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Photocatalytic Breakdown of Biomaterial by TiO_2 Mediated Photocatalysis: A Review

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Abstract: ***Photocatalytic degradation of biomaterials with TiO_2 a photocatalyst has attracted considerable interest owing to its potential in degrading a wide range of biomaterials. Homogeneous (undoped) and Heterogeneous (doped) TiO_2 based Photocatalytic biodegradation have been achieved in the presence of ultraviolet (UVA and UVC) and VIS irradiation. The degradation process effect the structural and functional properties of biomaterials. The objective of this review is to explore the effect of photocatalysis on different cells and viral particles. In addition, the review conveys comprehensive and fundamental assessments of the photocatalytic activity for breakdown of the nucleic acids, lignocelluloses materials, proteins and lipids.***

Abbreviations
TiO_2: Titanium dioxide, ROS: Reactive Oxygen Species, POC: Photocatalytic Oxidation, nm: nanometer, NPs: Nanoparticles, COD: Chem. Oxygen Demand, NAs: Nanotube array

Keywords: Photocatalysis, Biomolecules, Titanium dioxide, Breakdown, Degradation

1. Introduction

Chem. photocatalyst TiO_2 is the promising tools in the photocatalysis process because of its high activity potentials, chem. stability, no toxicity, and commercial availability. TiO_2 shows relatively high reactivity under ultraviolet light (<387nm). But, to develop photocatalysts exhibiting reactivity under visible light (> 400 nm) main part of the solar spectrum, different approaches by doping of TiO_2 are developed [1-8]. TiO_2 photocatalysis takes place by the following steps [9, 10] (Fig 1):

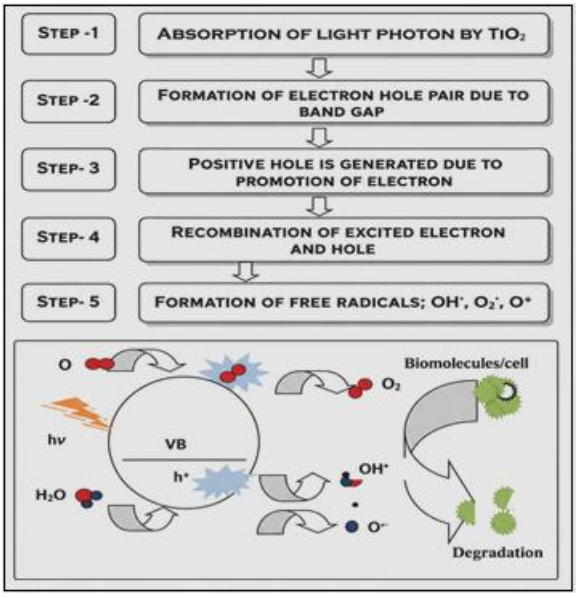

Figure 1: Formation Free radicals and Photocatalysis by TiO_2

Photocatalytic reactions at the surface of TiO_2 have received much importance in the present scenario due to diverse application in medicine, bioremediation, cosmetics, pharmacology and food. In general, it has been reported that the photocatalytic reactions proceed mainly by the reactions with reactive oxygen species (ROS), such as OH radical ($^{\bullet}OH$) [11-13] superoxide radical ($^{\bullet}O_2^-$)[14] and H_2O_2 [15,16]. ROS are significantly important species, responsible for the photocatalytic oxidation (POC) of inorganic, organic and biomaterials. The POC provide fascinating framework for the breakdown of biomaterials.

Effect of Photocatalysis on biomaterials is extensive field of research due to wide range of application. Biomaterials are living organism or substances produced by them. The living organisms are microorganism, plants and animals. Four major types of macromolecular substances produced by the living system are lipids, nucleic acids, and proteins. These macromolecules are essential for survival of life.

This review paper sequentially describes the cellular and viral degradation by photocatalysis in different environmental conditions. In the later section the degradation of biomolecules: genetic materials, lignocelluloses, protein and lipids is explained.

Effect of Photocatalysis on cellular and Viral particles:
The disinfection property of TiO_2 is attributed to surface generation of reactive oxygen species (ROS) and free metal ions formation. The ROS; HO•, O_2•, HO_2• are primarily responsible for inactivation of bacteria by oxidation of cellular components and membrane disruption [17]. The TiO_2 based photocatalyst has a great potential for inactivation of different types of cells and viral particles [18]

(Table 1.1). Effect of TiO_2 and near-UV light on *E. coli* resulted in increase in cell permeability to small molecules such as o-nitrophenol -d–galacto-pyranosideside (ONPG), and the leakage of large molecules such as β-d–galactosidase after 20 min followed by a damage of cytoplasmic membrane and intracellular components [19]. Potassium ion (K^+) is a vital component in polysome for regulation of protein synthesis. It is also indicator of cell membrane permeability. K^+ concentration in solution enhanced gradually as photocatalytic treatment time increased, along with cell structure destruction. K^+ leakage from bacterial cells due to cell membrane permeability, leads to loss of cell viability [20-22]. *E. coli* photo-killing due to the TiO_2 under light irradiation in a batch reactor was confirmed by Fourier transform infrared spectroscopy (ATR-FTIR) and atomic force microscopy. Formation of peroxidation products due to photocatalysis of *E. coli* results in structural changes in cell wall, leading to bacterial lysis [23]. Human colon carcinoma cell line (Ls-174-t) cells were effectively killed by photo-excited TiO_2 nanoparticles *in vitro*. The survival ratio decreased rapidly with increasing TiO_2 concentration (>200µg/ml). The rupture of cell membranes and decomposition of essential intracellular components accelerate cell death through a series of oxidized chain reactions and ROS [24]. UV radiation (280-400 nm) driven TiO_2 photocatalysis of cyanobacteria, *Microcystis aeruginosa* leads to cell lysis due to cell wall attack by the reactive species. The cell wall breakage enhances cell membrane permeability which accelerate release of microcystin-LR (MC-LR) and toxins in aqueous medium [25]. In recent years, to enhance the area of application, researchers has developed the second generation of TiO_2 photocatalysts. In this process, photocatalytic activities are carried under visible light irradiation. This substituted UV-light by sunlight to make use of solar energy for practical applications and enhance its photocatalytic. This shift of radiation from UV to VIS radiation was achieved by the doping of TiO_2 with different doping agents. Nitrogen-doping of TiO_2 substrates increased the bactericidal activity of microorganism *E. coli* as compare to pure TiO_2 and carbon-doped TiO_2 substrates [26]. TiO_2 doped with AgI is effective for killing *E. coli* and *S. aureus* pathogenic bacteria under visible light irradiation. The photocatalyst change the cell membrane permeability by reactive species, leading to leakage of intracellular substances [27]. Montmorillonite supported TiO_2 (TiO_2/Mmt) has irreversibly decomposed and dissolved cell components which leads to 99% inactivation of bacteria cells [28]. Palladium oxide and nitrogen-doped titanium oxide (PdO/TiON) photocatalysts exhibit high damage to microbial cell wall and cell membrane of *Eischerichia coli, Pseudomonas aeruginosa* and *Staphylococcus aureus* as compare to photocatalytic activity by either palladium-doped (PdO/TiO_2) or nitrogen-doped titanium oxide (TiON) under visible light (0.4-1.6 mW/cm^2) illumination [29]. The formation of Peri-nuclear vesicles in (Chinese hamster Ovary cells) CHO-K1 cells after treatment with Al_2O_3 and TiO_2 during 24 h was detected. Genotoxic effects and Sister chromatid exchange (SCE) frequencies were significantly increased due to lipid peroxidation and oxidative DNA damage [30]. The ROS triggers the photo-destruction of cancer cells after photocatalytic activity of Ag/AgBr/TiO_2 NPs. This resulted in 40-60% decrease of cell viability [31]. Visible-light-driven (VLD) graphitic carbon nitride (g-C_3N_4)/TiO_2 hybrid photocatalyst, completely inactivate, *E. coli* K-12 within 180 min under 500 nm VL irradiation. Bacterial cell damage, leads to a leakage of intracellular components through photocatalytic inactivation [32]. The response of lung and dermal cells to oxidative stress by photocatalysis with TiO_2- and Fe-N nanoparticles is dose and time dependent. The lung cells was more sensitive due to rate of ROS molecules formation and the cellular antioxidant capacity to neutralize them [33]. Graphene oxide (GO) nanosheets decorated with Ag, TiO_2 nanoparticles, and ZnO nanoflowers (GO– Ag–TiO_2@ZnO) inhibit the growth of microbial adhered cells and prevent biofilm formation. Antibacterial activity arises due to damage of cellular membranes by formation of ROS and the NPs accumulation in the cytoplasm [34].

TiO_2 suspensions under the influence of UV/VIS light are used for viral inactivation. Inactivation level of bactriophage MS2 increased to 99.9% after the addition of 2 µM ferrous sulfate. The iron-catalyzed Fenton reaction requires ferrous ion as it increases the formation of hydroxyl ions which is primarily responsible for the viral degradation [35]. UV light with a TiO_2 photo-catalyst generate, hydroxyl (OH.) and superoxide (O^{2}•) radicals under UV light, which attack the protein capsid and binding sites of adenovirus and bacteriophages; MS2, PRD1, phi-X174 [36], viral protein and genome of rotavirus, astrovirus, and feline calicivirus (FCV) [37]. TiO_2 photocatalysis is beneficial for inactivating viruses in an indoor environment. Quantitative polymerase chain reaction (qPCR) and bovine serum albumin degradation assume that viral inactivation is caused by outer viral protein disorder and not by viral RNA reduction by reactive oxygen species produced during TiO_2 photocatalysis [38]. Photocatalytic oxidation of viral particles distort the capsid shell, replicase and maturation proteins. The proteins loss result in the leakage and rapid destruction of RNA genes. This damage enhances the viral death without growth [39].

Table 1.1: Cell and Viral particle degradation by TiO_2 Photocatalyst

Biomaterial	Dopant ratio	Wavelength (nm)	Degradation efficiency (%)	Mechanism	References
E. coli (ATCC 27325)	No dopant	356	96	Increase in permeability due to cell wall damage, damages cell wall followed by a progressive damage of cytoplasmic membrane and intracellular components	[19]
Human colon carcinoma cell lines Ls-174-t	No dopant	315-400	88	Accumulation of ROS on the surface of cell membranes and in the cytoplasm	[24]
E. coli K12	No dopant	600	100	Formation of the peroxidation products due to the photocatalysis of E. coli changes cell wall membranes as the precursor events,	[23]

				leading to bacterial lysis	
E. coli (strain OP50)	No dopant	600	80-95	Formation of ROS results in cell damage.	[26]
E. coli DH 4R and (S. aureus ATCC 6538	No dopant	>420	99	ROS leads to change in the cell membrane permeability and a resultant leakage of intracellular substances.	[27]
E. coli, *P.aeruginosa*, *S. aureus*	(Pd, N)-doped TiO_2	>400	100	Production and separation of the charge carriers under visible-light illumination.	[29]
Escherichia coli (ATCC 11229) and *Staphylococcus aureus* (ATCC 6538)	TBOT:EtOH:HNO_3:H_2O = 1:15:3:0.3	365	99	The bacterial cells are irreversibly decomposed and some cell components are dissolved.	[28]
HeLa (human cervical carcinoma)	TiO_2:CTAB:$AgNO_3$=1:1.2:0.2	400-800	99.90	The ROS triggers the photo-destruction which resulted in 40-60% decrease of cell viability.	[31]
E. coli K-12	1.0 g NH4F , 1.0 g melamine and a piece of Ti foil	500	100	Bacterial cell damage, leads to a leakage of intracellular components through photocatalytic inactivation.	[32]
Candida albicans, Staphylococcus aureus, Enterococcus faecalis, Escherichia coli, Pseudomonas aeruginosa	anatase (~85%) and brookite (~15%)	347-400	Proportional decline in cell number	Formation of ROS molecules formation and the cellular antioxidant.	[33]
B. anthracoides, E. coli, P. multocida, and P. multocida	---	557-700	---	The formation of ROS (reactive oxygen species and the NPs accumulation in the cytoplasm.	[34]
Microbes in waste water	Ag-doped TiO_2 NPs :titanium butoxide =1:4.2	400-700	80.70	The ROS generated by the UV excitation of TiO2 attack cell membranes, RNA, DNA, 87 proteins, and lipids, and causing microorganisms deceased.	[52]
MS2 viron	Fe 0.5%	300-400	99.9	Hydroxyl radical oxidation is primarily responsible for the viral degradation.	[35]
Bacteriophages	No dopant	200-400	4 log inactivation	hydroxyl (OH.) and superoxide (O2•) radicals under UV light, attacks the protein capsid and binding sites.	[36]
Qβ and T4 bacteriophages	No dopant	315-400	6 log inactivation	viral inactivation is caused by outer viral protein disorder and not by viral RNA reduction by ROS.	[38]

Effect of Photocatalysis on Biomaterials

TiO_2 mediated photocatalysis has been used significantly for degradation of biomolecules (Table 1.2). This section provides comprehensive assessment of genetic material, lignin, protein and lipids degradation. ROS generated in the photocatalysis are involved in a variety of oxidative effects, responsible for destruction of genetic supra-molecules DNA. Photocatalytic UV-A irradiation causes DNA breakage leads to the inactivation of *Saccharomyces cerevisiae* [40]. pBR 322 DNA was irradiated with 5J/cm2 of UVA in the presence of TiO_2 and photodynamic DNA strand-breaking activity was due to hydroxyl radicals. These radicals react with hydrogen atoms of DNA bases and create lesions in DNA [41]. Photo-irradiated TiO_2 particles catalyze the copper-mediated site-specific DNA damage via the formation of hydrogen peroxide rather than that of a free hydroxyl radical. This DNA-damaging mechanism may participate in the photo-toxicity of TiO_2 in presence of Cu^{2+} by cleaving guanine residue [42].The photoactive bioinorganic TiO_2 and dexoyribonucleic acid was combined using enediol ligand dopamine (DA)as bridging ligands. The triads TiO_2/DNA/DA were capable of light induced manipulation of biomolecules by extended charge pair separation. Consequently, extended charge separation by multiple electron transfers result in cleavage of DNA [43]. Ti-O reacts with P═O to form P-O-Ti-O and the mechanism of binding is related to phosphate groups of DNA. This binding cause breakage in DNA strand due to distortion in the phosphate backbone of DNA [44]. The photodynamic DNA strand breaking activity of UV assisted TiO_2-PCO (photocatalytic oxidation) resulted in *E. coli* bactericidal phase in liquid culture. The interaction of UV light and semiconductor particles results in generation of highly reactive oxygen species (ROS) such as $OH^{\cdot}$, $O^{2\cdot}$, $HO_2^{\cdot}$, which are capable of destroying microorganisms [45]. Treatment *of Bacillus anthracis* in water by photocatalytic (UVA/TiO_2) result, the loss of plasmid pXO_2 (which contains the three toxin genes, *cya*, *lef*, and *pagA*). Hydroxyl radicals generated in the process are, responsible for breaking the plasmid DNA strands as a result the bacterial inactivation occurs [46]. The exposure of TiO_2 Engineered nanoparticles (ENPs) to human keratinocyte cells (HaCaT) effects the gene expression. These alterations in the expression profile may lead to the mutagenicity; carcinogenicity and cytotoxicity of the exposed cells [47]. TiO_2 NPs exposed to visible light from 400 to 800 nm (energy dose of 14.5 kJ/m^2 for 24 h or UVA light at 370 nm for 30 min (energy dose of 10 kJ/m^2) induce the formation of DNA lesions [48]. Doping of TiO_2, with vanadium and nitrogen for photocatalysis, has high efficiency under visible light for breaking DNA which causes bacterial degradation [49]. Graphene-based photocatalysts (TiO_2-rGO-PH) reduced antibiotic resistance genes (ARGs); clarithromycin and erythromycin of *E.coli* most efficiently. Photocatalysis was done by ROS mechanism O2· and HO· leading to inactivation of bacteria [50]. Photocatalytic degradation of plasmid-mediated floR, sul1, and sul2 gene with TiO_2-modified polyvinylidene fluoride (PVDF) membrane in the

genome was more efficient than those located in plasmid [51]. Ag doped-TiO_2 photocatalytic degradation resulted in 80.7% rDNA degradation at calcination temperature of 85 °C, and heating rate of 8 °C/min. The ROS generated by the UV excitation of TiO_2 attack cell membranes, RNA, DNA, proteins, and lipids which causes microbial death [52].

Lignin is second most plentiful biopolymer on globe, constituting 30% of the dry weight of softwood and 20% of the hardwood [53]. Lignin is major chem. oxygen demand (COD) components and colour pollutant of the effluents. Therefore, lignin degradation is of major environmental interest. Total oxidation of hazardous organic compounds by using advanced oxidation processes (AOP's) has been reported a promising treatment [54]. The generation of reactive organic species (ROS) have been extensively studied due to their ability to catalyse of a wide range of organic substrates. Photocatalysts, TiO_2 has the ability to degrade organic water pollutant from a number of organic pollutants [55,56]. TiO_2, absorbed on Lignin sulfonic acid sodium salt was desorbed under the influence of UV light (λ>310 nm) by lignin degradation accompanied by the formation of SO_4^{2-}. Lignin was depolymerized and aromatic ring was opened, which produced oxygenated aliphatic intermediates; formic acid, acetic acid, glycolic acid formaldehyde and of glyoxylic acids [57]. The exposure of lignin with TiO_2 and UV-visible radiation (> 300 nm) degrades phenolate groups and hydroxylation of aromatic structures generates hydroxyl radicals [58]. Doping of Photocatalyst (TiO_2) with platinum (Pt/TiO_2) enhanced the degradation of lignin in acidic solution as compared to alkaline pH [59]. Photocatalysis of rice husk (RH) over TiO_2 in H_2O_2 aqueous solution under UV irradiation produced alkanes, aldehydes and ketones. Phthalates and arenes confirmed the lignin degradation [60]. Photo-degradation of a herbaceous lignin with a TiO_2/polyethylene oxide (PEO) + methyl linoleate (ML) photocatalyst system had high photocatalytic activity. The methyl linoleate (ML) produced by photocatalyst has hydrophobic molecular structure. It works as initiator and attack the lignin and unsaturated polyester to cleave carbon–carbon bond [61]. Loading of TiO_2 by Ag increases the production of reactive oxygen species which enhances lignin degradation efficiency of photocatalysis process [62]. Oxidation of the lignin in wheat straw, release; vanillic acid, ferullic acid and acetic acid due to TiO_2 photocatalysis [63, 64]. TiO_2/lignin-based carbon composite photocatalysis synthesized by sol-gel microwave technique enhances photocatalytic activity. The photocatalyst enhanced lignin conversion up to 40.28 % and produced high value chem.s, such as vanillin after photocatalysis [65]. Addition of Fe_2O_3–TiO_2 and NiO–TiO_2 nanoparticles in anaerobic digestion (AD) of wheat straw increased degradation of lignocelluloses. This process increased chem. oxygen demand (COD) and volatile fatty acids (VFAs) concentration after degradation [66].

The TiO_2 photocatalytic oxidation of the different proteins; serum albumin, ovalbumin and gamma globulin reveals the slow oxidation of aliphatic amino acids; Gly and Asp like in the Fenton oxidation. The Fenton process involve the oxidation of α-hydroxy acids to the corresponding α-keto acids or in the oxidation of 1,2-glycols to ydroxyl aldehydes. This process apply the use of a redox couple consisting of hydrogen peroxide and ferrous ion. But in amino acid, Phe (phenylalanine) which lack of an activating group on the aromatic ring, make the system less amenable to degradation [67]. TiO_2 has a strong affinity for phosphorylated peptides and a high potential in field of phosphoproteomics. Proteolytic digests of three different auto phosphorylation forms of the 153-kDa homodimeric cGMP-dependent protein kinase were analyzed. Proteolytic digestion with trypsin generates too small fragments, containing threonine-84 [68]. The amino acids which contain –OH (Ser), -NH (Trp, His), or $–NH_2$ (Asn) in their side chain are susceptible to photocatalytic oxidation. These interact with the basic terminal OH groups more preferably by the side chain in photodecomposition on a TiO_2 surface. The photodecomposition rates increased in the order of Phe < Ala < Asp < Trp < Asn < His < Ser [69]. UVB irradiation cause changes in the protein conformation which, results in denaturation. Photocatalytic mechanism enhanced binding and protein oxidation [70]. TiO_2 films modified with silver (Ag–TiO_2) caused conformational changes in the β-amyloid, through photocatalytic mechanism [71]. Photocatalysis promote the formation of high molecular weight soy protein isolate (SPI) dextran conjugates, induced by TiO_2 photocatalysis. Moreover, significant changes of secondary structure occurred in SPI-dextran conjugates. TiO_2 photocatalysis promotes the structural changes in the α –helix, β –sheet, β –turns, and random coil of protein and enhanced the protein-polysaccharide copolymerisation [72]. Phosphorylation on peptide oxidation induced by TiO_2 photocatalysis is fast and easy method for oxidation of biomolecules. Tyrosine is the most preferentially oxidized amino acid. Hydroxyl radical initiated oxidation reactions results in hydroxylation of non-phosphorylated tyrosine. But the phosphorylation inhibits the oxidation reaction significantly. Moreover, the oxidation of tyrosine residue is more likely to be mediated by hydroxyl radicals than by surface holes [73].

Different studies has revealed that photocatalysis with TiO_2 has impact on lipid peroxidation by the formation of ROS. 17-β-oestradiol was 98% destroyed by photocatalysis over the immobilised TiO_2 powder on Ti-6Al-4V alloy. The concentration of oestradiol was determined by HPLC with fluorescence detection [76]. Phosphatidyl-ethanolamine, lipid polysaccharide (LPS), and cardiopilin from *E. coli* were used for TiO_2 photocatalysis leading to the cell membrane degradation. Photocatalysis decay the isolated cis CC−H, $-CH_2$, and $-CH_3$ groups and of the acyl-ester bond of the fatty acid in glycerol backbone. The process also induced spectral shifts in the CH_2 vibrations and changes in the asymmetric phosphate ester (C−(PO_4)-−C) stretching vibrations. Photocatalytic peroxidation occur at the TiO_2 surface through heterogeneous mediated processes and a homogeneous chain radical peroxidation of PE (l-α-phosphatidyl-ethanolamine) in aqueous solution [77]. Photocatalysis over an immobilised TiO_2 help to remove estrogenic activity of for 17beta-estradiol, 17alpha-ethinylestradiol and estrone. Without TiO_2 catalyst, the rate of UVA photolysis of the steroid substrates varied. The order effective rate of photolysis 17alpha-ethinylestradiol> estrone> 17β-estradiol (0.42, 0.2 and < 0.1 times) was achieved [78]. The interactions of TiO_2 with phospholipid

bilayers of cell membranes under UVA changes the phospholipid structure. Hydration effects at the semiconductor–phospholipid interface is helpful in the degradation of dimyristoylphosphatidylcholine (DMPC) and dimyristoylphosphatidylethanolamine (DMPE) bilayers [79]. Different level of TiO_2 concentration induce quite variable lipid peroxidation on ultraviolet B (UVB) irradiation. The extent of lipid peroxidation caused by the same TiO_2 pigment in different emulsions was even more variable than the effects of different pigments in the same system [80]. The oxidation kinetics of lipid vesicles are similar to the oxidation of *E. coli* cells in photocatalytic systems with TiO_2. This oxidation validate the importance of membrane peroxidation as an important process in the mechanism of photocatalytic disinfection. The production of both malondialdehyde (MDA) and lipid hydroperoxide (LOOH), byproducts supported the oxidation of membrane [81]. Hydroxyl radicals adsorbed on the surface of TiO_2 (Ti-OH groups) account for 70–100% of the photocatalytic peroxidation of linoleic acid under UVB irradiation for the production of malondialdehyde. The absorption of UV radiation by TiO_2 induces the production of valence band holes (hþ), ROS such as $HO^{\cdot}$, O_2, H_2O_2, and singlet oxygen ($^1O_2$), all are able to initiate oxidative processes. The holes trapped on the surface of TiO_2 are involved into lipoperoxidation to a significant extent. The reaction between carboxylic acids and holes is the oxidation of the –COOH group rather than the peroxidation of the double bonds [82]. Ag modified TiO_2 nanotube arrays (Ag/TiO_2 NAs) were employed as a photocatalyst for degradation of 17α-ethinylestradiol (EE2). By the application of Ag/TiO_2 NAs photocatalytic degradation of EE2 and inactivation of *E. coli* were enhanced in an analogical trend. The Ag/TiO_2 NAs exhibited the antimicrobial activity even in the absence of light. The Ag perfomed a function; of disinfection agent and dopant of the modified TiO_2 NAs photocatalysis by forming a Schottky barrier on the surface of TiO_2 NAs [83]. TiO_2 immobilized on supports (UV-A/TiO_2) as photocatalyst degrades steroid hormones: norethisterone and danazol in aqueous medium. Enhanced degradation in the presence of H_2O_2 is due to the traditional oxidation, but high concentration of H_2O_2 reduced the degradation process due to excessive oxidant scavenging radicals. The photolytic degradation is attributed to photo-oxidation of substrates from the singlet oxygen generated photochem.ly from the oxygen dissolved in the reaction mixture [84]. Arlos [85] observed that TiO_2 has potential applications for the removal of EDCs (endocrine disrupting compound); Estrone (E1), 17-estradiol (E2), 17-ethinylestradiol (EE2) and estriol (E3). The UV-LED irradiated immobilized TiO2 on porous titanium sheets have the potential for removal of these compounds. The total estrogenic activity was decreased below the detection limits within 120 min at pH 4. The pH 8 and pH 11 treatments showed slower removal of total estrogenicity, similar to those observed for the disappearance of individual estrogen. Degradation of phenol-containing estrogens can be attributed to hydroxylation (OH addition) and direct hole oxidation followed by subsequent ring opening mechanisms in the molecule. Mai [86] additionally predicted that the two carbon atoms in the phenol moieties are more susceptible to attack via OH radical and direct hole oxidation. The photocatalytic degradation of the estrogens 17β-estradiol and 17α-ethynylestradiol by TiO_2 immobilized in carbonaceous materials, prepared by sol-gel was performed. Under UV-A radiation and the synthesized photocatalysts almost complete removal of both estrogens was achieved in less than 10 minutes, the nanocomposites (TiO_2) and activated carbon (TiO_2-AC) has the similarity between the degradation potential but, no synergistic effects between AC and TiO_2 could be assumed [87]. Iron-doped TiO_2 nanoparticles (Fe-TiO_2) were photo-catalitically investigated under high and low values of UV radiation. The Fe^{3+} concentration (0.3%) played a key role in the photocatalytic generation of hydroxyl radicals (•OH) which enhanced the photocatalytic activity for estrol degradation under UV irradiation [88]. Non- Cellulosic gums from industrial hemp fibers was removed by hybrid pretreatment method that incorporates visible-light-activated photocatalysis using TiO_2/carbon quantum dots (TiO_2/CQDs) with pectinase enzymatic hydrolysis [92].

Table 1.2: Summary of TiO_2 mediated degradation of Biomaterial

Biomaterial	Dopant Ratio	Wavelength (nm)	Degradation efficiency (%)	Mechanism	Reference
Plasmid pBR322 DNA	No dopant	300-410	75	Active oxygen species, especially hydroxyl radicals react with hydrogen atoms of DNA bases and create lesions in DNA.	[41]
Human genes	No dopant	365	---	Formation of hydrogen peroxide results in DNA damage.	[42]
Chinese hamster ovary (CHO-K1 line) genes	No dopant	---	40	Due to lipid peroxidation and oxidative DNA damage.	[30]
S. cerevisiae (BY4742) genetic material	No dopant	315-400	90	Oxidation reaction breaks DNA molecules.	[40]
Escherichia coli (ATCC 25922), *Listeria monocytogenes* (KCCM 40307), and *Salmonella 89 Typhimurium* (ATCC 14028)	No dopant	254	6 log reduction	Generation of highly reactive oxygen species (ROS) such as $OH^{\cdot}$, $O^{2\cdot}$, $HO^{2\cdot}$, are capable of destroying microorganisms.	[45]
B. anthracis NCTC 10340 genetic material	No dopant	350-400	67	Hydroxyl radicals results in efficient inactivation by breaking the plasmid DNA strands.	[46]

human keratinocyte (HaCaT) genes	No dopant	---	---	DNA damage, response against stress, cell cycle, transportation and secretion, immune response and apoptosis.	[47]
Escherichia coli (K-12, MG1655)	Nitrogen: Vanadium= 1:2 atom%	510	49	Production of hydroxyl radicals, follows cell membrane deterioration or inhibiting cellular functions by damaging DNA.	[49]
E. coli genetic material	No dopant	solar irradiation	100	Photocatalysis was done by ROS mechanism O2· and HO· leading to inactivation of bacteria.	[50]
Bacteria in waste water	No dopant	254	98.90	Formation of ROS.	[51]
Coniferous wood lignin	No dopant	200-350	4.3	Hydroxyl radical causes oxidation of lignin.	[57]
Eucalyptus grandis Lignin	TiO_2 and H_2O_2	>350nm	50	Formation of hydroxyl radical, electron transfer and hydroxylation of the lignin aromatic structure in the presence of TiO2 under uv light.	[58]
Lignin from pulp and paper industry	Pt:TiO_2 = 1%:99%	439-590	40	Attraction of hydroxyl radical to the double bond is the major cause of lignin destruction.	[59]
Herbaceous lignin	TiO_2 2 mg, PEO 100 mg, and ML 10.0 g.	400	51%	Production of Reactive oxygen species facilitate autooxidation thereby degradation of lignin.	[61]
Rice Husk Lignin	No dopant	365	100%	Hydroxyl radical play a crucial role in the oxidation of small molecules and oxidative depolymerization of macromolecules.	[60]
Paper or pulp processes, wood extractions Lignin	1%wt ratio of Ag loading on TiO_2	365	33.8%	Reactive Oxygen Species lead to cleavage Ag+ and Ag0 phases and improve photocatalytic activity in lignin conversion.	[62]
Wheat straw Lignin	No dopant	200-400	56%	Oxidation of the lignin in wheat straw, release the sugars from the lignocellulosic structure of straw.	[63]
Lignin from Biomass waste	titanium (IV) butoxide and acethylacetone =1:1	365	40.28 %	Ligin dehydration and decomposition of aliphatic chains changes the structure of Ti-lignin composite. Ligin absorbs electrons from photogeneration.	[65]
Wheat straw Lignin	5.0 wt% NiO/TiO_2 and 5.0 wt% Fe_2O_3/TiO_2	200	67%	Ti based nanoparticles effects electron transfer reactions.	[66]
Wheat straw Lignin	No dopant	254	28%	Productions of free radicals on the surface of substrate.	[64]
Bovine serum albumin	TiO_2 with 65% anatase, 35% rutile	370	99%	Degradation is caused by oxidation due to hydroxyl radical.	[67]
Protein	No dopant	320-380	3.5 to 24.5 µM	photocatalysis of amino acids by ROS.	[69]
Human serum albumin	TiO_2 and 0.001 M of $AgNO_3$	365	Conformational change of the protein.	Changes in the protein conformation, resulting in denaturation and enhanced binding and oxidation, induced through a photocatalytic mechanism.	[70]
Amyloid	TiO_2 and 0.001 M of $AgNO_3$	365	Disordered conformation changes of the -amyloid	UVB irradiation, causing conformational changes in the β-amyloid, through photocatalytic mechanism.	[71]
Cheese industry	No dopant	254	100%	Changes in the original molecular weight cutoff of the membrane and degradation of the polarisation-layer by TiO_2.	[74]
SPI-dextran	No dopant	300–450	68.8%	Higher photocatalytic power promote the formation of high molecular weight SPI-dextran conjugates, induced by TiO2 photocatalysis.	[72]
Tyrosine-Phosphopeptides	TiO_2 and 0.01% NH_4OH	225	100%	Phosphorylation on peptide oxidation induced by TiO_2 photocatalyst.	[73]
Whey protein nano-fibrils	No dopant	200-800	100%	Lipid peroxidation and antioxidant activity.	[75]
Steroid hormone	Ti-6Al-4V	280 -315	98%	Unprotonated hydroxyl radical, PhO·, which can then react directly at the TiO2 surface.	[76]
E. coli LPS	TiO_2) 100 g/L and PEG2000 30 g/L	366	30%	The photocatalytic peroxidation of lipid polysaccharide (LPS) leads to the cell wall degradation.	[77]
Yeast LPS	No dopant	540-620	50% in 10min	Lipid peroxidation.	[78]
E. coli LPS	No dopant	365	---	Formation of free radicals induces degradation	[79]
cholesterol-lowering	TiO_2 films	365	0.052 ± 0.008	The formation of hydroxyl radicals leading to the	[89]

statin drugs	deposited on both sides of SiO_2			formation of different hydroxy derivatives.	
Linoleic Acid	No dopant	535	---	TiO_2 induced peroxidation of linoleic acid at different pH values. lipo-peroxidation activity, particularly with the most reactive TiO_2.	[90]
Porcine skin lipids	No dopant	535	---	Peroxidation of lipids on ultraviolet B (UVB) irradiation, in the presence of TiO_2.	[80]
E. coli LPS	Ag/TiO_2	254	30%	Oxidation decomposition of EE2	[83]
Steroid hormones	No dopant	365	93.86%	Degradation is caused by singlet oxygen produced by photochemically.	[91]
Yeast LPS	No dopant	365	Inefficient degradation of 17β-estradiol	Immobilized TiO2 through the thermal-chem. oxidation of porous titania sheets.	[85]
Steroid hormones	TiO_2-Activated Carbon weight ratio20%	320-400	90%	Synergetic effect hinders the electron/hole pair combination and improves the overall efficiency of the photochem. process.	[87]
Steroid hormones	No dopant	365	93.46%	Free radicals cause degradation	[84]
Estrogen	0.3 Fe-TiO_2	280	0.25 min^{-1}	Generation of hydroxyl radicals (•OH) and estriol (E3) degradation.	[88]

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