Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29390

305 (2023) 2–16
September

Recent advances in water and wastewater disinfection by nano-photocatalysis

M. Bodzek[a,*], K. Konieczny[b], A. Kwiecińska-Mydlak[c]

[a]*Institute of Environmental Engineering Polish Academy of Sciences, Marii Curie-Skłodowskiej 34, 41-819 Zabrze, Poland, email: michal.bodzek@ipispan.edu.pl*
[b]*Department of Energy and Environmental Protection, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland, email: krystyna.konieczny@polsl.pl*
[c]*Institute for Chemical Processing of Coal, Zamkowa 1, 41-800 Zabrze, Poland, email: akwiecinska@ichpw.pl*

Received 19 December 2022; Accepted 8 February 2023

ABSTRACT

Recently, nano-photocatalysis has appeared as an efficient and green method of disinfection. It has been found that the process allows deactivation of various types of microorganisms. The antibacterial effect has already been checked on a number of gram-positive and gram-negative bacteria including *Escherichia coli*, *Staphylococcus aureus*, and others. Moreover, the actions targeted on destruction of fungi, algae and viruses have also been performed. Despite intensive research on novel photocatalysts, titanium dioxide (TiO_2) remains the most commonly used material due to its properties. Additionally, TiO_2 can be easy modified using physical and chemical methods, what allows for its wide use in industrial scale. One possibility for modification is the use of photocatalysts in the form of nanoparticles. This review gives the latest developments in the deactivation of microorganisms in water and wastewater using photocatalysts in nanoforms.

Keywords: Photocatalysis; Nanoparticles; Disinfection; Water and wastewater treatment

1. Introduction

Industrial expansion accompanied by economic and civilization growth affect water resources and often leads to contamination of water streams and water scarcity (especially in regard to surface and ground water resources used for potable water production). It is a highly undesired effect, as it becomes a serious, worldwide problem, harmful not only to environment, but also to human health. The access to fresh and sanitary safe water is a fundamental of sustainable development. However, it is estimated that more than 1/6 of human population suffers because of poor water quality, which leads to death to millions of people, especially children. One of the most important issue is related with microbial water contamination, especially transmission of mutated species resistant to antibiotics, such as Methicillin Resistant *Staphylococcus aureus* (MRSA) and *Clostridium difficile* (*C. diff*) [1]. Due to these facts, novel methods of water treatment, targeted on removal and decomposition of not only chemical pollutants like organic compound and heavy metals, but also enabling elimination of microorganisms are seek for. The latter are desired to be used as colloidal solutions or surface coats, which should characterize with high efficiency and stability [2–7].

Photocatalysis as disinfection method of water and wastewater has been widely studied since the 1990s [1–5]. The experiments is related to novel materials, the use of visible light for excitation of photocatalysts and complete mineralization of pollutants which has been evaluated [2]. However, there are problems, which need further research and solution, namely, the reduction of energy band gap of photocatalysts, and fabrication of new photo-catalysts with low band gap [8–11]. In this range, nano-photocatalysts

* Corresponding author.

Presented at the 3rd International Conference on Strategies toward Green Deal Implementation – Water, Raw Materials and Energy (ICGreenDeal2022), 5–7 December 2022, held online by the Mineral and Energy Economy Research Institute, Polish Academy of Sciences

1944-3994/1944-3986 © 2023 Desalination Publications. All rights reserved.

(1–100 nm) are an ideal solution because they meet the above-mentioned requirements.

Nanoparticles (NPs) have strong antimicrobial properties. Different from chemical disinfectants, nanomaterials produce less toxic disinfection by-products, do not have such strong oxidizing properties and are inert in water [12]. The most commonly used nanomaterials in the water and wastewater disinfection are titanium dioxide (TiO_2), zinc oxide (ZnO) and carbon-based nanoparticles [13,14].

The presented paper reviews the current state on the art on the use of nano-photocatalysis in water and wastewater disinfection. Fundamentals of process mechanism and discussion on microorganisms used in investigation of disinfection processes are also included. The results of the research on the use of different types of nano-photocatalysts and possible methods of their modification has been shown. A short summary on the use of the process to remove organic compounds present in water and wastewater is also given in order to highlight the possible combined effect of the treatment with the use of the discussed method.

2. General photocatalysis mechanism

In the photocatalysis process, a light radiation is involved in initiation of photocatalytic reaction by bombarding of a photocatalyst surface with photons [15–17]. The detailed mechanism of the photocatalysis is quite a complex subject but the basic principle is the same. Upon irradiation of the light with the energy equal or more than the band gap of the semiconductor photocatalyst, the electrons (e^-) are excited from the valance band of the catalyst to the conduction band (e^-_{CB}), leaving the holes behind in the valance band (h^+_{VB}) [3–5,8,11,18] [Eq. (1) and Fig. 1].

$$\text{Photocatalyst} + h\nu \rightarrow h^+_{VB} + e^-_{CB} \quad (1)$$

These photo-generated electrons and holes can possibly recombine by releasing the heat between 10 and 100 nanoseconds (Eq. 2) [20]. This recombination of the electrons and holes causes the low quantum efficiency of the photocatalyst. This recombination process of the electrons and holes can be reduced significantly if these charge-carrier species are separated by the addition of suitable scavenger or

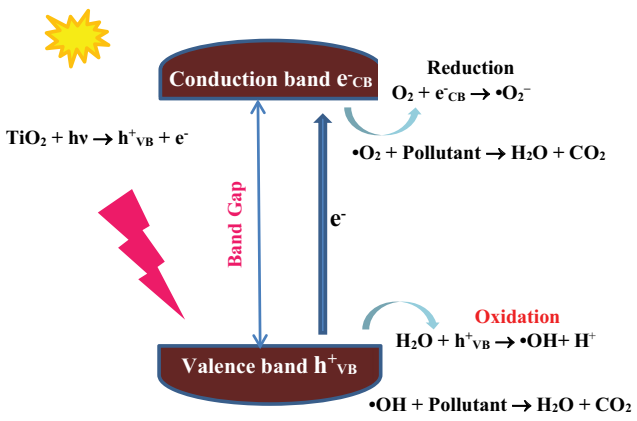

Fig. 1. Mechanisms of photocatalysis (compiled from [8–10,19]).

incorporation of some of the trap sites on the surface as a result of producing defects, surface adsorbents, or other sites.

$$e^-_{CB} + h^+_{VB} \rightarrow \text{heat} \quad (2)$$

In conduction band (e^-_{CB}), e^- reacts with oxygen, forming two radicals: peroxyl ($^{\bullet}O^{2-}$) and hydroperoxyl ($^{\bullet}OH_2$), while in the valence band (h^+_{VB}) water is oxidized with the formation of hydroxyl radicals ($^{\bullet}OH$) and hydrogen ions (H^+) [Fig. 1 and Eqs. (3) and (4)] [8–10]. If impurities are present in solution then they degrade to water (H_2O) and carbon dioxide (CO_2) [4,9–10].

$$e^-_{CB} + O_2 \rightarrow {}^{\bullet}O^{2-} \quad (3)$$

$$h^+_{VB} + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad (4)$$

Most photocatalysts are activated under near ultraviolet (UV) light (300–400 nm), which is a result from the high energy "transfer band" of many photocatalysts, such as 3.2 eV for TiO_2. Sunlight-based photocatalysis requires a large surface area [21]. In order to use sunlight in the photocatalysis of contaminants found in water and wastewater, the photo-catalysts used so far must be modified [18]. A number of successful attempts have been made to modify semiconductor catalysts with a wide "band gap" to shift light absorption to the visible range. In order to increase the range of absorbed light, what is crucial in case of photo-degradation and photo-mineralization of contaminants present in water and wastewater, modification of properties of involved photocatalysts [22]. Such procedures are very advantageous due to the free access and availability of natural light. A number of successful modifications of semi-conductive photocatalysts of wide transition band dedicated to shipment of absorption toward visible light have been made. Such photocatalysts, however, characterize with significantly lower photoactivity due to favoring of recombination process [3,23]. Among available modification techniques one may distinguish [3,11,22]:

- addition of transition metals (manganese, copper, nickel, cobalt, etc.) or non-metals (nitrogen, sulphur, boron, halogens, etc.) to semi-conductive photocatalysts;
- mixing of different semi-conductors, application of mesoporous supports;
- application of nanotechnology to modification of photocatalyst (nanostructured photocatalysts (ns-PhC), addition of dyes or organic polymers to ns-PhC, coating of photocatalysts surface with metallic nanoparticles (NPs) induced with visible light plasma).

Such modifications can change the fermi level and delay the electron-hole recombination process. For example, doping of metals (Au, Ag, Cr, Si, Co, Mg, Mn, Fe, Fe, Al, In and Ga) to photocatalytic material may decrease both energy of band gap and rate of recombination of e^-/h+ pairs, as electrons excited by radiation have a tendency to migrate to noble metals, of lower Fermi energy, while electron holes remain on a photocatalyst surface [7,21,22]. The combination

of semi-conductors with nanoparticles of noble metals like silver (Ag), gold (Au), platinum (Pt) and palladium (Pd) increases photocatalytic activity of final composites according to two possible mechanisms, which are shown in Fig. 2 [24,25].

3. Photocatalytic removal of organic compounds

Photocatalysis is widely used in water and wastewater treatment to degrade pollutants into harmless products, primarily using metal oxide semiconductor nanoparticles, mainly TiO_2 and ZnO [3,6,18,26–31].

Endocrine disrupting compounds (EDCs), that is, compounds which disrupt functioning of hormonal system, are harmful group of chemicals, which are disposed to natural waters and cause undesired changes in biochemical activity of endocrine processes, what results in serious health effects. The recent researches have shown, that EDCs appear more often in natural water as well as in wastewater, even after biological treatment. Among EDCs one may find endogenic hormones, natural organic compounds produced by fungi (mycoestrogens) and plants (phytoestrogens), as well as wide range of anthropogenic micropollutants including polyaromatic hydrocarbons (PAHs), surfactants, plant protection products (pesticides, herbicides and insecticides), preservatives, phthalates, phenolic compounds (alkylphenols, bisphenols), synthetic hormones, pharmaceutical compounds and personal care products [26,32–36].

Nano-TiO_2 photocatalyst is frequently used to pesticides removal. Compounds like endosulfan, quinalphos, imidacloprid, chlorpyrifos, dichlorvos, phosphamidon and aldrin has been successfully degraded using commercial Degussa P25 TiO_2 as well as ZnO in the form of nanoparticles, [37,38]. Water soluble pesticides of carbamate type (cymoxanil, dimethoate, methomyl, oxamyl, pyrimethanil and 1,3-dichloroproen) has been completely mineralized during heterogeneous photocatalysis carried out under solar UV light radiation and using nano- TiO_2 in pilot scale process [39]. Pesticides like thiabendazole, imazalil and acetamiprid, chlorpyrifos, lambda-cyhalothrin and diazinon have been efficiently degraded in reactor with immobilized sunlight activated photocatalyst containing TiO_2 [40]. The magnetic photocatalytic system comprised of $Fe_3O_4/SiO_2/TiO_2$ has been used to degradation and mineralization of pesticides like acephate, omethoate and methyl parathion [41] to inorganic

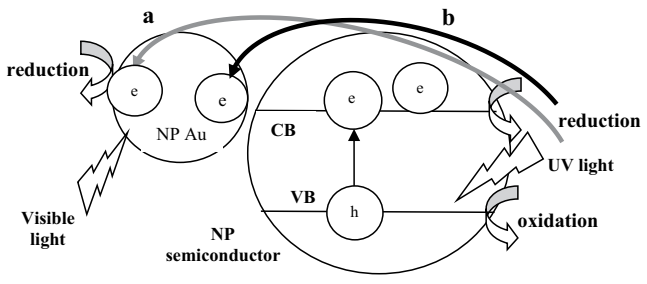

Fig. 2. Enhancement of photocatalytic activity of metal/semiconductor composites: (a) mechanism of charge separation and (b) mechanism of charge transfer (compiled from [24–26]).

products and any organic carbon has not remained in the treated stream.

Photocatalysis is one of the most important methods applied to removal of organic dyes from wastewater, especially having carcinogenic and mutagenic effect on living organisms. Nano-metal oxides (TiO_2 and ZnO) show the high efficiency degradation of a lot of dyes detected in water and wastewater [42]. For example, the methyl orange and methylene blue degraded by nano-ZnO in the form of powder and nanowires is faster than commercial TiO_2, due to the large active surface [22]. Also nanocomposite photocatalyst made of ZnO and CuO shows high mineralization of Acid Red 88 dye in wastewater compared to non-modified ZnO [43]. Similarly, nanocomposite polyaniline/ZnO shows removal of methylene blue and malachite in 99 at low dose equal 0.4 g/L [44], and nanoparticles of γ-Fe_2O_3 degrade Bengal rose and methylene blue at visible light radiation with high efficiency [45].

Photocatalysis is found to be suitable technique of the removal of pharmaceuticals and personal care products (PPCPs). Zhang et al. [46] have revealed, that NPs of TiO_2 have high photodegradation efficiency of chemotherapeutic and antibiotic doxorubicin carbamazepine, venlafaxine, fluoxetine, atenolol, sulfamethoxazole, ibuprofen, atorvastatin, naproxen, trioxolane, triclocarban and their metabolites [47]. The photocatalysis mechanism of consists of surface adsorption of the compound on NPs of TiO_2 and oxidation by UV induced electron holes. Immobilized TiO_2 in the form of quartz fibers filters and porous TiO_2 sheets and nanowires have been applied to treat wastewater containing pharmaceuticals (naproxen, carbamazepine) and personal care products (theophylline) at wavelength 30–100 nm [48]. TiO_2 nanocomposites modified with graphene (Gr-TiO_2) photo-catalytically degrade carbamazepine from drinking water and complete removal is obtained at the dose 25.14 mg/L Gr-TiO_2 after 5 min under UV radiation of intensity 1.35 mW/cm^2 [49]. Photocatalytic removal of carbamazepine, diclofenac and sulfamethoxazole by composite materials comprised of a semiconductor-carbon nanomaterial reveals significant increase of efficiency already under sunlight radiation [50]. TiO_2 photocatalysis has been degraded of gemfibrozil and 17β-estradiol in 95% and 93%, respectively at pH of 5 and TiO_2 dose 1.5 g/L. 17β-estradiol have been degraded by nanocrystalline TiO_2, modified with nitrogen and graphene oxide below its detection [51].

The use of photo-catalysis is also effective in the removal of phenolic xenoestrogens from water and wastewater The research included octylphenol, nonylphenol, bisphenol A and bisphenol F as well as 2-chlorophenol, 4-chlorophenol and 2,6-dichlorophenol [52,53]. It was found that on the removal efficiency depends on such parameters as pH and phenol concentration and structure, irradiation intensity, surface properties, and adsorption effect of intermediate products. In the study, Degussa TiO_2 and TiO_2-based composite photo-catalysts such as $InVO_4/TiO_2$ were used, which showed complete degradation for 2-chlorophenol, while in comparison, the removal efficiency on was 50.5% with TiO_2 [54].

Photocatalysis is proven to efficiently degrade and mineralize variety of organic compounds, which are harmful to human health, especially in regard to endocrine system

functioning. The contaminants, which are of the highest concern are pesticides, pharmaceuticals and personal care products, detergents, phenolic compounds, chloro- and non-halogenated organic derivatives have been successfully removed by the process. One should also note that this is especially important due to the fact, that a number of these compounds are highly persistent contaminants, which during treatment may form even more harmful by-products or keep their activity even after a series of conventional oxidative treatment techniques [26]. Despite many research showing that TiO_2 and its nanocomposite are able to decompose endocrine disruptors, only several research discusses the final toxicity of the treated stream. Nevertheless, photocatalysis, except for its high usability in organic compounds elimination, has become regarded as an efficient, "green" method of water and wastewater disinfection. It has been observed, that photocatalytic antimicrobial effect can be obtained in regard to many types of microorganisms [10,18].

4. Water and wastewater disinfection by nano-photocatalysis

Water and wastewater treatment methods should allow not only for removal of chemical contaminants, but also microbial ones such as viruses, bacteria, fungi or moulds. Photocatalytic inactivation of microorganisms is a complex process and its efficiency depends on a range of factors such as type of microorganisms, their concentration and physiological stage [18]. Moreover, type, morphology, concentration and phase (suspended or immobilized) of photocatalyst are crucial for efficient process performance. Among different microorganisms, *Escherichia coli* is the most often used in testing and optimization of photocatalysis parameters as well as in designing of novel photoreactors [17,18]. However other microorganisms like *Pseudomonas aeruginosa*, *Salmonella typhimurium* and *Enterobacter cloacae* have been used in research on their photocatalytic deactivation in order to prove the suitability of the process toward removal of biologically active microbial species.

4.1. Photocatalytic disinfection mechanism

Radicals generated during the photocatalysis. called also reactive oxygen species (ROS), are the most probable mechanism of bacteria degradation, and cell's death is caused by the damage of cell wall membrane [18,26,55,56]. The leakage of potassium ions and intercellular substances such as RNA and proteins leads to complete destruction of cells [26,55]. Antibacterial activity decreases after addition of ROS sweeper, but it is not completely stopped due to formation of highly reactive hydrogen peroxide. Hence, antimicrobial activity results from a synergic action of all types of ROS formed during photocatalytic reaction [26]. The progress in investigations of photocatalytic disinfection mechanism leads to understanding and description of the most probable mechanism of cellular wall damage [18,26,55]. It has been proven that peroxidation of phospholipid component of cellular wall due to the possible ROS attack results in its decay. Lipids peroxidation results in formation of malonic dialdehyde, while continuous radiation allows for the aldehyde mineralization to carbon dioxide (CO_2) and water (H_2O) [18,26,55].

Pigeot-Rémy et al. [57] have investigated bacterial cells and evaluated the possibility of their growth together with integrity of cellular walls in the dark and under visible light radiation. The authors have stated that TiO_2 particles reveal potential antibacterial features before the light radiation is applied, while the increase of TiO_2 content limits the growth of bacteria cells due to perturbations observed in wall's permeability. The particles cause the breakage in the integrity of cellular wall, what leads to the improved deactivation effect. On the other hand, the permeability of cellular wall remains unchanged at the presence of silica nanoparticles. It results from the difference in electrostatic charge between particular particles and cellular wall. Under further radiation, the inactivation effect is continued by the oxidative attack of ROS on cells RNA and DNA formed during photocatalytic treatment with UV light [57].

Wang et al. [58] have investigated dominant ROS responsible for deactivation of *E. coli* under visible light radiation using TiO_2 microspheres doped with boron (B) and nickel (Ni). Hydrogen peroxide (H_2O_2) generated in the system has been defined as the most dominant specie. Hydroxyl radical ($^{\bullet}OH$), on the other hand, which is present in the solution and on the catalyst surface, enhances H_2O_2 formation.

Matai et al. [59] have investigated antibacterial mechanism revealed by Ag-ZnO composite and have effectively defined probable inactivation pathways. The first pathway is based on direct interaction of the composite with a bacterial cell. It may be caused by surface oxidation followed by dissolution of Ag and Zn ions. The interaction may be also achieved by direct contact of composite particles with cellular wall based on electrostatic interactions. The second pathway relies on the damage of cellular wall by ionic potential or generated ROS. The third method of inactivation is based on change/inhibition of DNA replication by ions or ROS interaction with hydrocarbon-phosphate groups, which cause changes in protein genes responsible for functioning of the cell. Finally, possible damage of a cellular wall leads to the leakage of intercellular substances, which ends with lysis of a cell.

It should also be noted that lipid peroxidation, DNA and protein leakage studies, demonstrated irreversible comptonization of bacterial cell membrane, metabolism and morphology with simultaneous validation using electron microscopy and fluorescent staining [60]. Additionally, time dependent increase in membrane by-product 4-hydroxy-2-nonenal (4-HNE), which acts as a suicidal molecule synergistically acting on the bacteria for enhancing the rate of disinfection, confirms the disinfection of the targeted bacteria. The current reports about deleterious and detrimental effect of the solar-photocatalytic disinfection process on the resistance pattern of the bacteria, which showed substantial down-regulation of antibiotic resistance as compared to traditional chemical-based disinfection techniques.

Hence, the proceedings in determination of a mechanism of antibacterial actions of a photocatalyst may be defined as [18]:

- Coenzyme A degradation,
- Cellular wall malfunctions observed in transmission electron microscopy (TEM) images,
- Metabolic activity damage as confirmed by resazurin assay,

- Hydrogen peroxide production,
- Scanning electron microscopy microphotographs and C_{14} labelling for visualization of colonies disappearance,
- Peroxidation of phospholipid component of cellular wall,
- Change in fatty acid composition (increase omega 9 fatty acids) of the membranes (desaturation due to oxidative stress) supports ROS attack,
- Determination of toxic nature of nanoparticles and detection of materials of cellular nucleus as potential target of inactivation actions,
- Identification of dominant ROS types and indication that hydroxyl peroxide is the main specie responsible for inactivation occurrence.

To sum up, ROS are crucial in destruction of microorganisms using semiconductive materials and UV radiation, whereas the strongest effect is assigned to hydroxyl radicals (•OH) [17]. The inactivating properties of hydroxyl radicals lies in high oxidation potential and non-specific reactivity. Hydroxyl radicals formed on nano-TiO_2 surface, during their contact with water, characterize with long lifespan and may penetrate cellular wall and damage DNA, similarly as H_2O_2, as well as cause peroxidation of lipids (Fig. 3) [51,61].

Photocatalytic mechanism, which leads to antimicrobial effect, starts with destruction of cellular wall membrane, what results in leakage in intracellular substances such as RNA and proteins, followed by complete cell destruction and death [54]. The leaked material is oxidized at photocatalytic sites of a semiconductor. It has been found, however, that the presence of extracellular polymeric substance (EPS) may lead to the decrease of antibacterial activity due to its competition toward ROS. Hence, it is important to remove EPS from the reaction environment in order to obtain desired disinfection effect [62]. Apart EPS, bacterial contaminants also face competition from the already generated disinfected by-products in the system after a few minutes of photocatalytic treatment. Moreover, generated ROS are able to create so called oxidative stress in aqueous phase what additionally enhances the overall disinfection effect.

Multidrug-resistant bacteria (MDR bacteria) are bacteria that are resistant to three or more classes of antimicrobial drugs [63]. MDR bacteria have seen an increase in prevalence in recent years and pose serious risks to public health. These bacteria employ various adaptations to avoid or mitigate the damage done by disinfectants. These bacteria employ various adaptations to avoid or mitigate the damage done by antimicrobials. That is why MDR bacteria may possess certain defence mechanisms to counter the photocatalytic stress.

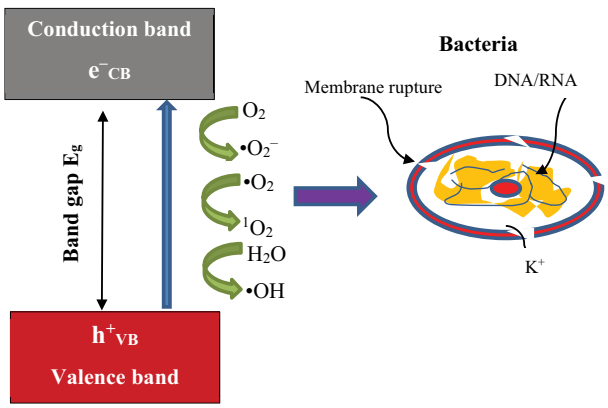

Fig. 3. Photocatalytic inactivation bacteria (compiled from [51,61]).

The post-photocatalytic bacterial reactivation/regrowth is one of the important parts of photocatalytic disinfection. Bacterial regrowth occurs through three mechanisms: (1) reactivation from a viable but non-culturable (VBNC) state, (2) repair of photo-induced DNA damage, and (3) reproduction of surviving bacteria in disinfected water. The literature shows that bacterial regrowth occurs at different degrees, depending on disinfection processes and post-disinfection storage conditions [64].

4.2. Photocatalytic disinfection with titanium dioxide

The nano-TiO_2 photocatalyst shows the ability to deactivate pathogenic organisms in water and wastewater. Studies have shown that nano-TiO_2 particles (Degussa P25) activated by sunlight deactivate both gram-negative and gram-positive bacteria, fungi, protozoa and cysts [18,55,56]. The effectiveness of photocatalytic deactivation of bacteria with nano-TiO_2 can be arranged in the following order: *E. coli* > gram-negative bacteria (other than *E. coli*) > gram-positive bacteria (other than *Enterococcus* sp.) > *Enterococcus* sp. [65]. The differences in the photocatalytic effectiveness of bacteria are due to the various structure of their cell wall and susceptibility to the oxidative damage of its components. In addition, the bactericidal efficacy of TiO_2/UV disinfection depends on the concentration and size of the photocatalyst particles, pH, temperature and radiation intensity as well as the initial concentration of bacteria and the presence of associated contaminants [66]. The presence of organic substances can reduce the efficiency of bacterial inactivation by TiO_2 photocatalysis by up to 40%/UV [67]. The results of other work suggest that high concentrations above 10^8 IU/mL underlie the weakening of the photocatalytic effect of nano-TiO_2 [55]. Another parameter is also the polymorphic form of nano-TiO_2, namely, the greatest antibacterial activity, shows a mixture of anatase and rutile in a ratio of 4:1 [55]. Also, a mixture of anatase and rutile TiO_2 doped with carbon in a ratio of 80/20 provides effective inactivation of *S. aureus* under visible light radiation [68].

TiO_2 in the form of nanotubes (NT) is one of the most favourable morphologies for the removal of microorganisms from water and wastewater due to its high specific surface area and good light absorption [17,69,70]. This was confirmed by studies of the effectiveness of germicidal nanotubes against *E. coli* and *S. aureus*, in which removal of 97.53% and S. 99.94%, respectively, was achieved within 24 h of UV irradiation [69]. In addition, hydroxyl radicals on the TiO_2 surface were found to determine inactivation, as indicated by the length-to-diameter ratio of the nanotube shape (100 μm and 20 nm). In another study on the inactivation of *E. coli*, *P. aeruginosa* and *S. aureus* with TiO_2 nanotubes, it was shown, the calcination temperature of NT TiO_2 affected the inactivation efficiency of bacteria [63]. As the temperature

and the rutile content increased, there was a decrease in bacterial inactivation to less than 1 $\log_{10}$ at 600°C and 800°C. At lower temperatures (non-calcined and 200°C), *E. coli* showed a high level of inactivation (2.7 $\log_{10}$ reduction) [70].

4.3. Disinfection with TiO_2 nanocomposites

TiO_2 composites have a higher inactivation efficiency against microorganisms in water and wastewater disinfection than pure TiO_2. There is a lot of dopants of TiO_2 that have been applied for the inactivation of microorganisms, some examples include nitrogen, silver, sulphur, carbon, nickel, copper, palladium, zirconium dioxide (ZrO_2) tin dioxide (SnO_2), molybdenum, iron, boron and cerium [26].

Pure silver is known as one of the most interesting antimicrobial materials. Silver nanoparticles, when used as TiO_2 doping, enable the semiconductor activation already in visible light [71]. The recent researches have also shown that Ag doped TiO_2 reveals significantly improved inactivation of bacteria. For example, the presence of 1 wt.% of Ag in TiO_2 shortens UV-A radiation period for complete removal of *E. coli* four times [72]. Ag nanoparticles improve TiO_2 photoactivity by the slowing of charge carriers recombination and/or by the increase of absorption surface. It is also supposed, that visible light absorption by Ag nanoparticles surface induces transfer of electrons to TiO_2, what leads to charge separation and thus allows for activation of the material under visible light range [71]. Hence, Ag-TiO_2 nanocomposites are promising photocatalytic materials suitable to be used in processes carried out under visible light radiation.

The introduction of Ag nanoparticles on the surface of TiO_2 films (Ag/TiO_2) results in anti-bacterial activity against *E. coli* under visible and sunlight [73]. The resulting composite has more active sites on the surface to deactivate bacteria, due to the high surface concentration of OH groups as well as the H_2O content, which resulted in the formation of more silver ions. The main mechanism for the release of silver ions was the interdiffusion of water and silver nanoparticles through the pores of the TiO_2 layer. The antibacterial activity of the nanocomposite layer irradiated with sunlight was several times higher than that of the anatase (a-TiO_2) layer. Therefore, the Ag-TiO_2/Ag/a-TiO_2 photo-catalyst can be considered as one of the effective and durable antibacterial nano-composite materials.

Reddy et al. [72] described the formation of catalyst composed of Ag-TiO_2 and hydroxyapatite (HAP). The addition of hydroxyapatite increased the disinfection capacity of Ag-TiO_2, resulting in complete disinfection of *E. coli*. The study showed that in HAP-Ag-TiO_2 composite, titanium is present as tetravalent and silver as Ag^0. It was also found that HAP irradiation causes surface changes of the PO_4^{3-} group, which translates into increased photocatalytic activity of the composite. The TiO_2/Ag_3PO_4 was also tested for disinfection of *E. coli* bacteria and *Fusarium graminearum* fungi under visible light [74], which reduced its survival rate to about 2. The disinfection mechanism involved damage to the cell wall by attacking oxygen-containing radicals [74].

Also composites AgI/TiO_2 and AgBr/TiO_2 have antimicrobial properties toward *E. coli* and *S. aureus* under visible light radiation [55]. The complete degradation of cellular wall has been observed in TEM images, whereas intermediate products such as aldehydes, ketones and carboxylic acids have been identified using Fourier-transform infrared spectroscopy. These results have indicated that photocatalytic destruction of cellular wall is the main reason of microorganisms death. Moreover, electrostatic interaction between bacteria and catalyst significantly influences on disinfection efficiency basing on *E. coli* inactivation results obtained at different conditions.

Rtimi et al. [75] have presented results of the research on the use of sputtered Cu/TiO_2 foils to bacteria inactivation. Cu and TiO_2/Cu sputtered films have allowed for complete inactivation of *E. coli* carried out in dark conditions, while such an effect has not been observed in case of TiO_2. The presence of Cu has enhanced inactivation of bacteria under simulated sunlight radiation of low intensity, what influences on practical use of such materials. Composite layers formed during plasma sputtering allow for significant metal savings in regard to layers formed using conventional sputtering methods. The leakage of Cu during bacteria inactivation has been monitored using inductively coupled plasma mass spectrometry analyses, which show that the content of copper is in ppb range, that is, below cytotoxic level established in human health standards. Similarly, a TiO_2-ZrO_2 composite on polyester (PES) with Cu doping showed a strong bactericidal effect. Inactivation increased threefold for the Cu-containing composite compared to the Cu-free composite, at low concentration of Cu (0.01–0.02 wt.%). The antibacterial properties are evident from the strong affinity between the phosphate and the thiol group in the negatively charged bacterial cell wall with copper (a strong electron donor) [76].

Fisher et al. [77] described molybdenum-doped titanium dioxide that effectively inactivated brewing microorganisms, that is, 5-log for bacteria after 4 to 24 h and 1-log for fungi after 72 h in the dark. The research suggests that composites may have dual function – antimicrobial and photocatalytic, and TiO_2-Mo coating may act as a secondary barrier to help prevent the accumulation of microbial contaminants on surfaces of brewing installations during long production runs. The TiO_2(Eu)/CuO nanocomposite exhibits bactericidal properties against bacteria of the *Enterococcus* species [78], with higher activity obtained against *Enterococcus faecalis* than against *Enterococcus faecium*. The mechanism of the antibacterial action of the composite was based on the selective binding of CuO to the surface of the microorganism. Titanium dioxide doped with boron and/or cerium (B/Ce-TiO_2) exhibits antibacterial properties against *S. aureus* [79]. In the case of boron. the composite obtained enhanced antibacterial properties due to the narrowing "band gap" of the TiO_2, increasing of the catalyst surface area, the presence of B instead of oxygen O, and the formation of B–O–B bonds. In materials with cerium, Ce^{3+} and Ce^{4+} ions co-occur. Photocatalytic and antibacterial properties are demonstrated by cotton fabrics coated with TiO_2-1% Fe–N nanoparticles obtained by hydrothermal method and annealed at 400°C [80]. Antibacterial efficacy depends on the composition of the composite, the type of bacteria and the incubation time. The TiO_2 in the composite consisted primarily of an anatase phase and in 15%–20% brucite, containing Fe^{3+} ions and nitrogen.

TiO_2 composites containing nickel ferrate ($NiFe_2O_4$) are characterized not only by photo-catalytic properties, but also by magnetic properties, making it possible to recover the catalyst in a magnetic field [81]. The obtained $TiO_2/NiFe_2O_4$ and $TiO_2/NiFe_2O_4$/diatomite composites show effective antibacterial activity against *E. coli* strains. Bacterial inactivation in the presence of TiO_2 nanoparticles coated with $NiFe_2O_4$ is faster than in the absence of $NiFe_2O_4$, and the presence of diatomite increased the adsorption of microorganisms. Magnetic properties also characterize the antibacterial Fe_2O_3-AgBr composite, which effectively inactivates both gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacteria [82]. The mechanism of bacterial inactivation relies on the oxidative action of H_2O_2 generated by photocatalysis.

Rengifo-Herrera et al. [83] have doped nitrogen and sulphur compounds N–S to TiO_2 in order to study the impact of the semiconductor modification on *E. coli* photocatalytic inactivation. The authors have used thiourea as the source of N–S dopes to TiO_2 [83]. The formation of reactive oxygen species (ROS) has been found to depend on the dope properties, particles size and surface hydroxylation.

4.4. Photocatalytic disinfection with zinc oxide

Zinc nano-oxide (nano-ZnO), like TiO_2, exhibits significant antibacterial activity even at low concentrations. A number of both gram-positive and gram-negative bacteria have been studied, with the effectiveness of nano-ZnO being greater against the former [55,84]. The reason for this is the structure of the bacterial cell membrane, that is, the thicker cell membrane of gram-negative bacteria may block the penetration of nano-ZnO into the bacterial cell. For example, the bacteria *Pseudomonas* spp. are resistant to ZnO photocatalyst, while *Bacillus cereus* bacteria were destroyed after 2–4 h of contact with nano-ZnO [55,84]. Not only the nature of the bacteria, but also the size of nano-ZnO has a large effect on antibacterial activity due to the greater accumulation of nanoparticles on the surface and inside the cell membrane [55,84]. It was shown that the effect of nano-ZnO size on the inactivation of *S. aureus* was smaller than that for *E. coli*, due to differences in the structure and chemical composition of the cell membrane layers. *E. coli* bacteria have layers of peptidoglycan, lipid and lipopolysaccharide on the cell surface, while *S. aureus* only has a peptidoglycan layer [51,77].

Other factors influencing bacterial disinfection are the structure of ZnO nanoparticles and the type of radiation that activates photocatalysis. Studies have been carried out on the effectiveness of disinfection by ZnO nanoparticles immobilized on paper prepared from cellulose under visible light and in the dark [55,84]. Inactivation of gram-negative *E. coli* and gram-positive *Bacillus subtilis* bacteria in visible light was almost twice as high as in darkness, indicating the possibility of disinfecting water in sunlight.

Nano-ZnO also shows disinfecting activity on pathogenic fungi *Botrytis cinerea* and *Penicillium expansum*, with *P. expansum* fungi being more sensitive to ZnO [85]. The concentration of the nanocatalyst is of great importance in this case, that is, with increasing concentration the disinfection efficiency increases.

Studies have shown enhanced antibacterial activity of ZnO photocatalysts containing silver and gold nanoparticles deposited on the surface, introduced by photoreduction of metal compounds [86,87]. The Ag@ZnO photocatalyst has been tested in the disinfection of model gram-negative *Vibrio cholerae* 569B bacteria present in water using radiation sunlight [87]. The nano-composite system showed a deactivation rate of about 98% within 40–60 min of exposure to sunlight. In the case of the Au@ZnO composite, a low concentration of Au enhanced the antibacterial effect many times over, due to increased levels of ROS produced during the disinfection process [86].

Nano-ZnO disinfection studies have also been performed in municipal wastewater for the bacteria *Klebsiella pneumoniae*, *E. coli*, *Proteus* and *Staphylococcus epidermidis* and compared with the disinfection efficiency of chlorine and ultraviolet light [88]. It was shown that, similar to the model studies, the disinfection efficiency depended on the type of bacteria and the concentration of the nano-catalyst. Thus, nano-ZnO showed activity against *E. coli* and *Staphylococcus epidermidis*, but not *Klebsiella pneumoniae* and *Proteus*; moreover, activity increased with increasing nano-ZnO concentration. Thus, ZnO nanoparticles can be an antibacterial agent in wastewater treatment, especially as a complementary method to UV disinfection [81].

The studies demonstrated that nano-ZnO is very efficient in water and wastewater disinfection, especially as a method together with UV disinfection, and the better effect shows in relation to gram-positive than to gram-negative bacteria. Table 1 presents selective efficiency studies of nano-ZnO antibacterial activity against different bacteria [88–92].

4.5. Carbon based photocatalysts in water and wastewater disinfection

Very important photocatalysts used in water and wastewater disinfection are those that are based on carbon. It can be distinguish composites first of all with TiO_2 by their combination with graphene oxide, carbon nanotubes, fullerenes and graphitic carbon nitride g-C_3N_4. Also this group of photocatalysts has gain the attention in regard to their use in photocatalytic disinfection processes.

Cao et al. [93] have investigated inactivation of *E. coli* using composite comprised of titanium dioxide and graphene oxide (TiO_2-GO) exposed to visible light radiation. GO has been prepared using Hummer method, whereas the developed composite has characterized with better inactivation properties for bacteria *E. coli* compared to TiO_2 and graphene separately. Fernandes-Ibanez et al. [94] have studied the possible use of the same composite against *E. coli* and *F. solani* and compared the results with Degussa P25 (standard nanoparticles of TiO_2 with mixed anatase and rutile phases). The composite has shown faster disinfection effect than commercial photocatalyst and the reason of this fact has been related with formation of singlet oxygen. Akhavan and Ghaderilt [95] have prepared nanocomposites comprised of TiO_2 and reduced graphene oxide which have characterized with improved antimicrobial properties under sunlight radiation. This activity has been assigned to better light absorption or acceptance of electrons revealed by reduced

Table 1
Antibacterial efficiency of nano-ZnO for different bacteria at different ZnO concentrations

Bacteria type	Nano-ZnO concentration	Antibacterial test results
Staphylococcus aureus	0.1–0.3 μL	Zone of inhibition was 10–13 mm depending on nano-ZnO concentration
Escherichia coli	5–100 mM	Efficient anti-bacterial activity at investigated concentration range. For concentration <1 mM, no anti-bacterial activity found
Escherichia coli *Bacillus subtilis*	0.1–2.0 wt.%	For 2% dose of nano-ZnO complete deactivation of both bacteria was obtained, at >2% *Bacillus subtilis* was better deactivated than *Escherichia coli*
Staphylococcus aureus *Salmonella typhimurium*	(20–100) μg/mL	Minimum nano-ZnO concentration for both bacteria was *ca.* 40 μg/mL, and disinfection effect increase with concentration increase
Escherichia coli *Bacillus cereus* *Pseudomonas aeruginosa*	1 M ZnO	Zone of inhibition was *ca.* 21 mm for *Escherichia coli*, *ca.* 34 mm for *Bacillus cereus*, *ca.* 17 mm for *Pseudomonas aeruginosa*
Escherichia coli *Klebsiella pneumoniae* *Staphylococcus epidermidis*	0.01–50 mM	Zone of inhibition at 25 mM was: *ca.* 12 mm for *Escherichia coli*, *ca.* 18 mm for *Staphylococcus epidermidis* and *ca.* 0 mm for *Klebsiella pneumoniae*
Staphylococcus aureus *Escherichia coli* *Klebsiella pneumoniae* *Enterococcus faecalis* *Pseudomonas aeruginosa*	(20–100) μg/mL	Zone of inhibition at 20 μg/mL was: *ca.* 18 mm for *Staphylococcus aureus*, *ca.* 13 mm for *Escherichia coli*, *ca.* 10 mm for *Klebsiella pneumoniae*, *ca.* 10 mm for *Enterococcus faecalis* and *ca.* 25 mm for *Pseudomonas aeruginosa*
Escherichia coli *Pseudomonas aeruginosa* *Staphylococcus aureus* *Bacillus subtilis*	0.02925–30 mg/mL	Zone of inhibition at 0.938 mg/mL was: *ca.* 22 mm for *Escherichia coli*, *ca.* 24 mm for *Pseudomonas aeruginosa*, *ca.* 18 mm for *Staphylococcus aureus* and *ca.* 15 for *Bacillus subtilis*

graphene oxide, which sufficiently participates in charge separation and delays recombination process. Liu et al. [96] produced graphene oxide photocatalyst, with better deactivation properties of *E. coli* than TiO_2 nano-rods. The better performance was attributed to the interaction of two-dimensional graphene and surface of TiO_2. Also three component composites of nano-titanium dioxide, carbon dots (C-dots) and reduced graphene oxide (rGO) has been found to possess disinfection properties [97]. Photocatalytic activity of TiO_2/rGO (TR) and C-dots/TiO_2/rGO (CTR) against *E. coli* in buffer phosphate (pH = 7.0) in dark as well as exposed to simulated and natural sunlight has been investigated. The results showed that under sunlight, the inactivation of *E. coli* for CTR was 1.03 log at 60 min, and 0.58 for TR, while in darkness or simulated sunlight, the inactivation was virtually imperceptible. The reason was the transfer, electrons from TiO_2 to carbon atoms via nano-rGO, which were then transferred to O_2, forming $^{\bullet}O^{2-}$ radicals that ruptured the bacteria's cell membranes. In Fig. 4, the mechanism of exemplary degradation of pollutants/microorganisms with the use of TiO_2/graphene composite photocatalyst is shown [9,26].

ZnO/graphene oxide nanoparticles have revealed very high antibacterial activity, whereas minimum inhibiting concentration have been 25 g/L for *E. coli* and *S. typhimurium*, 12.5 g/L for *B. subtilis* and 25 g/L for *Enterococcus faecalis* [99]. During the disinfection process, a large number of oxygen-containing radicals were formed on the surface of the nano-photocatalyst, which caused the ZnO-GO composites to become antibacterial. The fabricated graphene oxide/zinc oxide (GO-ZnO) nano-catalyst by a simple hydrothermal method showed disinfecting activity for *E. coli*, with the deactivation efficiency being higher under visible light [100]. The reason for this phenomenon was the strong interaction between GO and ZnO.

Table 2 summarizes selected results of bacterial inactivation with graphene oxide-containing photocatalysts [96–101].

Carbon nanotubes (CNTs) also has antibacterial properties, against a range of microorganisms present in water and wastewater. First proves on such the CNTs activity has been obtained for single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs) applied to inactivation of *E. coli* by Kang et al. [102]. On the basis of their observations other applications of CNTs to microbiological inactivation of pathogens like *Micrococcus lysodeikticus*, *Streptococcus mutans*, *E. coli*, *Salmonella* spp. have been discussed [103]. The toxicity of CNTs to bacteria depends on a multitude of parameters, among which are the physicochemical properties of the nanomaterials and water/wastewater and the transport capabilities of the nano-catalysts [102]. The introduction of functional groups into CNTs has been found to increase their disinfection efficiency by increasing the dispersion and stability of CNTs [104]. CNTs are also introduced into semipermeable membranes (ultra- or microfiltration), which are used in water disinfection to remove bacteria and viruses [103].

Nanocrystalline TiO_2 and MWCNTs are important functional materials, which in recent years have gained

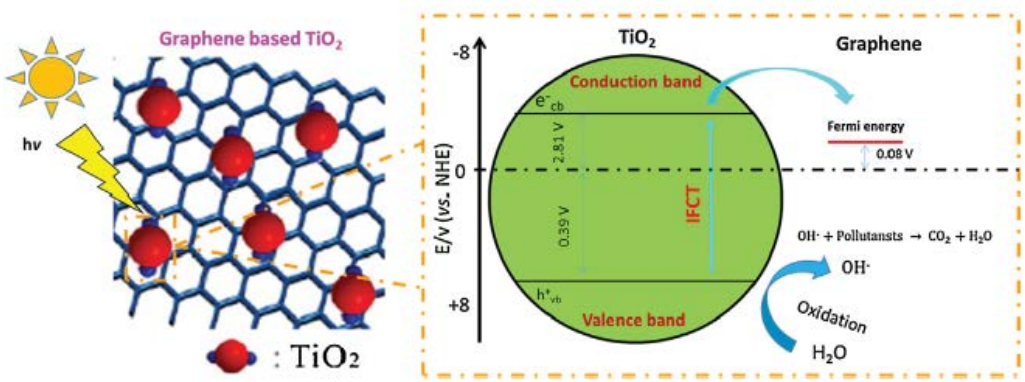

Fig. 4. The mechanism of exemplary degradation with the use of composite TiO_2/graphene photocatalyst (compiled from [26,98]).

Table 2
Deactivation bacteria with photocatalysts containing graphene oxide

Photocatalyst type	Catalyst activation radiation	Results of deactivation
rGO@film TiO_2	Sunlight	Complete deactivation of *Escherichia coli* bacteria
GO-TiO_2 nanowires	Sunlight	Complete deactivation of *Escherichia coli* bacteria
GO-ZnO-Ag	Visible	Deactivation of *Escherichia coli* bacteria in 99.99%
GO-CdS	Visible	Complete deactivation of *Escherichia coli* and *Bacillus subtilis* bacteria
rGO-C_3N_2-S	Visible	Complete deactivation of *Escherichia coli* bacteria
TiO_2-C-dots/rGO	Sunlight	Deactivation of *Escherichia coli* bacteria in 1.03 log

a wide interest in regard to their use in water disinfection. Composites comprised of TiO_2 and CNTs reveal efficient *E. coli* inactivation under visible light radiation [105]. Vertically arranged MWCNTs bundles has been deposited on thin Ni layer of ~5 nm thickness placed on Si support from gaseous phase enhanced with plasma at 650°C. Next, MWCNTs have been coated with TiO_2 using sol–gel method followed by calcination at 400°C, then crystallization of TiO_2 takes place and formation of Ti–C and Ti–O–C bonds. Composites calcined at 400°C have greater activity than composites calcined at 100°C. Photoinactivation of bacteria induced at visible light has increased in the following series: MWCNTs < TiO_2 < TiO_2/MWCNTs. Other bacterial disinfection studies of the TiO_2/MWCNT photocatalyst included *E. coli* and *S. aureus* bacteria under visible light radiation [106]. TiO_2/MWCNT exhibited faster disinfection than TiO_2 alone due to easier charge separation by MWCNTs.

Nanocatalysts containing TiO_2 with Fe and MWCNTs (0.1%–0.5%) have higher deactivation properties against a wide range of bacterial microorganisms, including *B. subtilis* and *P. aeruginosa*, than other TiO_2 and carbon-based nanocomposite photo-catalysts [107]. The reason is the ability of Fe-TiO_2-MWNTs nano-catalysts to generate more oxygen atom-containing radicals than other nanocomposites.

Ouyang et al. [108] have prepared nanocomposite containing of fullerene and TiO_2 (C_{70}-TiO_2) and investigated its antibacterial properties under visible light. Disinfection studies of water containing *E. coli* indicator bacteria showed that 73% of the bacteria died within 2 h, which is three times more than TiO_2 alone [108]. In addition, it was found, deactivation is associated with the formation of hydroxyl radicals, which play an important role in photo-catalytic disinfection. Another polyhydroxy-fullerene (PHF)-containing nano-photocatalyst is a transparent nano-TiO_2 coating with enhanced antibacterial potential, which has been used to inactivate *Aspergillus niger* spores, a fungus that commonly causes asthma [109]. The nanocomposite inactivated the spores three times faster than a TiO_2 coating containing no PHF.

The novel class of photocatalyst is based on graphitic carbon nitride g-C_3N_4, which characterizes with efficient disinfection activity for many toxic contaminant, including microorganisms and harmful pathogens, due to large adsorption, thermal stability and suitable band gap energy [110]. The disinfection ability is mainly due to generation of radicals containing oxygen atoms [111]. In order to increase the disinfection efficiency, it is proposed to modify pure g-C_3N_4 by (1) changing the texture and morphology of g-C_3N_4; (2) doping with metals (as Au, Pt, Ag Cu, Ni, Fe, Ni and Sn) and non-metals (as S, C, F, B, and P); and (3) combining with semiconducting materials (e.g., TiO_2, ZnO, CuO, CuO_2, BiOCl, $BiVO_4$, $Bi2MoO_6$, Bi_2WO_6, $In2S_3$, $SrTiO_3$, WO_3, AgX (X = Br, Cl and I) and GO) [110]. The modification results in a reduction of the energy band gap and an expansion of visible light absorption. Nitrogen-rich g-C_3N_4 can be an alternative to metal oxide-based photo-catalysts (TiO_2 and ZnO) in photo-catalytic disinfection water and wastewater.

The mesoporous structure of g-C_3N_4 is highly effective in deactivating *E. coli* bacteria due to a 20-fold larger catalyst surface area (190 m^2/g) than g-C_3N_4 with a normal structure, and the "electron holes" generated on the surface of g-C_3N_4

greatly facilitate bacterial inactivation [112]. Complete inactivation efficiency was obtained after 4-h visible light irradiation, while g-C_3N_4 alone can only destroy 77.1% of *E. coli* cells. Thurston et al. [113] studied the disinfection activity of g-C_3N_4 film against not only *E. coli* bacteria, but also *S. aureus*. The high disinfection efficiency of g-C_3N_4 was a result of its large surface area (72.2 m^2/g), reduced energy of "band gap" (2.86 eV) and efficient separation of photo-generated electron–hole pairs.

De-amination and functionalization of g-C_3N_4 can significantly increase the water disinfection activity compared to normal g-C_3N_4 and under visible light irradiation [114]. The introduction of –COOH and –C=O functional groups into the structure of g-C_3N_4 results in an *E. coli* inactivation efficiency of >99.9999% with lower catalyst consumption than the g-C_3N_4 catalyst without functionalization. The reason disinfection efficiency improvement of the functionalized g-C_3N_4 catalyst is that it effectively promotes electron–hole pair separation, enhanced H_2O_2 generation [114]. The g-C_3N_4 photocatalyst obtained from urea inactivated *Bacillus anthracis* (*B. anthracis*) endospores and *E. coli* bacteria after 4 h of visible light irradiation with an efficiency of about 5–3 log [115]. Also, inactivation of MS2 viruses using g-C_3N_4 was virtually complete in about 6 h [116].

The photo-catalytic efficiency of g-C_3N_4 can also be enhanced by incorporating metals into the photo-catalysts. Noble metals can play the role of charge carriers, extend light absorption into the visible region, and can absorb free electrons, promoting electron–hole charge carrier separation and enhancing the anti-bacterial efficiency of g-C_3N_4 through ROS generation [117–120]. Increased ROS generation on the surface of nano-Ag/g-C_3N_4 in the presence of visible light results in higher inactivation efficiency of *E. coli* bacteria and better ability to destroy proteins, nucleic acids and polysaccharides, compared to g-C_3N_4 [118]. The Ag/g-C_3N_4 photocatalyst has been shown to effectively destroy *S. aureus* bacterial cells in 99.4%, while g-C_3N_4 alone inactivates only29.6% [119]. The destruction of bacteria using the Ag/g-C_3N_4 catalyst contributes to the formation of a h^+ and $^{\bullet}O^{2-}$. Munoz-Batista et al. [120] have shown that g-C_3N_4 doped with Ag (Ag/g-C_3N_4) characterizes with much better efficiency in destruction of *E. coli* under both UV and VIS light radiation. Nanocomposites Ag/g-C_3N_4 reveal excellent disinfection effect that bare Ag-nanoparticles due to much better distribution and stability of Ag placed on g-C_3N_4.

Combining g-C_3N_4 with semiconductors enhances its photo-catalytic efficiency, due to the expansion of its exploitation capabilities in the visible region and effective separation of the e^-/h^+ pair, as there is a shift of electrons from higher CB to lower CB, and electron holes from higher VB to lower VB. Studies conducted on the combination of TiO_2 with g-C_3N_4 (g-C_3N_4/TiO_2), showed complete inactivation of *E. coli* under visible light within 180 min [121]. The use of a composite of g-C_3N_4 and TiO_2 nanotubes (TiNT) to remove *E. coli* resulted in bacterial survival rates for g-C_3N_4/TiNT and g-C_3N_4 of about 86% and about 16%, respectively [122]. Also, g-C_3N_4 quantum dots (QDs) immobilized on TiO_2 nanotubes (g-C_3N_4 QDs/TNA) showed complete elimination of *E. coli* when filtering water containing these bacteria [123]. In addition, combining semiconductors containing bismuth atoms, namely Bi_2MoO_6/g-C_3N_4 (BM/CNNs) and (g-C_3N_4/Bi_2O_4) showed higher photo-catalytic activity in inactivating *E. coli* K-12 than g-C_3N_4 under visible light [124,125]. For the latter composite (g-C_3N_4/Bi_2O_4), the removal efficiency of *E. coli* was 6 log, compared to 1.5 log for g-C_3N_4 and 4 log for Bi_2O_4 during exposure to visible light [125]. Also, g-C_3N_4 and graphene oxide (GO) composites have also been used to disinfect of *E. coli* bacteria in 97.9% by a 100 μg/mL GO/g-C_3N_4 composite after 120 min of visible light irradiation, with antimicrobial activity occurring under both aerobic and anaerobic conditions [126]. Similarly, fullerene (C_{60} and C_{70}) in combination with g-C_3N_4 showed antimicrobial activity against *E. coli* under visible light than g-C_3N_4, with the C_{70}/C_3N_4 composite showing higher activity than the C_{60}/C_3N_4 photocatalyst [127].

5. Possibilities of industrial application

A number of studies have been examined for photocatalytic disinfection. From them, it can be concluded that the inactivation of microbes is dependent on a number of properties, for example, the composition of the material, effective design of the reactors, the concentration and the irradiation source. Future studies in this direction have to be carried out along with the toxicological assays for evaluating the applicability of the process and also for further development.

Although a lot of work has been done on basic photocatalytic research, there is still a gap between laboratory and industrial application. Laboratory studies can take no account of the cost, catalyst recycle, energy consumption, environmental protection, and other issues, but only to prove the feasibility and mechanism of the photocatalytic system. However, in the case of amplifying industrial application, there are various uncontrollable factors in the actual production process, and the preparation conditions of the catalysts will not be as controllable and stable as in the laboratory [128]. Therefore, the development of economical, feasible, and stable large-scale preparation methods is the key to realize the industrial application of photocatalytic systems. The improvement and optimization of the reactor is also an important factor for the industrial application of photocatalytic technology [129,130]. It is necessary to optimize the system design of the reactor to achieve the optimal photocatalytic efficiency, since a well-designed reactor can not only improve the reaction efficiency, but also reduce the waste of energy and catalyst and improve the economic benefit.

Kim et al., investigated the removal efficiencies of mixed EDCs, in two different scales of rotating and flat-type TiO_2 photocatalytic reactors (Fig. 5) and compared the reactor performances on removal efficiency [131]. Several operational parameters such as hydraulic retention time (HRT), initial concentrations, single and mixed compounds, UV intensities, and dissolved oxygen, effect of the average solar UV intensities, effect of Cr(VI), pH on EDC-removal process were demonstrated under outdoor solar irradiation. The results revealed that for the both photocatalytic reactors (rotating and flat-type) decrease in HRT increased degradation efficiency because of increased mass transfer [132].

However, several important challenges remain with respect to their commercial use. First, it is necessary to

Fig. 5. Photographs of photocatalytic scale-up reactors including TiO_2 (a) flat-type reactor (b) rotating-type reactor (compiled from [129,130]).

remove particles from water as they may negatively interfere in secondary treatment processes or, due to their inherent toxicity, may present a risk for the environment (biomass) or water consumers. Second, electrostatic or van der Waals interactions among nanoparticles to form larger aggregates may be useful to obtain particle sizes easily trapped by traditional filtration methods or to induce spontaneous precipitation. Their size may also increase due to interactions with organic matter dispersed in solution (humic and fulvic acids, carbonaceous materials, among others). Core–shell nanoparticles involving a ferromagnetic layer is another attractive option as the latter may be used to remove nanoparticles by simply applying a strong external magnetic field. Functionalization of their surfaces to maintain their solubility, increase their stability against aggregation, decrease their chemical reactivity at a wide range of pH values, or avoid interactions with chemical substances present at solution is also key for their eventual consideration in wastewater treatment procedures. Biological interactions with other organisms (not only microbes, but also other phyla such as invertebrates, vertebrates, and plants) may prove to be another challenge, as the nanoparticles may biodegrade, suffering biologically induced chemical and physical transformations, which affects their stability and chemical reactivity, or even changes their biological activity from nontoxic to highly toxic or vice versa. All these problems make the field more attractive for further research in order to overcome the difficulties and better exploit the unique properties of nanomaterials for wastewater treatment.

6. Conclusions and future perspectives

The inactivation of bacteria has becoming an important research area in recent years for a number of applications, including in the environmental and in hospitals. There has been an extensive amount of studies into photocatalysis disinfection since its first discovery. The specific biocide activity of some nanomaterials against microorganisms present in wastewater is a very attractive property for their incorporation for water and wastewater disinfection. Titania still remains to be the photocatalyst of choice in many cases. This is due to a number of things which include low lost, nontoxicity and high oxidizing ability. In order to produce TiO_2 that is activated by both UV and visible light a number of improvements have been developed. These include forming composites (either with two of the titania phases or TiO_2 and another photocatalyst) and the use of dopants/chemical modifiers or additives in order to narrow the band gap. Both of these methods have been studied and been proven effective. TiO_2 composites have a higher inactivation efficiency against microorganisms in water and wastewater disinfection than pure TiO_2. There is a lot of dopants of TiO_2 that have been applied for the inactivation of microorganisms, some examples include nitrogen, silver, sulphur, carbon, nickel, copper, palladium, zirconium dioxide (ZrO_2) tin dioxide (SnO_2), molybdenum, iron, boron and cerium. There has been a growing interest in examining photocatalysts other than TiO_2. The studies demonstrated that nano-ZnO is very efficient in water and wastewater disinfection, especially as a method together with UV disinfection, and the better effect shows in relation to gram-positive than to gram-negative bacteria. Very important photocatalysts used in water and wastewater disinfection are those that are based on carbon. It can be distinguish composites first of all with TiO_2 by their combination with graphene oxide, carbon nanotubes, fullerenes and graphitic carbon nitride g-C_3N_4. Also this group of photocatalysts has gain the attention in regard to their use in photocatalytic disinfection processes.

The rate of photocatalytic degradation strongly depend on adsorption of a given contaminant on a photocatalyst surface. It is also valid for photocatalytic inactivation of microorganisms. In order to assure efficient photoinactivation, microbes need to interact with a photocatalytic material surface. Reactive oxygen species (ROS) generated during the process firstly damage lipopolysaccharide layer of cellular wall, next they react with peptidoglycan layer, and finally oxidize lipid layer and peptides. The destruction of these layer results in the leakage of potassium ions

from cellular interior, what influences on cells viability. This leakage leads to the loss of crucial cell functions and finally causes death of a cell.

The future development of nano-disinfection containing metal/metal oxides and carbon based nanoparticles should focuse on:

- improving disinfection efficiency through different manufacturing strategies,
- proper clarification and understanding of the role and mechanism of interaction of the nano-material with the microorganisms,
- progress in scaling up the production of commercial nano-photocatalysts,
- determination of the extent of environmental release of nano-photocatalysts and their toxicity.

References

[1] L. McKibben, T. Horan, J.I. Tokars, G. Fowler, D.M. Cardo, M.L. Pearson, P.J. Brennan, Guidance on public reporting of health care associated infections: recommendations of the Healthcare Infection Control Practices Advisory Committee, Am. J. Infect. Control, 33 (2005) 217–226.

[2] L. Feng, D. Astruc, Nanocatalysts and other nanomaterials for water remediation from organic pollutants, Coord. Chem. Rev., 408 (2020) 213180, doi: 10.1016/j.ccr.2020.213180.

[3] Molinari, P. Argurio, M. Bellardita, L. Palmisano, Photocatalytic Processes in Membrane Reactors, E. Drioli, L. Giorno, E. Fontananova, Comprehensive Membrane Science and Engineering, 2nd ed., Elsevier, Oxford, 2017, pp. 101–138.

[4] P.A.K. Reddy, P.V.L. Reddy, E. Kwon, K.H. Kim, T. Akter, S. Kalagara, Recent advances in photocatalytic treatment of pollutants in aqueous media, Environ. Int., 91 (2016) 94–103.

[5] X. Qu, P.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, Water Res., 47 (2013) 3931–3946.

[6] E. Friehs, Y. AlSalka, R. Jonczyk, A. Lavrentieva, A. Jochums, J.G. Walter, F. Stahl, T. Scheper, D. Bahnemann, Toxicity, phototoxicity and biocidal activity of nanoparticles employed in photocatalysis, J. Photochem. Photobiol., C, 29 (2016) 1–28.

[7] F. Petronella, C. Truppi, A. Ingrosso, T. Placido, M. Striccoli, M.L. Curri, A. Agostiano, R. Comparelli, Nanocomposite materials for photocatalytic degradation of pollutants, Catal. Today, 281 (2016) 85–100.

[8] M. Bodzek, M. Rajca, Photocatalysis in the treatment and disinfection of water. Pt 1: Theoretical backgrounds, Ecol. Chem. Eng. S, 19 (2012) 489–512.

[9] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: a review, Water Res., 44 (2010) 2997–3027.

[10] O.K. Dalrymplea, E. Stefanakos, M.A. Trotz, D.Y. Goswami, A review of the mechanisms and modeling of photocatalytic disinfection, Appl. Catal., B, 98 (2010) 27–38.

[11] T. Bora, J. Dutta, Applications of nanotechnology in wastewater treatment—a review, J. Nanosci. Nanotechnol., 14 (2014) 613–626.

[12] S.K. Loeb, P.J.J. Alvarez, J.A. Brame, E.L. Cates, W. Choi, J. Crittenden, D.D. Dionysiou, Q. Li, Gi. Li-Puma, X. Quan, D.L. Sedlak, T.D. Waite, P. Westerhoff, J.-H. Kim, The technology horizon for photocatalytic water treatment: sunrise or sunset?, Environ. Sci. Technol., 53 (2019) 2937–2947.

[13] M.T. Amin, A.A. Alazba, U. Manzoor, A review of removal of pollutants from water/wastewater using different types of nanomaterials, Adv. Mater. Sci. Eng., 2014 (2014) 825910, doi: 10.1155/2014/825910.

[14] M.L. Zambrano-Zaragoza, R. González-Reza, N. Mendoza-Muñoz, V. Miranda-Linares, T.F. Bernal-Couoh, S. Mendoza-Elvira, D. Quintanar-Guerrero, Nanosystems in edible coatings: a novel strategy for food preservation, Int. J. Mol. Sci., 19 (2018) 705, doi: 10.3390/ijms19030705.

[15] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S. Dunlop, J.W. Hamilton, J.A. Byrne, K. O'shea, A review on the visible light active titanium dioxide photocatalysts for environmental applications, Appl. Catal., B, 125 (2012) 331–349.

[16] S. Malato, J. Blanco, D.C. Alarcon, M.I. Maldonado, P. Fernandez-Ibanez, W. Gernjak, Photocatalytic decontamination and disinfection of water with solar collectors, Catal. Today, 122 (2007) 137–149.

[17] C. Byrne, G. Subramanianc, C.P. Suresh, Recent advances in photocatalysis for environmental applications, J. Environ. Chem. Eng., 6 (2018) 3531–3555.

[18] P. Ganguly, C. Byrnea, G. Subramanianc, C.P. Suresh, Antimicrobial activity of photocatalysts: fundamentals, mechanisms, kinetics and recent advances, Appl. Catal., B, 225 (2018) 51–75.

[19] S. Banerjee, D.D. Dionysiou, S.C. Pillai, Self-cleaning applications of TiO_2 by photo-induced hydrophilicity and photocatalysis, Appl. Catal., B, 176–177 (2015) 396–428.

[20] J. Zhang, B. Tian, L. Wang, M. Xing, J. Lei, Photocatalysis: Fundamentals, Materials and Applications, Springer, Singapore, 2018.

[21] M. Anjum, R. Miandad, M. Waqas, F. Gehany, M.A. Barakat, Remediation of wastewater using various nanomaterials, Arabian J. Chem., 12 (2019) 4897–4919.

[22] M. Ni, M.K.H. Leung, D.Y.C. Leung, K. Sumathy, A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production, Renewable Sustainable Energy Rev., 11 (2007) 401–425.

[23] A. Turki, C. Guillard, F. Dappozze, Z. Ksibi, G. Berhault, H. Kochkar, Phenol photocatalytic degradation over anisotropic TiO_2 nanomaterials: kinetic study, adsorption isotherms and formal mechanisms, Appl. Catal., B, 163 (2015) 404–414.

[24] O.A. Ibhadon, P. Fitzpatrick, Heterogeneous photocatalysis: recent advances and applications, Catalysts, 3 (2013) 189–218.

[25] S. Linic, P. Christopher, D.B. Ingram, Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy, Nat. Mater., 10 (2011) 911–921.

[26] M. Bodzek, K. Konieczy, A. Kwiecińska-Mydlak, Nano-photocatalysis in water and wastewater treatment, Desal. Water Treat., 243 (2021) 51–74.

[27] C. Tian, Q. Zhang, A. Wu, M. Jiang, Z. Liang, B. Jiang, H. Fu, Cost-effective largescale synthesis of ZnO photocatalyst with excellent performance for dye photodegradation, Chem. Commun., 48 (2012) 2858–2860.

[28] A.S. Adeleye, J.R. Conway, K. Garner, Y. Huang, Y. Su, A.A. Keller, Engineered nanomaterials for water treatment and remediation: costs, benefits, and applicability, Chem. Eng. J., 286 (2016) 640–662.

[29] S.T. Lin, M. Thirumavalavan, T.Y. Jiang, J.F. Lee, Synthesis of ZnO/Zn nano photocatalyst using modified polysaccharides for photodegradation of dyes, Carbohydr. Polym., 105 (2014) 1–9.

[30] S. Ahmed, M. Rasul, R. Brown, M. Hashib, Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review, J. Environ. Manage., 92 (2011) 311–330.

[31] R. Fagan, D.E. McCormack, D.D. Dionysiou, S.C. Pillai, A review of solar and visible light active TiO_2 photocatalysis for treating bacteria, cyanotoxins and contaminants of emerging concern, Mater. Sci. Semicond. Process, 42 (2016) 2–14.

[32] M. Bodzek, Membrane separation techniques – removal of inorganic and organic admixtures and impurities from water environment – review, Arch. Environ. Prot., 45 (2019) 4–19.

[33] M. Gmurek, M. Olak-Kucharczyk, S. Ledakowicz, Photochemical decomposition of endocrine disrupting compounds–a review, Chem. Eng. J., 310 (2017) 437–456.

[34] A. Cesaro, V. Belgiorno, Removal of endocrine disruptors from urban wastewater by advanced oxidation processes (AOPs): a review, Open Biotechnol. J., 10 (2016) 151–172.

[35] K. Sornalingam, A. McDonagh, J.L. Zhou, Photodegradation of estrogenic endocrine disrupting steroidal hormones in

aqueous systems: progress and future challenges, Sci. Total Environ., 550 (2016) 209–224.
[36] Z. Mirzaei, F. Chen, Haghighat, L. Yerushalmi, Removal of pharmaceuticals and endocrine disrupting compounds from water by zinc oxide-based photocatalytic degradation: a review, Sustainable Cities Soc., 27 (2016) 407–418.
[37] M. Muneer, M. Qamar, M. Saquib, D.W. Bahnemann, Heterogeneous photocatalysed reaction of three selected pesticide derivatives propham, propachlor and tebuthiuron in aqueous suspensions of titanium dioxide, Chemosphere, 61 (2005) 457–468.
[38] M.A. Rahman, M. Muneer, Photocatalysed degradation of two selected pesticide derivatives, dichlorvos and phosphamidon, in aqueous suspensions of titanium dioxide, Desalination, 181 (2005) 61–172.
[39] I. Oller, W. Gernjak, M.I. Maldonado, L.A. Pérez-Estrada, S. Malato, Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale, J. Hazard. Mater., 138 (2006) 507–517.
[40] S.J. Jafari, G. Moussavi, H. Hossaini, Degradation and mineralization of diazinon pesticide in UVC and UVC/TiO_2 process, Desal. Water Treat., 57 (2016) 3782–3790.
[41] L. Zheng, F. Pi, Y. Wang, H. Xu, Y. Zhang, X. Sun, Photocatalytic degradation of acephate, omethoate, and methyl parathion by Fe_3O_4@SiO_2@mTiO_2 nanomicrospheres, J. Hazard. Mater., 315 (2016) 11–22.
[42] S.H. Chan, T. Yeong, T. Wu, J.C. Juan, C.Y. Teh, Recent developments of metal oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment of dye wastewater, J. Chem. Technol. Biotechnol., 86 (2011) 1130–1158.
[43] P. Sathishkumar, R. Sweena, J.J. Wu, S. Anandan, Synthesis of CuO-ZnO nano-photocatalyst for visible light assisted degradation of a textile dye in aqueous solution, Chem. Eng. J., 171 (2011) 136–140.
[44] V. Eskizeybek, F. Sari, H. Gulce, A. Gulce, A. Avci, Preparation of the new polyaniline/ZnO nanocomposite and its photocatalytic activity for degradation of methylene blue and malachite green dyes under UV and natural sun lights irradiations, Appl. Catal., B, 119 (2012) 197–206.
[45] A.K. Dutta, S.K. Maji, B. Adhikary, C-Fe_2O_3 nanoparticles: an easily recoverable effective photo-catalyst for the degradation of Rose Bengal and methylene blue dyes in the wastewater treatment plant, Mater. Res. Bull., 49 (2014) 28–34.
[46] Y. Zhang, B. Wu, H. Xu, H. Liu, M. Wang, Y. He, B. Pan, Nanomaterials-enabled water and wastewater treatment, NanoImpact, 3–4 (2016) 22–39.
[47] D.E. Curry, K.A. Andrea, A.J. Carrier, C. Nganou, H. Scheller, D. Yang, B. Youden, Y. Zhang, A. Nicholson, K.D. Cui, S. Oakes, S.L. MacQuarrie, M. Lu, X. Zhang, Surface interaction of doxorubicin with anatase determines its photodegradation mechanism: insights into removal of waterborne pharmaceuticals by TiO_2 nanoparticles, Environ. Sci. Nano, 5 (2018) 1027–1035.
[48] R. Liang, A. Hu, W. Li, Y.N. Zhou, Enhanced degradation of persistent pharmaceuticals found in wastewater treatment effluents using TiO_2 nanobelt photocatalysts, J. Nanopart. Res., 15 (2013) 1990, doi: 10.1007/s11051-013-1990-x.
[49] I.A. Appavoo, J. Hu, Y. Huang, S.F.Y. Li, S.L. Ong, Response surface modeling of carbamazepine (CBZ) removal by graphene-P25 nanocomposites/UVA process using central composite design, Water Res., 57 (2014) 270–279.
[50] A.S. Mestre, A.P. Carvalho, Photocatalytic degradation of pharmaceuticals carbamazepine, diclofenac, and sulfamethoxazole by semiconductor and carbon materials: a review, Molecules, 24 (2019) 3702, doi: 10.3390/molecules24203702.
[51] V.M. Mboula, V. Héquet, Y. Andrès, Y. Gru, R. Colin, J. Doña-Rodríguez, L. Pastrana-Martínez, A. Silva, M. Leleu, A. Tindall, Photocatalytic degradation of estradiol under simulated solar light and assessment of estrogenic activity, Appl. Catal., B, 162 (2015) 437–444.
[52] J. Rashid, M.A. Barakat, S.L. Pettit, J.N. Kuhn, $InVO_4$/TiO_2 composite for visible-light photocatalytic degradation of 2-chlorophenol in wastewater, Environ. Technol., 35 (2014) 2153, doi: 10.1080/09593330.2014.895051.
[53] K.K. Singh, K.K. Senapati, C. Borgohain, K.C. Sarma, Newly developed Fe_3O_4–Cr_2O_3 magnetic nanocomposite for photocatalytic decomposition of 4-chlorophenol in water, J. Environ. Sci., 52 (2017) 333–340.
[54] R.A. Doong, C.Y. Liao, Enhanced photocatalytic activity of Cu-deposited N-TiO_2/titanate nanotubes under UV and visible light irradiations, Sep. Purif. Technol., 179 (2017) 403–411.
[55] M. Bodzek, Nanoparticles for water disinfection by photocatalysis: a review, Arch. Environ. Prot., 48 (2022) 3–17.
[56] M. Bodzek, K. Konieczny, M. Rajca, Membranes in water and wastewater disinfection – review, Arch. Environ. Prot., 45 (2019) 3–18.
[57] S. Pigeot-Rémy, F. Simonet, E. Errazuriz-Cerda, J. Lazzaroni, D. Atlan, C. Guillard, Photocatalysis and disinfection of water: identification of potential bacterial targets, Appl. Catal., B, 104 (2011) 390–398.
[58] W. Wang, L. Zhang, T. An, G. Li, H.Y. Yip, H.Y. Wong, Comparative study of visible-light-driven photocatalytic mechanisms of dye decolorization and bacterial disinfection by B–Ni-codoped TiO_2 microspheres: the role of different reactive species, Appl. Catal., B, 108 (2011) 108–116.
[59] I. Matai, A. Sachdev, P. Dubey, S.U. Kumar, B. Bhushan, P. Gopinath, Antibacterial activity and mechanism of Ag–ZnO nanocomposite on *Staphylococcus aureus* and GFP-expressing antibiotic resistant *Escherichia coli*, Colloids Surf., B, 115 (2014) 359–367.
[60] S. Das, A.J. Misra, A.P.H. Rahman, B. Das, R. Jayabalan, A.J. Tamhankar, A. Mishra, C.S. Lundborg, S.K. Tripathy, Ag@SnO_2@ZnO core-shell nanocomposites assisted solar-photocatalysis downregulates multidrug resistance in *Bacillus* sp.: a catalytic approach to impede antibiotic resistance, Appl. Catal., B, 259 (2019) 118065, doi: 10.1016/j.apcatb.2019.118065.
[61] N.S. Leyland, J. Podporska-Carroll, J. Browne, S.J. Hinder, B. Quilty, S.C. Pillai, Highly efficient F, Cu doped TiO_2 anti-bacterial visible light active photocatalytic coatings to combat hospital-acquired infections, Sci. Rep., 6 (2016) 24770, doi: 10.1038/srep24770.
[62] K. Davididou, E. Hale, N. Lane, E. Chatzisymeon, A. Pichavant, J.F. Hochepied, Photocatalytic treatment of saccharin and bisphenol-A in the presence of TiO_2 nanocomposites tuned by Sn(IV), Catal. Today, 287 (2017) 3–9.
[63] A.-P. Magiorakos, A. Srinivasan, R.B. Carey, Y. Carmeli, M.E. Falagas, C.G. Giske, S. Harbarth, J.F. Hindler, G. Kahlmeter, B. Olsson-Liljequist, D.L. Paterson, Multidrug-resistant, extensively drug-resistant and pandrug-resistant bacteria: an international expert proposal for interim standard definitions for acquired resistance, Clin. Microbiol. Infect., 18 (2012) 268–281.
[64] M. Wang, M. Ateia, D. Awfa, C. Yoshimura, Regrowth of bacteria after light-based disinfection — what we know and where we go from here, Chemosphere, 268 (2021) 128850, doi: 10.1016/j.chemosphere.2020.128850.
[65] J. Bogdan, J. Szczawiński, J. Zarzyńska, J. Pławińska-Czarnak, Mechanizmy inaktywacji bakterii na powierzcniach fotokatalitycznych, (Mechanisms of bacterial inactivation on photocatalytic surfaces), Med. Weter, 70 (2014) 657–662 (in Polish).
[66] D. Friedmann, C. Mendive, D. Bahnemann, TiO_2 for water treatment: parameters affecting the kinetics and mechanisms of photocatalysis, Appl. Catal., B, 99 (2010) 398–406.
[67] A.D. Belapurkar, P. Sherkhane, S.P. Kale, Disinfection of drinking water using photocatalytic technique, Curr. Sci., 91 (2006) 73–76.
[68] V. Etacheri, G. Michlits, M.K. Seery, S.J. Hinder, S.C. Pillai, A highly efficient $TiO_{2-x}C_x$ nano-heterojunction photocatalyst for visible light induced antibacterial applications, ACS Appl. Mater. Interfaces, 5 (2013) 1663–1672.
[69] J. Podporska-Carroll, E. Panaitescu, B. Quilty, L. Wang, L. Menon, S.C. Pillai, Antimicrobial properties of highly efficient photocatalytic TiO_2 nanotubes, Appl. Catal., B, 176 (2015) 70–75.
[70] M. Garvey, E. Panaitescu, L. Menon, C. Byrne, S. Dervin, S.J. Hinder, S.C. Pillai, Titania nanotube photocatalysts for effectively treating waterborne microbial pathogens, J. Catal., 344 (2016) 631–639.

[71] M.K. Seery, R. George, P. Floris, S.C. Pillai, Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis, J. Photochem. Photobiol., A, 189 (2007) 258–263.
[72] M.P. Reddy, A. Venugopal, M. Subrahmanyam, Hydroxyapatite-supported Ag-TiO_2 as *Escherichia coli* disinfection photocatalyst, Water Res., 41 (2007) 379–386.
[73] O. Akhavan, Lasting antibacterial activities of Ag-TiO_2/Ag/a-TiO_2 nanocomposite thin film photocatalysts under solar light irradiation, J. Colloid Interface Sci., 336 (2009) 117–124.
[74] B. Liu, Y. Xue, J. Zhang, B. Han, J. Zhang, X. Suo, L. Mu, H. Shi, Visible-light driven TiO_2/Ag_3PO_4 heterostructures with enhanced antifungal activity against agricultural pathogenic fungi *Fusarium graminearum* and mechanism insight, Environ. Sci. Nano, 4 (2017) 255–264.
[75] S. Rtimi, O. Baghriche, C. Pulgarin, J.C. Lavanchy, J. Kiwi, Growth of TiO_2/Cu films by HiPIMS for accelerated bacterial loss of viability, Surf. Coat. Technol., 232 (2013) 804–813.
[76] S. Rtimi, C. Pulgarin, R. Sanjines, V. Nadtochenko, J.C. Lavanchy, J. Kiwi, Preparation and mechanism of Cu-decorated TiO_2-ZrO_2 films showing accelerated bacterial inactivation, ACS Appl. Mater. Interfaces, 71 (2015) 12832–12839.
[77] L. Fisher, S. Ostovapour, P. Kelly, K. Whitehead, K. Cooke, E. Storgårds, J. Verran, Molybdenum doped titanium dioxide photocatalytic coatings for use as hygienic surfaces: the effect of soiling on antimicrobial activity, Biofouling, 30 (2014) 911–919.
[78] R. Michalski, E. Dworniczek, M. Caplovicova, O. Monfort, P. Lianos, L. Caplovic, G. Plesch, Photocatalytic properties and selective antimicrobial activity of TiO_2(Eu)/CuO nanocomposite, Appl. Surf. Sci., 371 (2016) 538–546.
[79] Y. Wang, Y. Wu, H. Yang, X. Xue, Z. Liu, Doping TiO_2 with boron or/and cerium elements: effects on photocatalytic antimicrobial activity, Vacuum, 131 (2016) 58–64.
[80] M.S. Stan, I.C. Nica, A. Dinischiotu, E. Varzaru, O.G. Iordache, I. Dumitrescu, M. Popa, M.C. Chifiriuc, G.G. Pircalabioru, Y. Lazar, Photocatalytic, antimicrobial and biocompatibility features of cotton knit coated with Fe-N-Doped titanium dioxide nanoparticles, Materials, 9 (2016) 789, doi: 10.3390/ma9090789.
[81] Y. Chen, K. Liu, Fabrication of magnetically recyclable Ce/N co-doped TiO_2/$NiFe_2O_4$/diatomite ternary hybrid: improved photocatalytic efficiency under visible light irradiation, J. Alloys Compd., 697 (2017) 161–173.
[82] T.W. Ng, L. Zhang, J. Liu, G. Huang, W. Wang, P.K. Wong, Visible-light-driven photocatalytic inactivation of *Escherichia coli* by magnetic Fe_2O_3–AgBr, Water Res., 90 (2016) 111–118.
[83] J.A. Rengifo-Herrera, C. Pulgarin, Photocatalytic activity of N, S co-doped and N-doped commercial anatase TiO_2 powders towards phenol oxidation and *Escherichia coli* inactivation under simulated solar light irradiation, Sol. Energy, 84 (2010) 37–43.
[84] E.A.S. Dimapilis, C.S. Hsu, R.M.O. Mendoza, M.C. Lu, Zinc oxide nanoparticles for water disinfection, Sustainable Environ. Res., 28 (2018) 47–56.
[85] L. He, Y. Liu, A. Mustapha, M. Lin, Antifungal activity of zinc oxide nanoparticles against *Botrytis cinerea* and *Penicillium expansum*, Microbiol. Res., 166 (2011) 207–215.
[86] W. He, H.K. Kim, W.G. Wamer, D. Melka, J.H. Callahan, J.J. Yin, Photogenerated charge carriers and reactive oxygen species in ZnO/Au hybrid nanostructures with enhanced photocatalytic and antibacterial activity, J. Am. Chem. Soc., 136 (2013) 750–757.
[87] S. Das, S. Sinha, M. Suar, S.I. Yun, A. Mishra, K. Suraj, K. Tripathy, Solar-photocatalytic disinfection of *Vibrio cholerae* by using Ag@ZnO core–shell structure nanocomposites, J. Photochem. Photobiol., B, 142 (2015) 68–76.
[88] F. Elmi, H. Alinezhad, Z. Moulana, F. Salehian, S.M. Tavakkoli, F. Asgharpour, H. Fallah, M.M. Elmi, The use of antibacterial activity of ZnO nanoparticles in the treatment of municipal wastewater, Water Sci. Technol., 70 (2014) 763–770.
[89] R. Menaka, R. Subiya, Synthesis of zinc oxide nano powder and its characterization using XRD, SEM and antibacterial activity against *Staphylococcus aureus*, Int. J. Sci. Res., 5 (2016) 269–271.
[90] A.M. El Saeed, M.A. El-Fattah, A.M. Azzam, Synthesis of ZnO nanoparticles and studying its influence on the antimicrobial, anticorrosion and mechanical behavior of polyurethane composite for surface coating, Dyes Pigm., 121 (2015) 282–289.
[91] G.R. Navale, M. Thripuranthaka, D.J. Late, S.S. Shinde, Antimicrobial activity of ZnO nanoparticles against pathogenic bacteria and fungi, JSM Nanotechnol. Nanomed., 3 (2015) 1033 (1–9).
[92] M.F. Elkady, H.H. Shokry, E.E. Hafez, A. Fouad, Construction of zinc oxide into different morphological structures to be utilized as antimicrobial agent against multidrug resistant bacteria, Bioinorg. Chem. Appl., 2015 (2015) 536854, doi: 10.1155/2015/536854.
[93] B. Cao, S. Cao, P. Dong, J. Gao, J. Wang, High antibacterial activity of ultrafine TiO_2/graphene sheets nanocomposites under visible light irradiation, Mater. Lett., 93 (2013) 349–352.
[94] P. Fernández-Ibáñez, M.Polo-López, S. Malato, S. Wadhwa, J. Hamilton, P. Dunlop, R. D'sa, E. Magee, K. O'shea, D. Dionysiou, Solar photocatalytic disinfection of water using titanium dioxide graphene composites, Chem. Eng. J., 261 (2015) 36–44.
[95] O. Akhavan, E. Ghaderi, Photocatalytic reduction of graphene oxide nanosheets on TiO_2 thin film for photoinactivation of bacteria in solar light irradiation, J. Phys. Chem., C, 113 (2009) 20214–20220.
[96] J. Liu, L. Liu, H. Bai, Y. Wang, D.D. Sun, Gram-scale production of graphene oxide–TiO_2 nanorod composites: towards high-activity photocatalytic materials, Appl. Catal., B, 106 (2011) 76–82.
[97] X. Zeng, Z. Wang, N. Meng, D.T. McCarthy, A. Deletic, J.H. Pan, X. Zhang, Highly dispersed TiO_2 nanocrystals and carbon dots on reduced graphene oxide: ternary nanocomposites for accelerated photocatalytic water disinfection, Appl. Catal., B, 202 (2017) 33–41.
[98] R. Ahmad, Z. Ahmad, A.U. Khan, N.R. Mastoi, M. Aslam, J. Kim, Photocatalytic systems as an advanced environmental remediation: Recent developments, limitations and new avenues for applications, J. Environ. Chem. Eng., 4 (2016) 4143–4164.
[99] P. Raizada, A. Sudhaik, P. Singh, Photocatalytic water decontamination using graphene and ZnO coupled photocatalysts: a review, Mater. Sci. Energy Technol., 2 (2019) 509–525.
[100] D. Wu, T. An, G. Li, W. Wang, Y. Cai, H.Y. Yip, H. Zhao, P.K. Wong, Mechanistic study of the visible-light-driven photocatalytic inactivation of bacteria by graphene oxide–zinc oxide composite, Appl. Surf. Sci., 358 (2015) 137–145.
[101] S.F. Anis, R. Hashaikeh, N. Hilal, Functional materials in desalination: a review, Desalination, 468 (2019) 114077, doi: 10.1016/j.desal.2019.114077.
[102] S. Kang, M.S. Mauter, M. Elimelech, Microbial cytotoxicity of carbon-based nanomaterials: implications for river water and wastewater effluent, Environ. Sci. Technol., 43 (2009) 2648–2653.
[103] A.S. Brady-Estévez, T.H. Nguyen, L. Gutierrez, M. Elimelech, Impact of solution chemistry on viral removal by a single-walled carbon nanotube filter, Water Res., 44 (2010) 3773–3780.
[104] L.M. Pasquini, S.M. Hashmi, T.J. Sommer, M. Elimelech, J.B. Zimmerman, Impact of surface functionalization on bacterial cytotoxicity of single walled carbon nanotubes, Environ. Sci. Technol., 46 (2012) 6297–6305.
[105] O. Akhavan, M. Abdolahad, Y. Abdi, S. Mohajerzadeh, Synthesis of titania/carbon nanotube heterojunction arrays for photoinactivation of *Escherichia coli* in visible light irradiation, Carbon, 47 (2009) 3280–3287.
[106] V.B. Koli, A.G. Dhodamani, A.V. Raut, N.D. Thorat, S.H. Pawar, S.D. Delekar, Visible light photo-induced antibacterial activity of TiO_2-MWCNTs nanocomposites

with varying the contents of MWCNTs, J. Photochem. Photobiol., A, 328 (2016) 50–58.
[107] V.B. Koli, S.D. Delekar, S.H. Pawar, Photoinactivation of bacteria by using Fe-doped TiO_2-MWCNTs nanocomposites, J. Mater. Sci.: Mater. Med., 27 (2016) 177, doi: 10.1007/s10856-016-5788-0.
[108] K. Ouyang, K. Dai, S.L. Walker, Q. Huang, X. Yin, P. Cai, Efficient photocatalytic is infection of *Escherichia coli* O157:H7 using C70-TiO_2 hybrid under visible light irradiation, Sci. Rep., 6 (2016) 25702, doi: 10.1038/srep25702.
[109] W. Bai, V. Krishna, J. Wang, B. Moudgil, B. Koopman, Enhancement of nano titanium dioxide photocatalysis in transparent coatings by polyhydroxy fullerene, Appl. Catal., B, 125 (2012) 128–135.
[110] R. Hao, G. Wang, H. Tang, L. Sun, C. Xu, D. Han, Template-free preparation of macro/mesoporous g-C_3N_4/TiO_2 heterojunction photocatalysts with enhanced visible light photocatalytic activity, Appl. Catal., B, 187 (2016) 47–58.
[111] P. Murugesan, J.A. Moses, C. Anandharamakrishnan, Photocatalytic disinfection efficiency of 2D structure graphitic carbon nitride-based nanocomposites: a review, J. Mater. Sci., 54 (2019) 12206–12235.
[112] J. Huang, W. Ho, X. Wang, Metal-free disinfection effects induced by graphitic carbon nitride polymers under visible light illumination, Chem. Commun., 50 (2014) 4338–4340.
[113] J.H. Thurston, N.M. Hunter, L.J. Wayment, K.A. Cornell, K.A. Urea-derived graphitic carbon nitride (u-g-C_3N_4) films with highly enhanced antimicrobial and sporicidal activity, J. Colloid Interface Sci., 505 (2017) 910–918.
[114] Z. Teng, N. Yang, H. Lv, S. Wang, M. Hu, C. Wang, D. Wang, G. Wang, Edge-functionalized g-C_3N_4 nanosheets as a highly efficient metal-free photocatalyst for safe drinking water, Chem., 5 (2018) 664–680.
[115] H. Zhao, H. Yu, X. Quan, S. Chen, Y. Zhang, H. Zhao, H. Wang, Fabrication of atomic single layer graphitic-C_3N_4 and its high performance of photocatalytic disinfection under visible light irradiation, Appl. Catal., B, 152–153 (2014) 46–50.
[116] Y. Li, C. Zhang, D. Shuai, S. Naraginti, D. Wang, W. Zhang, Visible-light-driven photocatalytic inactivation of MS2 by metal-free g-C_3N_4: virucidal performance and mechanism, Water Res., 106 (2016) 249–258.
[117] J. Xue, S. Ma, Y. Zhou, Z. Zhang, M. He, Facile photochemical synthesis of Au/Pt/g-C_3N_4 with plasmon-enhanced photocatalytic activity for antibiotic degradation, ACS Appl. Mater. Interfaces, 7 (2015) 9630–9637.
[118] W. Bing, Z. Chen, H. Sun, P. Shi, N. Gao, J. Ren, X. Qu, Visible-light-driven enhanced antibacterial and bio film elimination activity of graphitic carbon nitride by embedded Ag nanoparticles, Nano Res., 8 (2015) 1648–1658.
[119] J. Xu, Q. Gao, X. Bai, Z. Wang, Y. Zhu, Enhanced visible-light induced photocatalytic degradation and disinfection activities of oxidized porous g-C_3N_4 by loading Ag nanoparticles, Catal. Today, 332 (2019) 227–235.
[120] M.J. Munoz-Batista, O. Fontelles-Carceller, M. Ferrer, M. Fernández-García, A. Kubacka, Disinfection capability of Ag/g-C_3N_4 composite photocatalysts under UV and visible light illumination, Appl. Catal., B, 183 (2016) 86–95.
[121] G. Li, X. Nie, J. Chen, Q. Jiangae, T. An, P.K. Wong, H. Zhang, H. Zhao, H. Yamashita, Enhanced visible-light driven photocatalytic inactivation of *Escherichia coli* using g-C_3N_4/TiO_2 hybrid photocatalyst synthesized using a hydrothermal-calcination approach, Water Res., 86 (2015) 17–24.
[122] J. Xu, Y. Li, X. Zhou, Y. Li, Z.D. Gao, Y.Y. Song, P. Schmuki, Graphitic C_3N_4-sensitized TiO_2 nanotube layers: a visible-light activated efficient metal-free antimicrobial platform, Chem. Eur. J., 22 (2016) 3947–3951.
[123] Q. Zhang, X. Quan, H. Wang, S. Chen, Y. Su, Z. Li, Constructing a visible-light-driven photocatalytic membrane by g-C_3N_4 quantum dots and TiO_2 nanotube array for enhanced water treatment, Sci. Rep., 7 (2017) 3128, doi: 10.1038/s41598-017-03347-y.
[124] J. Li, Y. Yin, E. Liu, Y. Maa, J. Wan, J. Fan, X. Hu, *In-situ* growing Bi_2MoO_6 on g-C_3N_4 nanosheets with enhanced photocatalytic hydrogen evolution and disinfection of bacteria under visible light irradiation, J. Hazard. Mater., 321 (2017) 183–192.
[125] D. Xia, W. Wang, R. Yin, Z. Jiang, T. An, G. Li, H. Zhao, P.K. Wong, Enhanced photocatalytic inactivation of *Escherichia coli* by a novel Z-scheme g-C_3N_4/*m*-Bi_2O_4 hybrid photocatalyst under visible light: the role of reactive oxygen species, Appl. Catal., B, 214 (2017) 23–33.
[126] L. Sun, T. Du, C. Hu, J. Chen, J. Lu, Z. Lu, H. Han, Antibacterial activity of graphene oxide/g-C_3N_4 composite through photocatalytic disinfection under visible light, ACS Sustainable Chem. Eng., 5 (2017) 8693–8701.
[127] K. Ouyang, K. Dai, H. Chen, Q. Huang, C. Gao, P. Cai, Metal-free inactivation of *Escherichia coli* O_{157}:H_7 by fullerene/C_3N_4 hybrid under visible light irradiation, Ecotoxicol. Environ. Saf., 136 (2017) 40–45.
[128] X. Tang, O. Rosseler, S. Chen, S. Houzé de l'Aulnoit, M.J. Lussier, J. Zhang, G. Ban-Weiss, H. Gilbert, R. Levinson, H. Destaillats, Self-cleaning and de-pollution efficacies of photocatalytic architectural membranes, Appl. Catal., B, 281 (2021) 119260, doi: 10.1016/j.apcatb.2020.119260.
[129] K. Reilly, B. Fang, F. Taghipour, D.P. Wilkinson, Enhanced photocatalytic hydrogen production in a UV-irradiated fluidized bed reactor, J. Catal., 353 (2017) 63–73.
[130] B. Pieber, M. Shalom, M. Antonietti, P.H. Seeberger, K. Gilmore, Continuous heterogeneous photocatalysis in serial micro-batch reactors, Angew. Chem. Int. Ed., 57 (2018) 9976–9979.
[131] S. Kim, H. Cho, H. Joo, N. Her, J. Han, K. Yi, J.-O. Kim, J. Yoon, Evaluation of performance with small and scale-up rotating and flat reactors; photocatalytic degradation of bisphenol A, 17β-estradiol, and 17α–ethynyl estradiol under solar irradiation, J. Hazard. Mater., 336 (2017) 21–32.
[132] C. Byrne, G. Subramanian, S.C. Pillai, Recent advances in photocatalysis for environmental applications, J. Environ. Chem. Eng., 6 (2018) 3531–3555.