materials. TiO_2 uses started as suspended material in aqueous media. This suspension was fast faced by the difficulty to recover the catalyst after treating water. In the present review, we present the shift from the photocatalytic activity of Ti-based catalysts/photocatalysts for the disinfection of polluted water (TiO_2 in suspension) to the implementation of smart indoor surfaces (supported TiO_2) presenting self-sterilizing properties. In this review, we present the general context of the water issue as raised by the United Nations 2030-agenda, we show an overview of photocatalytic materials and we try to link the reported photocatalytic mechanisms for the disinfection process. At the end of this review, we stress the advantages of using supported photocatalytic thin films and the interfacial phenomena leading to bacterial killing without sacrificing the catalyst that can be easily reused.

Keywords: TiO_2; Photocatalysis; Thin Films; Disinfection; Interfaces.

1- Introduction

Mitigation of environmental pollution is an important universal issue that needs to be investigated [1-4]. The environmental pollution has occurred via point- and non-point sources. The major pollution sources are through agricultural, forestry and domestic activities by releasing fertilizers and pesticides [5,6], industrial activities [7], pharmaceutical [8,9]. Since water is one of the most crucial natural resources in the world for life, many methods for water treatment have been considered [9]. It has been reported that one-fourth cities in the world are still exposed to a lack of safe drinking water. Since in Latin America drought can significantly affect economic activities [10]. Availability to developed drinking water supplies in Latin America and Caribbean (LAC) has been expanded since the start of reform waves at the beginning of 1990s. The advancement of LAC countries was significant by world factors, notably since 2015. The only countries that had the highest access index of safe drinking water sources were developed countries, where 99% of people used safe drinking water (Figure 1). Also, sanitation services developed in LAC from 1990 to 2015 [11]. Moreover, in Asia and Africa and the collapse in the water area was very remarkable due to the demographic and economic growth. Although, water reuse has been considered in these countries [12] yet water resources are day after day scarce.

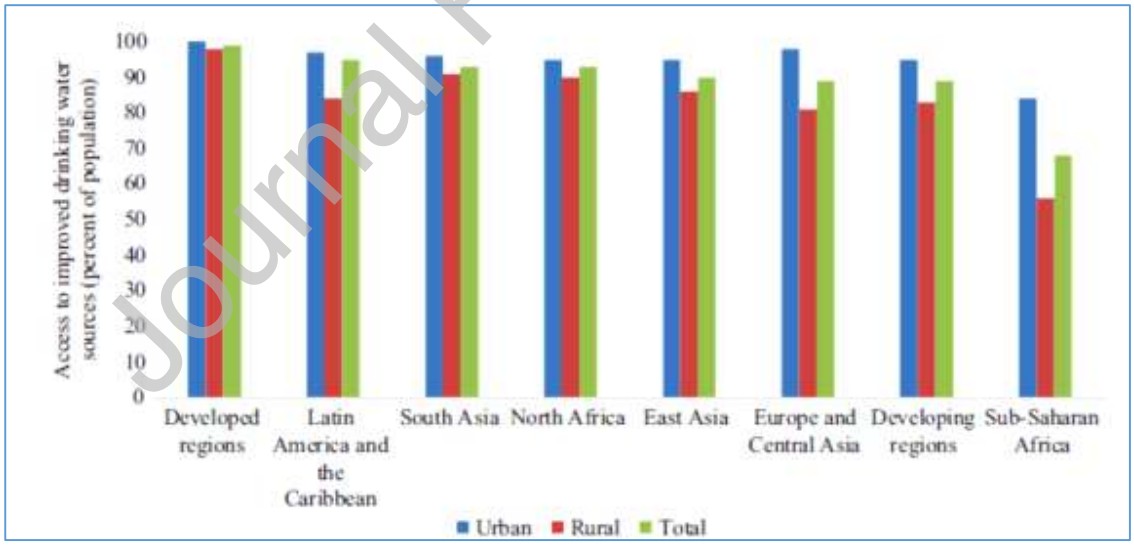


Figure 1. Access drinking water resources as evaluated by WHO [11].

Even though there are many natural water resources in the world, but only less than 1% of the global store is available for human consumption [13]. Water scarce was stressed in the World Health Organization (WHO) report in 2011 [14] affirming that there will not be enough drinking

water for the coming years. Furthermore, during its general assembly of 2015, the United Nations (UN) designed target goals that should be achieved for the best of the present and the coming generations. Seventeen Sustainable Development Goals (SDGs) arise as the pillar of the sustainability of humankind. One of the most urgent needs today is the accessibility to clean water and sanitation (SDG 6). Moreover, as water and energy are strongly allied, the water-energy nexus raised the need to recover the used water. SDG7 was designed for affordable clean energy. These goals include the achievements of safe drinking water and sanitation services and also economical and reliable energy [2].

Many traditional methods exist for water and wastewater treatment [15,16]. However, these methods could not effectively treat all contaminants and provide water that has standard factors for irrigation and/or human use. This area has been challenged by researchers working on alternative solutions to treat used water [3,4]. Many methods have been investigated such as adsorption, plasma, filtration and chlorination [17]. Later, the development of nanostructured tailored materials for water remediation has been growing during the last three decades [18]. Many nano-architectures have been reported to degrade organic pollutants [19,20], disinfect bacteria [21], inhibit viruses' growth [22] and remove malodors [23,24]. The reported nano-designs range from suspended nanoparticles, nanotubes, nano-spheres, nano-flocks, nanowires amongst others. In some cases, the combination of these nanostructures enhanced their catalytic activity [16]. Suspended nanomaterials were mainly used as adsorbents [25], disinfectant [26-28], filters [29], and reactive agents [30], which offer a large index for water treatment [31,32]. Fenton, photo-Fenton, catalytic ozonation, and photocatalysis mediating heterojunctions and Z-scheme catalysts are in their deep investigation today [33-37].

Due to the presence of several microorganisms in water and wastewater, the disinfection process has been considered worthwhile [38-40]. These microorganisms degrade water quality and endanger human/animal health [41]. Waterborne diseases are very dangerous and caused by water contamination due to bacteria, protozoa, virus and other microbes. As per WHO, the waterborne diseases account for about 3.6% of disease global burden and cause around 1.5 million human deaths yearly. WHO, assessed that 58% of that burden (or 842,000 deaths per year), is due to a lack of safe water, hygiene and sanitation [42]. Many approaches were adopted to disinfect water such as chlorination [43], ozonation [44] and photo-assisted systems [45]. According to the Environmental Protection Agency (EPA) [46] ozone is more efficient than chlorine for

disinfection, but it is not economically affordable [47]. Despite some drawbacks related to photons' diffusion, wavelengths and biomass accumulation, photo-disinfection is one of the most interesting applicable systems in the world. Many advanced materials were used for this purpose [48] but supported TiO_2 was used for self-cleaning grease, dyes stains, coffee and /or wine on textile fabrics because of its several advantages of excellent optical and electronic properties, stability, high oxidation power, low cost, etc. Antibacterial activity of sol-gel and colloidal supported TiO_2 films was also investigated [49,50]. Although these preparations showed self-cleaning and self-sterilizing under light, these colloidal/sol-gel TiO_2 coatings presented low adherence to the substrate and reproducibility [51,52]. The thickness of these coatings was not controllable and could be easily wiped-off [53,54]. The use of supported photocatalyst films allows the recovery of the catalysts/photocatalyst after use without harmful ions/particles release in the water matrix. Among others, anatase phase of TiO_2 is active only in UV radiation (<380 nm) as the band gap width is large (3.2 eV). Nevertheless, sunlight has only around 4% of UV light. To advance the photocatalytic activity of TiO_2 in sun light, there are many methods, which prevents electron-hole pair recombination, and/or rebounds the sorption of the photocatalyst from UV to visible light. The advancement of TiO_2 based materials are very important in photocatalytic degradation of the pollutants. Some papers are available [55, 56] in this area but much work has not been carried out and this the time to review the status of TiO_2 based photocatalytic thin films for photodegradation of the pollutants so that further advancements may be achieved by the researchers.

In this review, we expose the water scarcity and the necessity of wastewater treatment and reuse. Then, we illustrate some technologies used for water disinfection and organic pollutants degradation. Advanced oxidation processes are highlighted as green approaches for water disinfection. Titanium-based photocatalytic thin films for water/wastewater disinfection are reviewed. The mechanistic considerations are highlighted for each section.

2- Water consumption and reuse: Sustainable development goals (SDGs)

Accessible water for drinking consumption without any contaminated materials is the most important challenge in the world [57]. Over 1.2 billion people have no safe water to drink and are exposed to death due to water pollution-related diseases [58]. These challenges have caused the necessity of water resuscitation and reuse with its related critical issues. Even though water

resuscitation and reuse have experimented around the world, however, water reuse currently faces the huge volume of produced urban and industrial effluents [59]. Water reuse is a major interest that is increasing in many parts of the world, even in countries that are not normally exposed to water scarcity [60]. Many methods were used to achieve acceptable purified water for possible reuse [61,62]. These methods lead to direct [63] and indirect [64] reuse of treated wastewater.

The demand for natural resources use has been increasing during the last decades threatening human life and degrading ecosystems. Thus, these resources must be managed in a sustainable manner [65]. The United Nations has designed an agenda for the coming years to fulfill several sustainable development goals (SDGs). This 2030 agenda comprises 17 SDGs and 169 targets. It has been separately presented to countries with high pollution index to reduce the harmful agents to the environment [66]. Among these goals, SDG 6 has been focused on providing water by 2 targets. Target first (target 6.3) is designed to improve water quality by decreasing pollution, removing dumping and minimizing the release of hazardous chemicals and materials, halving the proportion of untreated wastewater, and growing recycling and safe reuse by 2030. Target second (target 6.4) is designed to considerably increase the efficiency of water use in all sectors and ensure sustainable harvesting and supply of freshwater to answer the lack of water and decrease the number of people suffering from water shortages by 2030 [67,68]. Also, reliable and economical energy sources are the aim of the SDG 7; another goal that indirectly relates to wastewater reuse. Besides, water and energy are linked together so that for producing energy, water is necessary and vice versa [69,70].

3. Non-conventional solutions for water treatment and emergence of antibiotic resistance

One of the main methods for water disinfection process is chlorination that was investigated for many years. However, harmful byproducts are produced leading to health complications, which warranted sophisticated research linking the production of these byproducts with some cases of human cancer [71]. The main issue is that certain groups exhibit considerable resistance to chlorination, such as viruses or parasites [72]. Deeper discussion of the chlorination process for wastewater disinfection is out of the scope of the actual manuscript. From another perspective, adsorption was used to treat polluted water. However, this process does not inactivate microorganisms in water. A. Fahad et al., recently reviewed the wastewater treatment techniques

and illustrated some of the non-conventional technologies. Figure 2 shows some unconventional processes used for water/wastewater treatment.

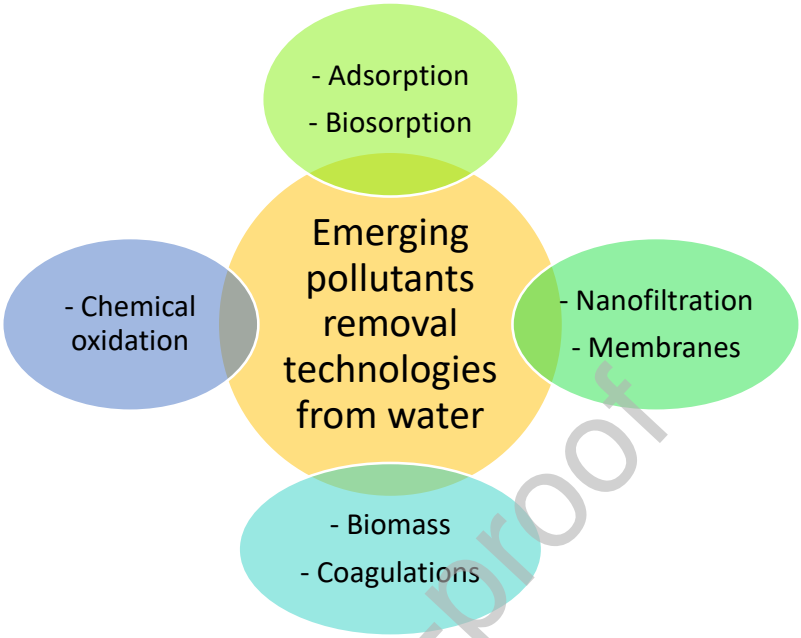


Figure 2. Some unconventional processes used for water/wastewater treatment

Recently, Karkman and co-workers [73] reported that wastewaters are hot spots for antibiotic-resistant-genes transfer. However, they specified that this concerns municipal, industrial and hospital wastewaters. This warrants the urgent need for new non-selective solutions for bacterial/microbial removal from non-desired media/environments. Antibiotic-resistant bacteria present a serious problem that raised up during the last few years [74-76].

Alexander Fleming, the pioneer of penicillin, warned at first sight of the potential importance of the development of microbial resistance [77]. Shortly, the evidence turned out to be alarming. Antibiotic resistance genes can then spread to other organisms [78]. The mixing of municipal and hospital wastewater effluents and their treatment in wastewater treatment plants (WWTP) could be the significant storages for antibiotic-resistance genes [75,79]. Therefore, antibiotic-resistant bacteria in the WWTPs sewage should be controlled in order to reduce the spread of pathogenic agents during the water reuse process [66].

To inactivate antibiotic-resistant bacterial strains in WWPTs, chemical disinfection was employed. Chlorine is a chemical disinfectant that its effectiveness and side effects have been

conflicted. Grabow et al., [80] examined the chlorination process on ampicillin-resistant bacteria in effluents. They found that chlorination decreased this strain, however other antibiotic-resistant bacteria were able to survive and grow [81,82]. Among these techniques and methods that have been studies for water treatment none of them could effectively remove all biological pollutants. Hence, finding an effective method for water disinfection is urgently needed.

4. Advanced oxidation processes as a non-selective solution for wastewater remediation

Advanced oxidation processes (AOPs) or advanced oxidation technologies (AOTs) is a green technology for the treatment/degradation of water and air pollutants [83,84]. AOPs include various methods such as ozone (O_3), Fenton (Fe^{2+}/H_2O_2), electrolysis, sonolysis, photolysis, photo-Fenton and photocatalysis. Despite their widespread lab-scale applications, their short half-life limited their use for the disinfection process in industrial set-ups [85,86,87]. AOPs are associated with the production of strong, non-selective oxidative radical (namely, reactive oxidative species, ROS) [88,89]. Fenton process includes Fe^{2+} or other metal types in mixture with H_2O_2 at usually acidic pH that is done for the degradation of organic pollutants. This process has several benefits and drawbacks. Dark run and relatively high reaction speed are the advantages of Fenton process. In contrast, the need for a post-treatment to remove the agglomerated iron after treatment and the high costs of pH adjusting when treating a large amount of water is the major problems in this method [90,91].

After the report by Matsunaga et al. [92] many studies were devoted to the issue of microbial abatement in water using suspended TiO_2. Titanium dioxide nanoparticles were dispersed in water and illuminated by UV light. Many other nano-sized particles were then used to treat water. Particles at the nano-size diffuse randomly in a fluid (liquid or gas) and ROS formation was harassed by photons with an energy greater than the band-gap energy of the used semi-conductor.

Later, some research groups and some industries tried to support TiO_2 on diverse substrates using different methods such as size-press technique, dip coating, spin coating and many other solution-based techniques belonging to the large field of wet chemistry. Many studies reported on the large-scale application of TiO_2 photocatalysis. The main drawback of these preparations is the low mechanical stability leading to NPs' leaching in the treated water. To recover these leached catalysts, ultrafiltration or a centrifugation post-treatment step was compulsory. However, due to the very small size of some nanoparticles, they adhere to the used reactor/flask or remain in the solution at very low amounts. This implies additional labor and costs [93].

Another AOT that was largely investigated is sonochemistry. The first experiment in sonochemistry was developed by Richards and Loomis in the 1920s. This method involves vibrations that are created by ultrasound (US) waves that encounter water molecules leading to the production of hydroxyl radicals (•OH). The range of the frequencies most used in sonochemistry goes from 20 to 1000 kHz, although the range of application is wider and can be extended until 3000 kHz [94]. Each cavitation/bubble collapses theoretically producing local pressures of ~2000 atm and temperatures around 5000 K in aqueous solutions. The major disadvantage of this method is the small diffusion distance of the produced radicals. These radicals stay near the vibrations (acoustic cavitation). This limits their use for the treatment of large volumes. Sonochemical processes were employed for the degradation of aromatic compounds, pesticides, endocrine disrupters, pharmaceuticals and disinfection agents in water [95-97]. Recently, Cairós et al., reported on the process behind the chemical effects of ultrasound cavitation, namely the rectified diffusion [98]. They resembled the cavitation bubbles to micro-reactors inside a liquid.

Electrochemical processes were also investigated to treat wastewater. An electrochemical reaction is defined as a process either caused or accompanied by the transfer of electrons between two substances - one a solid and the other a liquid. To effectively treat wastewaters, these processes were associated with direct electrochemistry (anodic oxidation) and indirect electrochemistry (electro-Fenton) and/or with sonochemical, physicochemical and photochemical treatment methods allowing the removal of pollutants from water in industrial, pharmaceutical and agricultural effluents [96,99].

Although all these methods have many advantages yet photocatalysis method among all the AOPs methods was reported to produce promising and significant results for water treatment. Photocatalysis contains heterogeneous and homogeneous processes [88]. Heterogeneous photocatalysis includes semiconductor materials like TiO_2, CdS, ZnO, ZnS, and ZrO_2 and homogeneous photocatalysis contains Photo-Fenton treatment [100], Photocatalytic Ozonation (O_3/UV) [101], Photolysis of hydrogen peroxide (UV/H_2O_2) [102], Peroxone Process (O_3/H_2O_2) [103,104], and Vacuum Ultraviolet (VUV) [105,106]. Photocatalytic processes were reported to remove Natural Organic Matter (NOM) [107-109], pesticides [110-112], pharmaceutical and personal care products (PPCPs) [113-115]. So far, many studies have carried out for bacterial inactivation in water [116]. Other research groups studied the photocatalytic fungal removal from wastewater [117]. Another significant group of water pollutants is viruses that were removed from

water by Fenton process [118,119]. Fenton reaction has effectively experimented with the deactivation of some viruses like MS2 coliphage or Echovirus [120,121]. Subsequently, some prokaryotic unicellular microorganisms have been also investigated because of their harmful effects on human health. Also, photocatalysis was seen to inactivate fungal cell like *Penicillium*, *Fusarium*, and *Aspergillus* from water and soil [122-124]. Besides, some kinds of yeasts and multicellular microorganisms specifically *Candida* and *Fusarium solani* respectively, have been inactivated by AOPs system [125-127].

5. Photocatalysis for water disinfection: form suspension to supported Ti-based photocatalysts

5.1. Background of TiO_2 photocatalysis

One of the most used photocatalysts is titanium dioxide. It has been widely used for water disinfection during the last two decades [45-47,128]. In 1972 photo-electrolysis of water was experimented by Fujishima and Honda [129]. Also, TiO_2 can catalyze pollutant oxidation [130,131] and kill the microorganisms [132-133]. In fact, TiO_2 coatings were prepared with a superhydrophobic property allowing water to spread on its surface. This allows the preparation of self-cleaning and anti-icing glass [134,135]. Although in early studies TiO_2 had not shown effectiveness in water disinfection, however, in recent years many publications reported on the high capability of this material [136]. TiO_2 is a semiconductor with a nearly 3.2 eV band gap. TiO_2 can absorb photons with wavelengths below 385 nm. During this process pair electron-hole produce. The photo-generated electrons will then migrate from the valance band to the conduction band. Besides, some processes may occur within this operation such as the production of some reactive oxygen species such as $O_2^{\bullet-}$ or $^{\bullet}OH$ and in the worst case, the photo-generated charges may recombine. In another way, in solution, it can react and produce H_2O_2, hydroperoxyl (also known as the perhydroxyl radical, which is the protonated form of superoxide with the chemical formula HO_2) and other radicals [137,138]. Along with the broad application of TiO_2 in this issue, many other applications with different materials have been reported as illustrated in Table1 [137]. At this level, it is necessary to revisit the photo-generated ROS from illuminated TiO_2. Figure 3 summarizes the photo-generated ROS and their possible permutations. Anodic reactions are induced by the photo-generated electronic holes mediating TiOH at the interface of TiO_2. This involves the formation of active radicals such as $O_2^{\bullet-}$, $HOO^{\bullet}$, H_2O_2. This pathway leads to the oxidation of the pollutant through these reactive species or by thermal oxidation. On the other side,

cathodic reactions are induced by the electrons photo-generated at the conduction band of the TiO_2. These electrons react with the surrounding water/water vapor/oxygen to start a cascade of permutations leading to the formation of various reactive oxygen species that are thermodynamically possible. This last aspect involves level energies and pH conditions allowing their formation.

TiO_2 has three polymorphs crystal structure: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). The naturally abundant form is Rutile; however, it presents the lowest free energy. The most important structure is anatase showing higher photocatalytic activity compared to rutile. This is particularly related to its high ability to inject and/or transport electrons, especially in photovoltaic devices. However, in general, approximately all studies have shown the mixtures of anatase and rutile. This mixture was more effective than pure anatase. Also, there are few studies about the mixture of anatase-brookite [163]. Anatase and brookite are polymorphs that can exothermally transform to rutile. This irreversible transformation happens in the range of temperature of 400-1200 °C depending on the size of the TiO_2 nanoparticles and whether they are supported over a heat-resistant substrate. The three crystalline structures are made up of distorted octahedra. Each octahedron represents a TiO_6 unit. Each unit consists of Ti^{4+} at the center coordinating six O^{2-} ions.

Table 1. Several applications of TiO_2 antimicrobial

Uses and application	Refs.
Building materials	[139,140]
Catheters to prevent urinary tract infections	[141,142]
Coatings for bioactive surfaces	[143]
Dental implants	[144,145]
Fabrics	[146,147]
Food packaging films	[148-150]
Surgical application	[151]
Orthodontic wires	[152]
Paint	[153]
Photocatalytic tiles for operating theatres	[154]
Plastics	[155-157]
Protection of marble from microbial corrosion	[158]
Surgical face masks	[159]
Tent materials	[160]
TiO_2-coated wood	[161]
TiO_2-containing paper	[162]

While it is the most used for photocatalytic environmental applications, TiO_2 anatase presents a wide bandgap (3.2 eV) allowing it to absorb mainly in the UV. Modified titanium dioxide can act in the visible by reducing its band gap. Due to the highest activity of bare TiO_2 in the UV compared to the modified one, deep investigations have been considered [154]. The first research in the disinfection process was carried out by Matsunaga and coworkers [90]. Theoretical calculations and mechanistic consideration were considered by many researchers [164]. Most of the calculations first-principles were dedicated to mass or surface sections of the TiO_2 anatase phase [165]. Displaying nanoparticles in realistic size (nanometric dimensions) by first-principle computations was carried out and a worldwide advancement is scarcely doable [166]. But, density functional theory (DFT), which is the self-consistent-charge density-functional tight-binding (SCC-DFTB) [167] is a strong tool to perform quantum mechanics studies of TiO_2 structures [168-171]. In this method, the interaction between nanoparticles and light and their photo-activity have been investigated [172-175]. Additionally, these calculations allowed the establishment of clear methodologies to create targeted structures, to predict the details of the photo-oxidation process and to determine the dimensions of water surrounding the nanoparticles with high precision [176-181]. After computational consideration, some results were obtained: there were some hydroxyl groups in the uncoordinated sites that they have surrounded spherical models that make them chemically stable [164]. These models should tolerate thermal annealing. In order to achieve high accuracy, B3LYP was used. However, the results were a bit different but the obtained pictures with DFTB were like those obtained when using DFT (B3LYP) method. This method has investigated the nanoparticles with around 4000 atoms and a diameter of 4.4 nm.

5.2. TiO_2 interaction with bacterial cells and OH-radical generation estimation

During the last two decades, many studies investigated the potential of TiO_2 for environmental remediation. PES fabrics impregnated with different loadings of TiO_2 have been recently reported for dyes degradation, indoor air treatment and microorganisms' inactivation in water [182-185]. The reduction of bacteria in the dark have been also considered. However, reduction process of bacteria in the dark was very slow and limited. Under light irradiation, the production of ROS was showed and quantified to lead to the total bacterial inactivation [186-187,137]. In this process, the interactions between TiO_2 and *E. coli* cell wall depend on two important factors which are pH and Lewis acid-base interactions [188,137]. Furthermore, the interactions NPs-NPs and NPs-cell walls

were also dependent on these parameters. TiO_2 NPs agglomerate/aggregate and *E. coli* cell wall adhere to these agglomerates. The bacterial cell wall presents lipopolysaccharide (LPS) at its external surface. Due to their charge, LPS groups are predominately able to bind NPs [184,44,187,188].

Thermodynamically, TiO_2 band positions allow the photo-generation of •OH radicals. As mentioned earlier, the diffusion of the reactive species leading to the inactivation of bacteria can be a major mechanism leading to *E. coli* death compared to the possible mechanical effect of TiO_2 aggregates. The estimation of the diffusion path of •OH radicals can be estimated according to the Smoluchowski simplified approximation $x^2 = D\tau$ [189]. Recently, Baghriche et al. [190] studied the diffusion path of the photo-generated •OH radicals at the interface of CuxO sputtered on polystyrene dishes in the presence of H_2O_2. They estimated the migration distance of •OH as follows.

•OH + MB → by-products/intermediates ($k = 10^{10}$ $M^{-1}s^{-1}$)

If we consider the concentration of MB= $3x10^{-5}$ M, $\frac{1}{\tau} = k_2 x\,[MB] = 10^{10} \times 3x10^{-5} = 3x10^{-5}$ s^{-1}

$\tau = \frac{1}{3\,10^{-5}}$ = $3.3x10^{-6}$ s (time of the encounter pair OH-MB)

The diffusion "D" for a small molecule like MB is about $5x10^{-6}$ cm^2/s, the diffusion distance "x" can be calculated as: $x^2 = D\tau$ by the inverse of the lifetimes the reaction rate of •OH in water with hydrogen peroxide.

$x^2 = 5x10^{-6} \times 3.3x10^{-6} = 16.5x10^{-12}$

$x = \sqrt{16.5\,10^{-12}}$ = $4x10^{-6}$ cm = 40 nm

Baghriche et al. [190] estimated the migration path of •OH radical to be 40-50 nm. Other photogenerated reactive oxygen species may migrate a little further depending on their size and lifetime. This is an open question that remains unanswered in relation to the multitudes of TiO_2 preparations, their light absorption ability and more importantly to the polluted matrix where they react. Furthermore, the photocatalytic activity might change depending on how firmly the reactant molecules are adsorbed on the photocatalyst surface. This was attributed to the diffusion of •OH to the bulk solution. The effect of water matrix will be discussed in section 7 below.

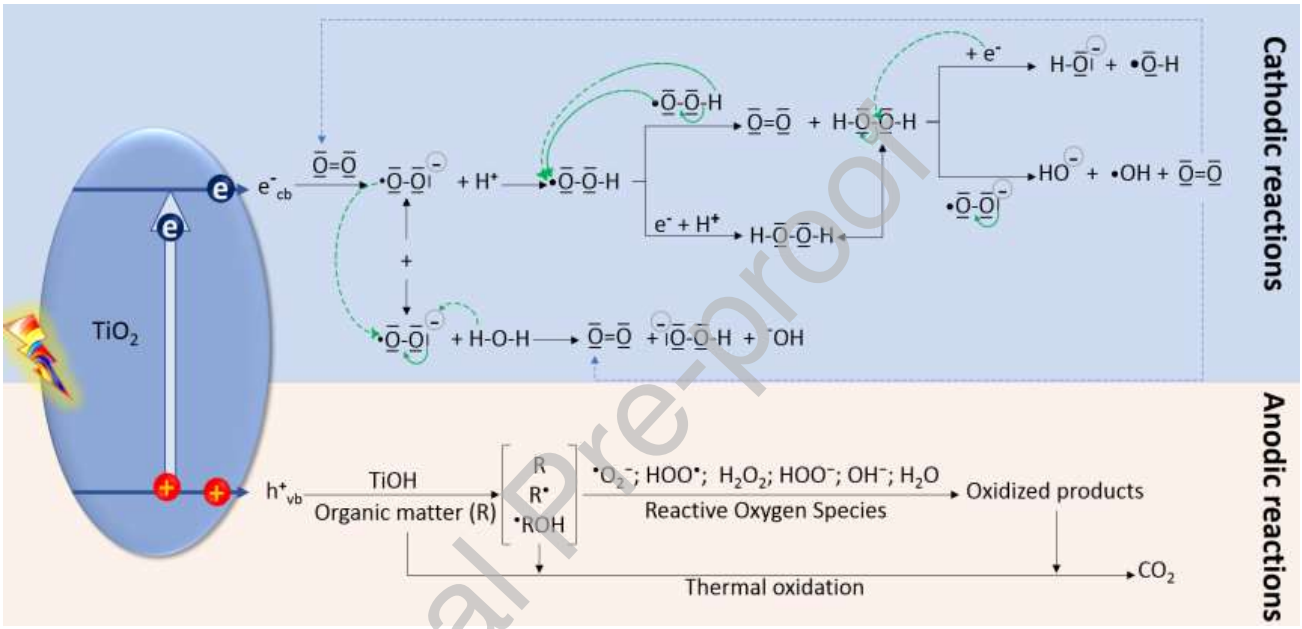


Figure 3. Possible photocatalytic generation of ROS and their permutation at the interface of TiO_2.

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5.3. Supported TiO_2 for bacterial inactivation

A study about TiO_2 supported on PE was early reported by Tennakone and co-workers in 1995 [191]. PE chose as a cheap and accessible polymer substrate due to its stability in presence of UV irradiation and oxidation process. Also, in a different report Ohtani et al., investigated [192] and found a remarkable degradation of PE happened when TiO_2 particles were implanted in the PE-bulk compared to when TiO_2 was just deposited on the surface. Rtimi et al., [184] used RF-plasma pretreatment method to create polar groups on the PE surface allowing covalent bonds with the deposited TiO_2. The prepared surfaces degraded pollutants and killed bacteria at the water-solid interface. Table 2 illustrates the technologies for the deposition of TiO_2 on different substrates.

Table 2. Updates on technologies used for the deposition of TiO_2 on different substrates.

Technology	Substrate	TiO_2 layers properties	Ref.
Liquid phase deposition	Glass	Partially crystalline after deposition at 50 °C from aqueous solution.	[193]
Chemical vapor deposition	Carbon fiber, aluminum plate, silica plate, and glass plates	The photocatalytic activity of TiO_2 loaded on carbon fiber was much higher than that of other catalysts.	[194]
Magnetron sputtering	flexible polyethylene terephthalate (PET)	Mixture phases of anatase and rutile TiO_2 thin films.	[195]
High power impulse magnetron sputtering (HiPIMS)	Polyethylene, polyethylene terephthalate (PET)	Thin layers were denser than thin films prepared by conventional magnetron sputtering. Excellent photoinduced hydrophilicity and high photocatalytic activity.	[163] [182] [195]
Nozzle-based robotic water-based inks for the direct writing of TiO_2	Flexible substrates	Bridging crystallite formation from the Ti-organic precursor into the TiO_2 crystalline phase, under ultraviolet (UV) exposure or mild heat treatments up to 150 °C.	[196]

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		Successful photocatalytic degradation of methylene blue.	
3D printing	Flexible substrates	Water-based inks for the direct writing of TiO_2 on flexible substrates is of paramount importance since it enables low-cost and low-energy intensive large-area manufacturing, compatible with roll-to-roll processing.	[197]
Low pressure cold spraying	Metallic substrate	The key parameter for the process seems to be temperature of working gas allowing the deposition of 100 µm thick TiO_2 from polymorphic feedstock.	[198]
Plasma Jet at atmospheric pressure	Wood	Titanium tetraisopropoxide (TTIP) was used as a precursor for TiO_2 deposition leading to improve the wood's stability against ultraviolet (UV) light.	[199]

There are many methods of deposition of TiO_2 on different substrates such as sol-gel [200], dip-coating [46], CVD [201], plasma-enhanced chemical vapor deposition [202], metal-organic chemical vapor deposition (MOVCD) [191] and spray-methods. However, none of these methods were convenient to deposit uniform and highly adhesive TiO_2 on non-heat resistant substrates like polyester, polyurethane, polyester. The sputtering methods have been shown to produce transparent thin TiO_2 layers. These pliable thin films showed fast bacterial inactivation under light irradiation. These methods damage the stability of bacterial so fast compared to other methods with non-pretreated PE [46]. The sputtering technique was mostly used for the deposition of metals and oxides thin films. Later, nitrides and oxynitrides appeared to be feasible by controlling the deposition parameters and the vacuum atmosphere [203]. The thin films issued from the sputtering technique showed crystalline structures and controlled surface roughness. The simplest sputtering apparatus consists of a vacuum chamber containing a metallic anode and cathode. The cathode is the material to be deposited named also as "target". This configuration allows the achievement of

a glow discharge in the residual gas in the vacuum chamber. It has been also shown that several KeV (applied voltage) and a little higher than 0.01 mbar (pressure) are enough to induce the sputtering process and to depose the thin film. During the sputtering process, ions are released from the discharge bombard to the molecules in the target (cathode) leading to atoms/molecules liberation from the cathode. These liberated atoms/molecules present high kinetic energy. In order to maximize the momentum transfer, the atomic weight of the bombarding ions should be almost that of the target's material(s). These atoms/molecules move straightly and hit on the substrate (anode) to start forming the desired thin film. The sputtering technique presents many advantages:

- It can be operated at an ultrahigh vacuum for high purity depositions.
- The composition of the sputtered films can be like the target's material.
- The sputtering sources are compatible with reactive gases such as oxygen.
- Materials presenting a high-melting-point can be easily sputtered.
- Multi-layered films presenting multi-oxides/nitrides/oxynitrides can be easily designed.

On the other hand, this technique does not allow the preparation of thick coatings because they require long operational times and high costs. In addition, when operating for a moderately long time, the sputtering rate decreases due to fatigue. Furthermore, it has been reported that the deposition of complex shapes is difficult. However, recently Rtimi et al., [204-205] reported and patented a modification of the sputtering process leading to uniformly coat a whole catheter.

6. Engineered photocatalytic TiO_2-based surfaces for wastewater treatment

6.1. Magnetron sputtered TiO2-based layers: DCMS vs. HiPIMS

The catalytic kinetic of supported TiO_2 films have been recently investigated by Verran et al., [206] Dionysiou et al., [207,208], Foster et al., [137], Bahnemann et al., [209-210] Byrne et al., [211], and Pillai et al., [212-214]. Wettability photo-switching has been observed during the bacterial inactivation or pollutant degradation at the interface of TiO_2 sputtered on PE fabrics/films [46]. In another work, an adhesive, uniform and recyclable TiO_2 films bind on PE by sputtering prepared under two different current energies that are applied to the targets. Magnetron sputtering was applied at different modes based on the current energy, namely direct current magnetron sputtering (DCMS) and high-power impulse magnetron sputtering (HiPIMS) [182]. By this method, TiO_2 particle sizes, Ti-ionic types, optical properties and crystal structures were shown to

be different. These sputtered thin films were applied for water treatment (bacterial inactivation and organic pollutant removal). Figure 4 shows the bacterial inactivation mechanisms at the interface of TiO_2-PE and the difference of the TiO_2 release [182]. The simplified mechanism for ROS generation at the interface of TiO_2 is given in equations 1-3 below and summarized in Figure 4C. The •OH-radical in eq. (3) is considered the strongest oxidant among the ROS-species.

$TiO_2 + light \rightarrow TiO_2(e^-) + TiO_2(h^+)$ eq.1

$(h^+) + H_2O \rightarrow H^+ + {}^\bullet OH$ eq.2

${}^\bullet OH/OH^-$ 1.90 eV eq.3

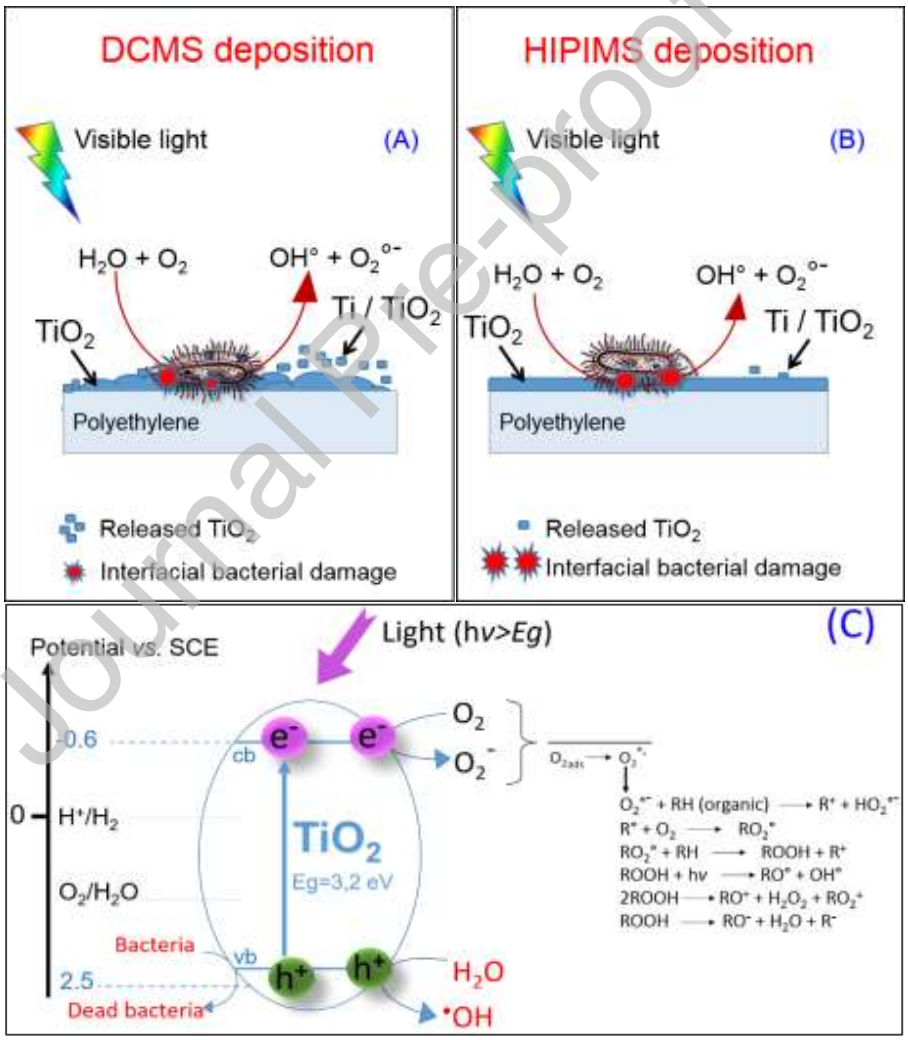


Figure 4. Interfacial bacterial inaction on TiO_2-PE surfaces sputtered by (A) DCMS and (B) HiPIMS [163]. (C) Photocatalytic mechanism leading to bacterial inactivation.

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In another hand, protective thin films are in a part prepared by magnetron sputtering. Titanium nitride layers showing strong mechanical and chemical resistance against oxidation/corrosion were industrialized for devices and interconnectors [215-217]. Gudmundsson et al., studied the high melting point, adhesion and diffusion barrier for metal ions in interconnectors [218]. Also, TiN and other nitrides co-sputtered with Ag and/or Cu have been investigated for the inactivation of Gram-negative and Gram-positive bacteria in the dark and under light [219,220,221]. Polyester-based sputtered membranes attracted attention because of their high stability over many cycles [221]. The photocatalytic activity was seen to be stable for 5-10 cycles. Once the photocatalytic activity drops down, these membranes can be refilled/re-sputtered to regain their initial photo-activity. This refill can be applied as many times as the substrate is mechanically stable. This allows a circular economy with the minimal side effect (release of toxic ions) leading to the destruction of the ecosystem.

In the past three decades, many reactors appeared in the literature based on photoactive materials [222]. Although these reactors presented different configurations, their efficiency was continuously questioned, especially for their scale-up and real applications. The photoreactors based on suspended materials rapidly vanished, however, the ones based on supporting materials are still under investigation. Some of these reactors used direct solar irradiation of simulated solar light. Solar light photons were concentrated by the mean of parabolic collectors concentrating the solar light. Recently, sputtered thin films on textiles were used in scale reactors. The results showed the sustainable water remediation up to 30 cycles [223-226]. In a recent study, Veziroglu et al., studied the photocatalytic and self-cleaning behavior of TiO_2 thin film decorated with PdO nanoparticles [227]. They showed that the co-existence of PdO and PdO_2 on the sputtered TiO_2 thin film fostered the charge separation efficiency leading to enhanced photocatalytic activity.

Sputtered cotton textiles showed self-cleaning and antibacterial activity properties [228-230]. Coated fabrics with semi-conductor materials were shown able to produce ROS under light irradiation [231-233]. Textile coating with semiconductors such as TiO_2, CuO and Cu_2O and their association showed light absorption in the visible range by decreasing the TiO_2 band gap [233-235] through intra-gap states or by lowering the photo-generated charge recombination through interfacial charge transfer (IFCT). Many other combinations involving TiO_2 have been studied for bacterial inactivation such as Pd-TiO_2, SiO_2-TiO_2 thin films [236], Fe^{+3}-doped TiO_2 thin film, TiO_2–Fe_2O_3 [237] and $NiFe_2O_4$–TiO_2 composites [238] in UVC region, doping TiO_2 with nitrogen

and sulfur [239,240], NiO/TiO_2 composite [241] in visible irradiation. The citation of all these systems is beyond the scope of the actual review.

6.2. TiO_2 embedded in polymeric matrices

For further inactivation of pathogenic bacteria, antibacterial nanocomposites based on TiO_2 have been studied. Titanium dioxide has been coupled to small organic molecules and/or metal oxides (frequently FeO_x, Ag_xO or Cu_xO) [242,243]. Titanium-polymer nanocomposites were also reported [217]. As it has been previously explained, the deposition of TiO_2 on a polymer largely depends on the interfacial chelating groups, the surface charge and hydrophilicity. A bottom-up approach to produce hybrid organic/inorganic photoactive films is the production of polymeric aqueous dispersions, e.g., waterborne latex. Different techniques were used to produce these hybrid polymeric dispersions such as mini-emulsion polymerization. This method showed high versatility because it allows the use of complex hybrid polymer particles. It also allows a high control of the inorganic material's dispersion throughout the polymer matrix leading to environmentally friendly fabrics. Bonnefond et al., prepared hybrid acrylic/TiO_2 films presenting antibacterial and self-cleaning properties [245,246]. The effect of the TiO_2 loading on the photo-activity of the prepared polymeric films was also investigated. Reactive oxygen species (mainly $^{\bullet}$OH-radicals) quantification was carried out by fluorescence. It was shown that the photo-generated $^{\bullet}$OH-radicals were proportional to the TiO_2 loading. A simplified mechanism is shown in Figure 5 showing the interfacial phenomena leading to the bacterial inactivation under solar light. Figure 6 summarizes the molecular mechanism happening at the interface bacteria/catalyst leading to the microorganism lysis.

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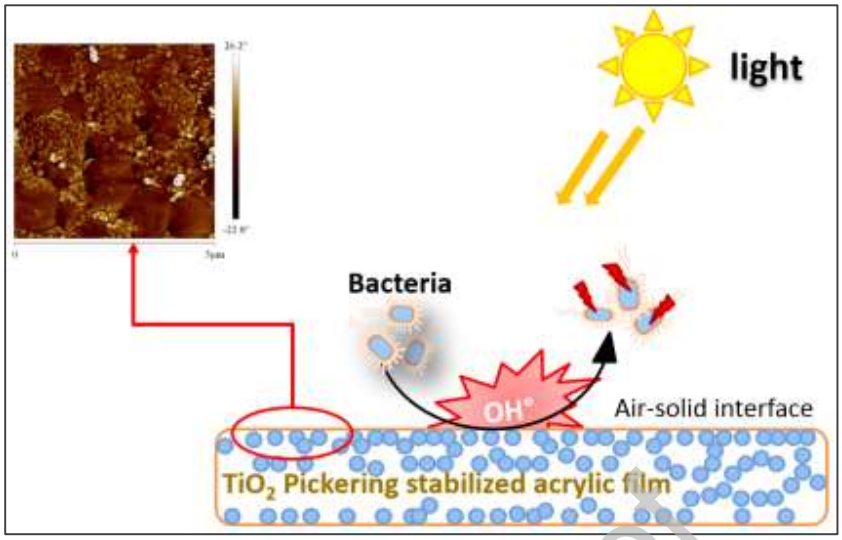


Figure 5. Pickering stabilizing acrylic polymer/TiO_2 inactivating bacteria under sunlight. Modified from reference [246].

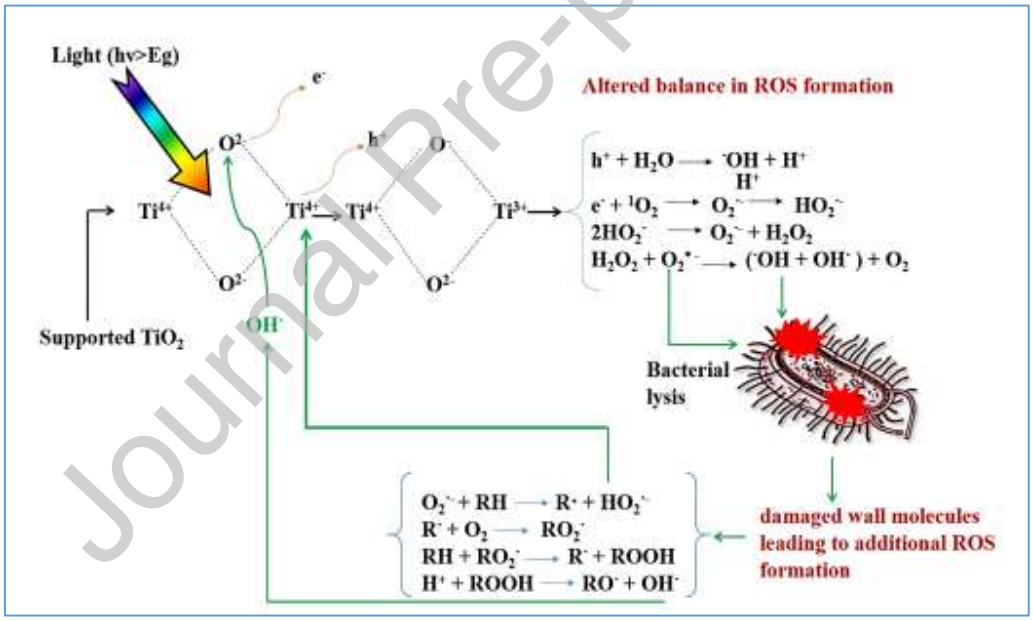


Figure 6. Molecular mechanism for bacterial inactivation at the interface of supported/embedded TiO_2 nanostructures.

However, it is worth mentioning that TiO_2 was reported to inactivate bacteria in the dark as well [244-247]. This activity was attributed to the impairment of the cell wall membrane's integrity. This in turns leads to bacterial loss of cultivability but not necessarily a loss of viability. This mechanism was seen to happen in two steps. The first consists of the agglomeration of the

practically neutral TiO_2 nanoparticles at the pH favorable for bacterial survival (physiological pH). The second step involves the translocation of the formed aggregates on the cell wall of the bacterial cells. Recently, a new interface was prepared by gradually functionalizing epoxide polymer with TiO_2 magnetized by iron oxide (Fe_3O_4). A magnetic field was then applied to the mixture and the magnetized nanoparticles migrated to one side. This side was seen to exhibit an antibacterial activity under solar simulated light. Figure 7a schematically shows the functionalization and the bacterial inactivation at the interface of the magnetized TiO_2 nanoparticles as prepared by Nardi et al. [247].

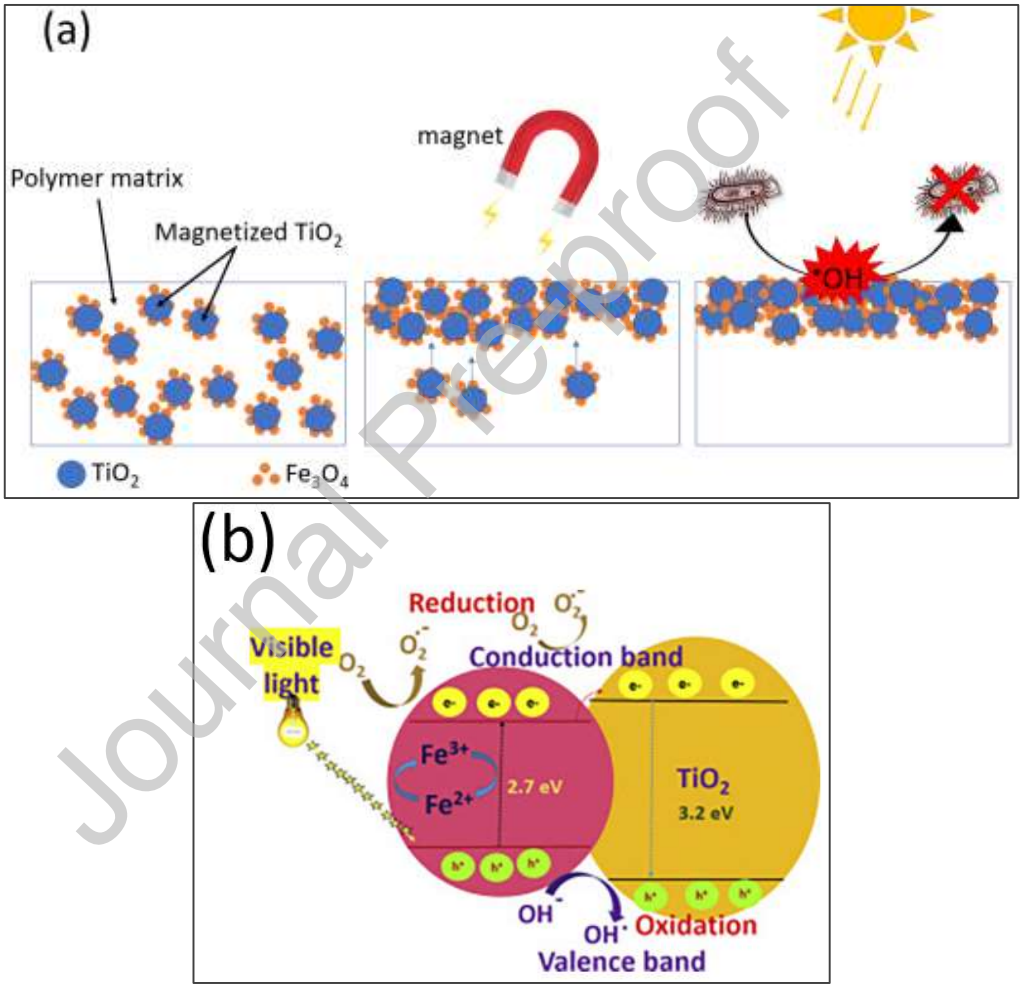


Figure 7. (a) functionally graded photocatalytic Fe_3O_4@TiO_2 core–shell nanoparticle in epoxy matrix: TiO_2 at the interface with bacteria [247], (b) Potential mechanism for pollutant degradation and microbial inactivation (Reproduced from Elsevier under license Nº 5281841055763) [216].

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The mechanism shown in Figure 7b shows the process of electron and hole hopping for the Fe_3O_4-TiO_2 composite. The magnetic Fe_3O_4 actively participates in the visible light absorption and acts as color center. The conduction band electrons of TiO_2 move to Fe_3O_4 due to the electrons hopping mechanism attracted by the photo-generated holes. This magnetically separable photocatalytic system allows the recovery of the catalyst after the desired reaction.

6.3. Effect of the water matrices on the TiO_2 photocatalysis

Water matrix has also an important role in the removal of pollutants by AOTs. In highly charged water, the removal efficiency is drastically influenced by suspended particles and dissolved components. However, dissolved components can have neutral, inhibitory, or promoting impacts and can affect the water disinfection process mediating photocatalysis [248-249]. Moreover, the presence of scavengers in water matrix could prevent the elimination of the dissolved organic matter (DOM) [250]. For example, $^{\bullet}OH$ scavengers can be natural organic matter, bromides, carbonates and bicarbonates types in neutral water [251]. Consequently, municipal or hospital wastewaters harboring a huge number of molecules represent different scavenging rates limiting the application of the photocatalytic wastewater treatment method in the industrial scale. On the other hand, when the complexity of the water matrix increases, the rate of pollutants removal decreased due to the presence of organic and inorganic materials competing to the catalytic active sites leading to their poisoning [252]. Also, other inhibitory factors in water matrix are mitigation of light and light absorption [253]. Therefore, the poisonous effect during the photocatalytic treatment can be attributed to the co-existence of organic and inorganic components in a complex water matrix [254-256]. The presence of inorganic salts in water matrix such as (NaCl, $FeCl_3$, $FeCl_2$, $AlCl_3$, $CaCl_2$), has also a negative effect on photocatalytic reactions and can even completely block these reactions when they are abundant (high concentration) in the wastewater [257]. TiO_2 catalyst can be disabled by inorganic salts through the competition between free radicals and blocking active sites on the catalyst surface [258]. Recently, Petala et al., reviewed the effect of water matrix on photocatalytic water remediation mediating TiO_2, $BiVO_4$, Ag and g-C_3N_4 [259]. The authors concluded that the negative role of complex water matrices is not always valid. Furthermore, Rioja et al., [260] studied and modelled the effect of water matrix on the photocatalytic degradation kinetics. They studied the photocatalytic degradation of clofibric acid (CFA) using TiO_2-P25 under UV light to study the effect of the water

matrix. They showed that the water matrix could affect the photocatalytic activity to an extend of 90%. In this review we will not detail further on this aspect as other authors already did.

7. Conclusion and Outlook

Water is now the gold-leaf of the future. Many zones of the world present already no more access to drinking water. People in these countries should move for many kilometers to access water. Today, water consumption is a global challenge still waiting for good practices. In this review, we exposed the difficulties facing the water reuse and the efficient technologies allowing acceptable water quality after treatment. Many technologies exist today to reuse water or to improve the quality of natural resources to be useful for humans. We addressed the advantages and limitations of some conventional and non-conventional wastewater treatment technologies. We also highlighted the emergence of advanced oxidation processes (AOPs) as a non-selective solution for wastewater remediation. Photocatalysis (one of these AOPs) was extensively tested for water disinfection. The testing went from suspended photo-active nanomaterials up to supported photocatalysts. Titanium dioxide and titanium based photocatalysts attracted the attention due to their availability and thermodynamic properties in relation with the thermodynamically favorable photo-generation of ROS. In this review, ROS permutation at the interface of TiO_2 was clearly elucidated. In the few last years, engineered photocatalytic TiO_2-based membranes and photo-reactors for wastewater treatment appeared to solve the high cost of recovery of a suspended photocatalyst. On the other hand, plasma-based technologies appeared to solve this challenge by preparing high adhesive photocatalytic layers leading to bacterial death at the interface by simple contact. However, these photo-active layers are largely affected by the water matrix and pollutant density. Porous materials presenting catalytic/photocatalytic active sites -event in their pores- may represent a step further towards efficient photo-responsive materials for environmental mitigation.

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CRediT author statement:

FH: Data curation & Writing - Original Draft

AAA and PNT: Validation

Journal Pre-proof

IA and SR: Supervision

SR: Conceptualization and Writing - Review & Editing.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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