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Nano-photocatalysis in water and wastewater treatment

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ABSTRACT

Industrial development, civilization growth and climate changes make water pollution a global critical issue. The efficient removal of contaminants from aquatic environment urgently requires the use of novel techniques. Among them, photocatalysis is undoubtedly one of the most promising method of mitigation of water pollution issues, especially if it is combined with the use of nano-catalysts and other nanomaterials. Despite intensive research on various photocatalysts (e.g., ZnO, ZnS, graphene based semiconducting composites, MoS_2, WO_3 and Fe_2O_3) it is titanium dioxide (TiO_2), which remains the most commonly used photocatalyst due to its low price, non-toxicity and high oxidation potential. Moreover, TiO_2 based photocatalysts can be easily activated on various surfaces, what enhances their industrial scale application. The presented paper is focused on the review of the latest achievements in the field of photocatalysis, especially regarding the application of nano-catalysts in water and wastewater treatment technologies. The use of the process to degradation of such harmful substances like endocrine disruptors (pesticides, pharmaceuticals, phenols, etc.), dyes, pathogenic microorganisms and heavy metals is also discussed.

Keywords: Nanotechnology; Nanomaterials; Photo-catalysis; Water and wastewater treatment

1. Introduction

Industrial development, continuous economic and population growth, climate changes and hazards related with water pollution and water stresses (including access to ground and surface water as well and potable water of good quality) have become global critical environmental and social issues. Hence, the assurance of access to clean and sanitary safe water, especially the one dedicated for drinking purposes, is a huge challenge. In 2001, US, European Union and other 90 countries established and signed so called Stockholm Convention, which forced all the countries to elimination or limitation of production, application and/or release of 12 key permanent organic pollutants (POPs), that is, aldrine, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Moreover, there are also other than organic contaminants of significant hazard, especially biologically active substances and heavy metals [1]. The increasing resistance of particular group of contaminants to commonly used chemical and biological treatment methods has gained the attention of international researches and specialists to develop and implement novel methods of treatment.

The development and application of nanomaterials has recently gained the global interest. Nanotechnology and nanomaterials reveal a great potential in water treatment due to their high efficiency and, thus, their use leads to widen the access to water sources of different origin. Except for

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adsorption and membrane filtration, photocatalytic degradation is an important and efficient strategy of removal of contaminants from water, especially if organic substances are the targeted ones [1–4]. In this context, the method is useable and "green" treatment technic, as due to the oxidation mechanism involved in it, it is able to mineralized a wide range of organic contaminants, even those containing heteroatoms, leasing finally to formation of inorganic products, that is, carbon dioxide CO_2, water H_2O, nitrates NO_3^-, sulphates SO_4^{2-}, phosphates PO_4^{3-}, etc. [2].

Photocatalysis has already been widely investigated for about 30 y, since the discovery of Fugishima and Honda, who in 1972 discovered the photocatalytic decomposition of water on TiO_2 electrodes [5]. Photocatalysts are used to conversion of energy in solar cells, hydrogen and hydrocarbons production and in degradation of contaminants present in water, wastewater and in air. Photocatalysis is also applied in health care, including sterilization as well as in cancerogenic therapies. Nevertheless, a number of researches on the development of novel, useable materials as well as on the improvement and modification of already available photocatalysts are carried out. Among them, nanosize particles (1–100 nm) are especially desired ones, as they reveal excellent photocatalytic potential due to unique physico-chemical properties [5]. Catalytic and photocatalytic oxidation belong to advanced oxidation processes group and they are used to removal of trace contaminants and hazardous biological pathogens from water. They are also used in the increase of biodegradation rate of organic and hardly biodegradable compounds, but they can also be applied as a polishing step to final elimination of organic substances, which remain after chemical and/or biological treatment [3,4].

Nanocatalysts characterize with the high surface to volume rate and reveal much higher catalytic affinity than their conventional analogues. Additionally, the energy of bandgap, crystalline structure and redox potential of semiconductors of nanosize are actually size dependent [6]. Moreover, nanocatalysts can be immobilized on variety of surface materials, what enhances their stability, while the finally obtained constructions are compatible with already operated photocatalyzers [7].

In the presented paper the latest achievements related with the modification on nanocatalysts and their use in photocatalytic removal of contaminants from water and wastewater as well as in disinfection are discussed.

2. Photocatalysis process fundamentals

Photocatalysis process is defined as the "change of the rate of chemical reaction or its initiation at the influence of UV or visible light radiation at the presence of a photocatalyst, which absorbs the light and is involved in a chemical transformation" [2,3,8]. During the photocatalysis process, a solid semi-conductive catalysts, after irradiation with the light of desired wavelength, generates on its surface active oxygen forms, which are able either to reduce or to oxidize chemical compounds adsorbed on a catalyst's surface [8–10]. The fundamentals of heterogeneous photocatalysis, which involves the use of a photocatalyst (e.g., TiO_2), is based on a chain of redox reaction, occurring on a catalyst surface [3,4,8,11], which are related with features of electrons on external orbital of photocatalyst molecules. When energy of photons (hν) delivered on a catalyst surface is equal or higher than the energy of the bandgap of the semiconductor, free electrons are transferred from valence band (VB) to empty conduction band (CB) within several femtoseconds (10^{-15} second). The dependence between energy of the bandgap and wavelength required for excitation of a semi-conductor is described by Eq. (1) [12]:

$$\lambda = 1240/E_g \tag{1}$$

where λ – radiation wavelength (nm), E_g – energy of bandgap (eV).

As a result pairs comprised of an electron (e^-) and an electron hole (h^+) are formed, what may be described by Eq. (2) [4]:

$$\text{Photocatalyst (PhC)} + h\nu \rightarrow \text{PhC}\ (e^- + h^+) \tag{2}$$

The generation of electron (e^-) – electron hole (h^+) pairs takes place within the whole volume of a photocatalyst, which is reached by radiation of desired energy. The reaction with a substrate takes place only if electron and electron hole are present on a PhC surface. If migration of electron hole and electron on a surface is shorter than recombination, the number of ($e^- + h^+$) pairs on a PhC surface increases and thus the process efficiency also increases [12]. Hence, the activity of a photocatalyst is the higher the longer is the lifespan of photo-excited electron holes and electrons. Electrons present in valence band and electron holes present in conduction band on a photocatalyst surface are carriers of captured electrons and thus they prevent recombination to occur directly after photoexcitation [9]. At the absence of so called electron scavenger, photoexcited electron recombines with valence band within several nanoseconds at simultaneous heat dispersion [Eq. (3)]:

Recombination of electron hole:

$$e^-_{CB} + h^+_{VB} \rightarrow e^-_{VB} + \text{heat} \tag{3}$$

Hence, the presence of scavengers (acceptors) of electrons (e.g., oxygen) is crucial for elongation of recombination and favorable performance of photocatalysis. Eq. (4) shows the way in which the presence of oxygen prevents electrons recombination by the formation of superoxide radical ($^\bullet O_2^-$).

Photo-excitation of free radicals:

$$(O_2)_{ads} + e^- \rightarrow {}^\bullet O_2^- \tag{4}$$

$^\bullet O_2^-$ radicals may be further protonated, what leads to formation of hydroperoxyl radical ($^\bullet HO_2$) followed by H_2O_2 formation, what is shown by Eqs. (5) and (6) [8,10]:

$${}^\bullet O_2^- + H^+ \rightarrow {}^\bullet HO_2 \tag{5}$$

$${}^\bullet HO_2 + {}^\bullet HO_2 \rightarrow H_2O_2 + O_2 \tag{6}$$

Moreover, hydroperoxyl radicals are also able to scavenge electrons, thus their presence allows to double recombination duration during photocatalysis process. On the other hand, interaction of electron holes with water particles and hydroxide ions leads to formation of highly reactive hydroxyl radicals [Eqs. (7) and (8)]:

Water oxidation:

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+ \tag{7}$$

Hydroxide ion oxidation:

$$OH^- + h^+ \rightarrow {}^{\bullet}OH \tag{8}$$

These radicals are bonded with hydrated photocatalyst surface and act as basic oxidants in photocatalysis system [Eqs. (9) and (10)] [9,10]:

Photodegradation caused by $^{\bullet}$OH radicals:

$$R - H + {}^{\bullet}OH \rightarrow {}^{\bullet}R' + H_2O \tag{9}$$

The role of electron hole:

$$R + h+ \rightarrow {}^{\bullet}R+ \rightarrow \text{by products/final product of degradation} \tag{10}$$

It has to be noticed, that the presence of water is crucial as it leads to formation of hydroxyl radicals ($^{\bullet}$OH), which enable photodegradation of dissolved organic compounds present in an aqueous phase.

In Fig. 1 the mechanism of formation of electron-electron hole pairs in valence and conduction bands after radiation of semi-conductive (nano)catalyst particles with the desired energy (hν) is shown [9,10]. A substance may be oxidized at the presence of a photocatalyst only if its redox potential is above a valence band of a semi-conductor. Oppositely in case of reduction, which may occur if redox potential of a substrate adsorb on a photocatalyst surface is below a conduction band. It results from the fact that after excitation electron holes participating in oxidation reaction are located in valence band, while electrons responsible for reduction are transferred to conduction band [8,12].

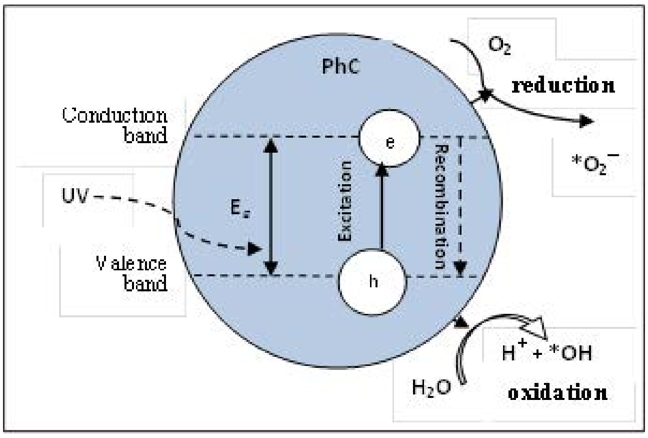

Fig. 1. The mechanism of formation of electron-electron hole pairs during photoexcitation of semi-conductive photocatalyst (E_g – bandgap).

Titanium dioxide (TiO_2) is the most often used, conventional photocatalytic semi-conductor applied in water and wastewater treatment processes due to its low toxicity, chemical and biological stability, low costs and availability [8]. TiO_2 appears in three main polymorphic forms, that is, anatase (tetragonal TiO_2), brookite (orthorhombic TiO_2) and rutile (tetragonal TiO_2) [11–14]. Anatase phase if found to be the most photocatalytically active due to the wide bandgap equal 3.2 eV [12]. Its photo-excitation leading to generation of electron-electron hole pairs followed by formation of $^{\bullet}$OH radicals requires higher energy than the energy of transfer from valence to conduction band (E_g). TiO_2 based photocatalysis, under UV, visible or sunlight radiation, also leads to formation of other highly reactive anionic radicals like $^{\bullet}O_2^-$ and $^{\bullet}O_2^{2-}$, which are able to decompose organic compounds. However, one has to noticed, that TiO_2 characterized with high absorption of UV light, while its absorption of visible light reaches up to several percent only. It corresponds to desired wavelength below 380 nm in case of anatase and below 400 nm in case of rutile.

The recent researches have shown the ability of many other photocatalyst to involve visible or natural light in photocatalytic process [13]. A number of studies on other than TiO_2 photocatalysts has also significantly increased [12]. They are mostly focused on photocatalytic decomposition of water, but also on other applications like water/wastewater treatment or air/gas cleaning [15,16]. In regard to chemical structure, one may distinguish oxide and non-oxide photocatalysts (Fig. 2) [15,16]. The impact of pH on valence and conduction bands of these compounds is one of the main difference between PhC categories.

Among most popular oxide photocatalyst titanate (TiO_3^{2-}), zinc oxide (ZnO), sodium tantalite ($Na(K)TaO_3$), iron (III) oxide (Fe_2O_3), manganese oxide (MnO_x), tungsten oxide (WO_3) can be found, while non-oxide PhC group includes zinc sulphide (ZnS), cadmium sulphide (CdS), silicon carbide (SiC) [10]. Despite the mentioned compounds, derivatives of fullerene (Fullerol and C60 bonded in poly(N-vinylpyrrolidone)), graphene, graphene oxide, carbon nanotubes as well as their composites with TiO_2 may also be regarded as potential photocatalyst for water and wastewater treatment [12].

WO_3 has narrower bandgap than TiO_2, and thus it can be activated by visible light (<450 nm). If combined with Pt doping, it reactivity may be increased by enhancement of multielectron O_2 reduction and e^-/h^+ separation [17].

Next to TiO_2 it is ZnO, which gains the high interest as a potential photocatalyst due to the low cost and similar to TiO_2 photodegradation mechanism [18–24]. ZnO reveals high photocatalytic and antibacterial activity [19,24]. ZnO nanostructures obtained from natural substances characterize with wide bandgap, what limits recombination stage. As in case of TiO_2, the addition of substance like carbon nitride (C_3N_4), silver, chromium, aluminum, tin, cobalt and graphene oxide on the photocatalytic effect of ZnO has been investigated [18–23]. The performed research indicate on the positive effect of admixtures presence in basin ZnO photocatalyst. Wang et al. [20] have found that the introduction of C_3N_4 to ZnO photocatalyst

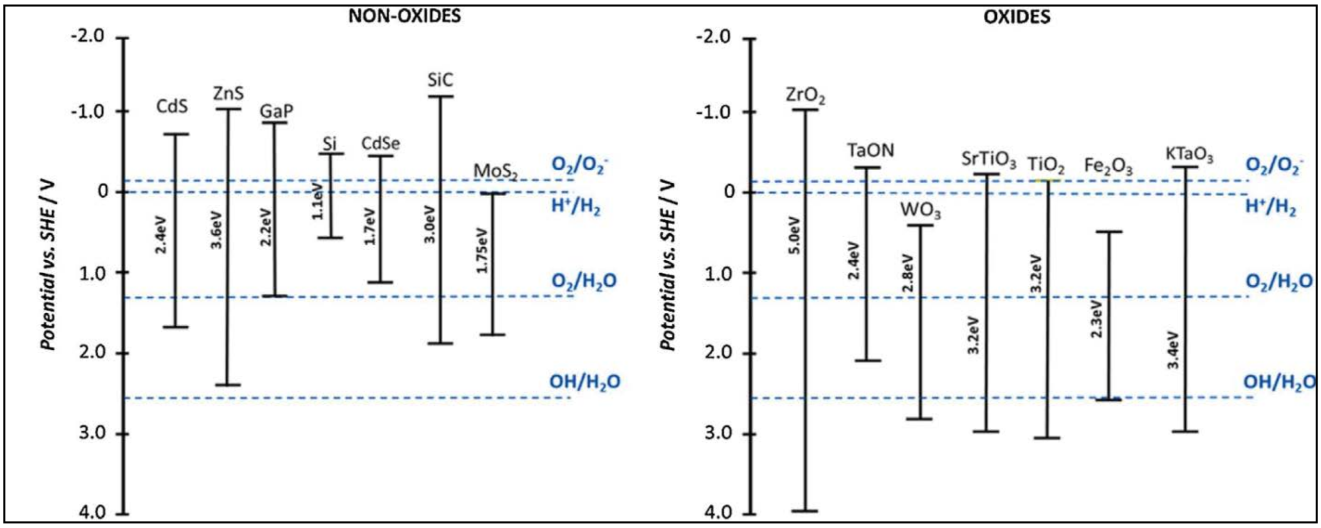

Fig. 2. The energy of bandgap of (a) non-oxide and (b) oxide photocatalysts at pH 7.

quintuples its photoactivity toward UV radiation. In case of the use of composite ZnO_{1-x}/graphene the photocatalytic effect toward UV and visible light may be increased 1.2 and 4.6 times, respectively [18]. Other research suggest, that nanoparticles of ZnO activated with a dye may be used to deactivation of bacteria and degradation of organic compounds under sunlight radiation [25].

CdS nanoparticles also gain a high attention in regard to their use as a photocatalyst applied to degradation of dyes in industrial wastewater due to the wide bandgap of 2.42 eV and activation under wavelength <495 nm [26].

Addition of noble metals also improves PhCs photoactivity as they act as electron scavengers and limit e^-/h^+ recombination simultaneously promoting charge separation [27]. Nanocomposites with different noble metals like Ag/ZnO, Au-CuS-TiO_2, Ag/AgBr/graphene oxide have revealed advantageous features in decomposition of some organic contaminants [28]. Other nanoparticles of MnO_x, ZnO and nanowires of β-MnO_2 may also be used as photocatalysts in advanced oxidation processes [18].

3. Modification of photocatalysts

The wavelength required to activation of most of photocatalyst usually covers the range characteristic to ultraviolet light (300–400 nm), which is delivered by UV lamps or partially by sunlight. It results of high energy of bandgap of many photocatalyst, including TiO_2 (3.2 eV). Sunlight, which reaches Earth comprises in 46% from visible light, in 47% in infrared light and only in 7% from UV light [10]. Photocatalytic systems dedicated to UV light delivered from sunlight require extremely high surfaces and thus generate high operational costs [10]. 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 [26]. 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 [2,6]. Among available modification techniques one may distinguish:

- 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) [3,11,29].

3.1. Nanostructural photocatalysts

The factor extremely influencing on recombination occurring between electron-electron hole is the size of photocatalyst particles. Smaller particles are found to be more active due to the larger active surface. It enables adsorption of larger amount of contaminants and generation of higher number of $^{\bullet}OH$ radicals. These effects are kept for lowering particles size up to ca. 10 nm. The application of nanostructural semi-conductive material to photocatalysis is more advantageous, as the most of photogenerated electron-electron hole pairs is available on a surface of a photocatalyst, while nanoparticles characterize with very high surface to volume ratio. Such nanocatalysts reveal much higher catalytic efficiency that their conventional analogues, as the energy of bandgap and crystalline structure of nano-size semi-conductors depend on the size of particles. Additionally, redox potential of electron holes and distribution of photo-generated charges also depend on the size of a nanoparticle [29]. The small size of the nanoparticles can provide high efficiency of surface trapping of photon-generated electrons and holes, thus increasing the probability of a photocatalytic process on the surface of the catalyst. Moreover, the immobilization of nanoparticles on variety of supports enhances the stability of a photocatalyst, while nano-composites obtained in such a way are compatible with existing photocatalytic reactors [6]. To sum up, the size of photocatalyst particles plays an important role in solid phase transformation, sorption and e^-/h^+ pair formation dynamics.

The difference in energy of band gap (E_g) of semi-conductors comprised of nanoparticles of several nanometers size in regard to materials of larger particles size is quite noticeable. In case of TiO_2 crystalline particles of size 1–10 nm the bandgap is ca. 0.2 eV higher than in case of monocrystals [17]. Below these value, effects related with e-/h+ recombination dominate processes involved in contaminants photodegradation.

Mercury selenide (HgSe) of crystallite size 50 nm characterizes with Eg 0.3 eV, while the same material formed from nano-crystals of size 0.3 nm reveals Eg higher by 2.9 eV [17]. Similar effect has also been observed for other semi-conductors like: PbSe, Ac_3As_2, ZnO, Zn_3P [17]. The widening of effective bandgap of semi-conductors composed of nanoparticles causes that the redox potential of photo-excited electrons and electron holes is higher. Shorter migration distance to the interior of a semi-conductor increase a number of electron-electron hole e-/h+ present on the surface, and thus the photocatalytic effect is better [17].

Zielińska-Jurek et al. [30] have observed that the limitation of microorganisms growth and photocatalytic activity of metal/metal oxide photocatalysts depend on metal particles size. The smaller metal' particles are the better degradation and antibacterial effect is. For example, photocatalytic activity in visible light during degradation of phenol based on the use of catalysts like Pt/TiO_2 and $Ag-Pt/TiO_2$ depends mainly on platinum nanoparticles size. DRS, XRD, TEM and BET measurements indicate that the most active photocatalyst contained Pt NPs of size ca. 3 nm and Ag NPs of size 6 nm doped on TiO_2 surface [30]. The antibacterial effect of silver nanoparticles (AgNPs), investigated in regard to *C. Albicans* yeast, gram-positive *S. Aureus* bacteria and gram-negative *Escherichia coli* bacteria depends on amount and size of AgNPs.

3.2. Hybrid/composite photocatalysts

3.2.1. Photocatalysts doped with nanoparticles

Doping of metals to photocatalytic material may decrease both energy of bandgap 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 [7,29]. Many metals is applied to modification of surface photocatalysts, that is, Au, Ag, Cr, Si, Co, Mg, Mn, Fe, Fe, Al, In and Ga [26,29]. 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. 3 [31,32]. The first mechanism is separation of charges in UV light, when metal nanoparticles acts as electron traps, what leads to reduction of charges recombinations and simplifies transport of photogenerated electrons to acceptor particles [31]. The second mechanism depends on charge transfer, which take place in visible light, when noble metals excited electrons are transferred to CB of a semi-conductor, what leads to improvement of light absorption revealed by composite photocatalysts [32]. The researches have also shown the advantageous effect of TiO_2 doping with lanthanum La^{3+}, yttrium Y^{3+}, cerium Ce^{4+}, palladium Pd^{2+} and neodymium Nd^{3+} in regard to photocatalytic oxidation of organic compounds [26]. La^{3+} and Ce^{4+} ions after their introduction to TiO_2 network, improve the adsorption of hydroxyl ions on TiO_2 surface, and thus improve photocatalytic activity. The research on modification of TiO_2 with Pd^{2+} and Nd^{3+} have shown better activity of composite material in regard to photo-oxidation of 2-chlorophenol than pure TiO_2 [26]. Both of these cations (Pd^{2+} and Nd^{3+}), due to the larger ionic radium than one of TiO_2 are located in junction position. In case of TiO_2 doping with Fe^{3+}, Cr^{3+}, Ca^{2+} and Na^+ ions the worsening of photocatalytic effect has been observed [26]. According to authors the doping with these ions creates additional recombination centres of photogenerated redox pairs.

Doping with non-metals like nitrogen, sulphur or carbon, is also applied in photocatalysts modification [4,25]. Doping with nitrogen anions has been found to be the most advantageous and suitable for industrial applications, but

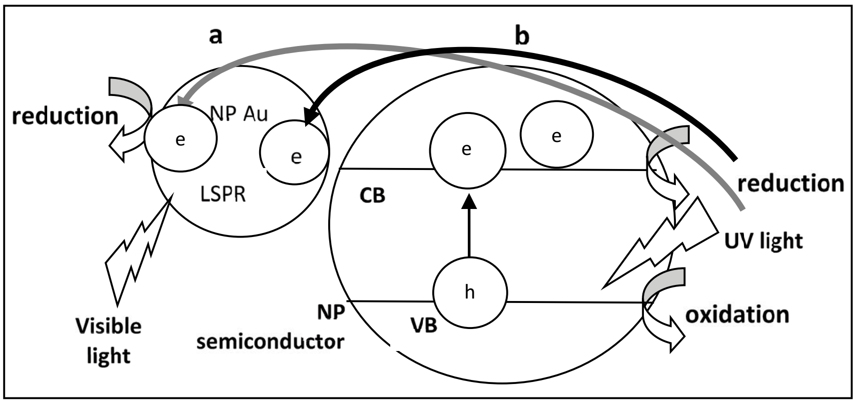

Fig. 3. The enhancement of photocatalytic activity of metal/semi-conductor composites: (a) mechanism of charge separation and (b) mechanism of charge transfer.

fluorine (F), iodine (I), chlorine (Cl), phosphorus (P) and boron (B) are also considered [5]. Doping with non-metals creates additional VB in semi-conductor, which decrease the energy of bandgap and forms localized states above VB, which ease transfer of electrons to other acceptors. Single or multiple doping with some nonmetals like carbon (C) or nitrogen (N) shifts photoactivity toward visible light range, as it is shown in Fig. 4 [33]. In case of N and S dopes, electron structure of $Ti_{1-x}S_xO_{2-x}N_y$ reveals the presence of intermediate energy states during photocatalysis process [28,34]. 2p orbital of nitrogen is used as the orbital of middle slit for electrons in valence band. Hence, electrons require less energy to be excited and to reach the conduction band. As only all electrons leave the valence band, positive electron gaps are formed in VB and the redox reactions may occur [28,34].

3.2.2. Combination of different semi-conductors, application of supports

One of the most important factors responsible for slow kinetics of photocatalysis with TiO_2 is fast recombination of e^-/h^+ pair. It has already been explained in chapter 3.1., that the decrease of TiO_2 particles size decreases recombination rate and increase interfacial transfer of charge carrier. Among available TiO_2 structures, rutile is the most stable in case of particles of size above 35 nm, while anatase is found to be more effective in formation of oxygen reach radicals for particles of size below 11 nm [35]. However, if the size of particles is reduced to several nanometers (ca. 10 nm), the surface recombination of electron holes and electrons is dominant and it decreases photocatalytic activity. Thus, the maximum photocatalytic activity of TiO_2 is obtained, when above discussed mechanism occur simultaneously, while this is only possible for particles appearing in nanosizes. The high photocatalytic efficiency has also been proved for mixed structures of anatase and rutile and anatase and brookite. It happens due to the fact, that excited electrons from higher-energy CB in anatase can be transferred to lower-energy CB of rutile allowing for efficient charge separation [36]. In case of anatase and brookite mixtures, excited electrons from CB in brookite may be transferred to CB of anatase [35]. It is caused by the fact, that CB of brookite if ca.0.2 eV higher than CB of anatase [26]. The electron transfer slows down recombination between electron-electron hole and improves photocatalytic activity in visible light range [36].

Similar phenomenon takes place in nanostructural composite of CdS/TiO_2, which contains CdS semi-conductor of narrow band split, excited by the light of lower energy, which leads to transfer of photogenerated electrons to TiO_2, while electron holes remain in CdS (Fig. 5) [37]. In visible light, conjugated CdS/TiO_2 nano-composite possesses higher efficiency of photodegradation of organic contaminants, also in regard to gaseous benzene [5]. Similar effect has been observed of modified CdS-chitosan photocatalyst, which has been proven to be highly efficient in photodegradation of model organic dyes [38]. Among other nanostructural composite photocatalyst CuO/ZnO suitable for degradation carried out under visible light or ZnO/polyaniline are mentioned [39,40].

Supports applied to immobilization of photocatalyst particles may play crucial role in photocatalytic activity characteristic of the final material. The support material should offer features like (1) stability toward applied radiation range, (2) large specific surface area, (3) strong adhesion of photocatalyst particles, (4) high transparency and (5) efficient adsorption affinity to contaminants [41]. A number of various transparent and non-transparent supports have been investigated, while the most often used materials are polymeric materials, silica gel, activated carbon and glass [42]. Despite intensive research on immobilizing supports features, several aspects including transparency, long-term stability under UV radiation, hydrophobicity, fragility and weight of a surface need further investigations and improvements [43].

3.2.3. Hybrid systems based on carbon materials

In recent years, carbon-based photocatalyst have been introduced as a new group of hybrid photocatalysts [44] of exceptionally large specific surface area (2,630 m^2/g) and effective electrons mobility.

In case of photocatalyst comprise of TiO_2 and graphene it is believed, that photoelectrons from TiO_2 are transferred to graphene, what significantly limits recombination

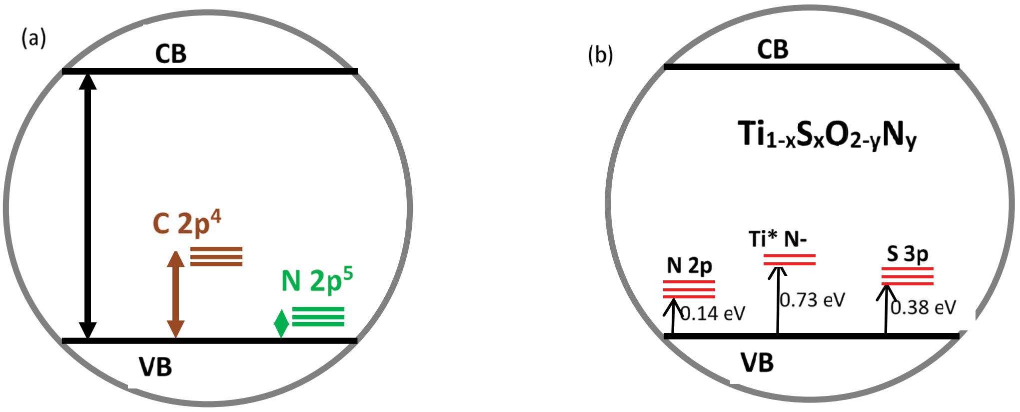

Fig. 4. The schema of nonmetal dopes in semi-conductor particles: (a) C and N doping and (b) N and S doping.

and elongates lifespan of electron-electron hole pairs [45]. The use of visible light to photodegradation has widen already popular application of composite graphene/TiO_2 catalysts due to the possible decrease of bandgap energy. In Fig. 6, the mechanism of exemplary degradation using MB dye with the use of TiO_2/graphene composite photocatalyst is shown [45]. Integration of graphene with nano-TiO_2 may be performed either by mechanical mixing or by chemical binding, while the latter creates a strong interaction between TiO_2 nanoparticles and graphene sheets [46]. Composites composed of graphene and other semi-conductive materials may significantly influence electrons mobility due to interfacial transfer of electrons during photocatalysis process. Moreover, graphene has the ability to promote photo-induced electrons separation and creation of electron holes in photocatalyst structure [47].

Except for graphene, hybrid composite based on activated carbon and TiO_2 have also gained interest, as they reveal simultaneous effect of adsorption and photocatalysis [48]. Such composites minimize limitations related with mass transfer in effective TiO_2 applications [49]. The improvement of efficiency of these composites results from the fact, that generated hydroxyl radicals may easily react with neighborhoodly adsorbed, concentrated contaminants, and additionally the need of separation of nano-TiO_2 from water stream is also eliminated [48,50,51]. Among the most important features of AC/TiO_2 composites there are: (a) simple recovery; (b) lower affinity to deactivation; and (c) increased photodegradation efficiency, what makes these materials more reliable and universal in comparison with materials composed only of TiO_2 [48]. Despite above-mentioned benefits resulting from the use of AC/TiO_2 composites, their application in industrial scale requires to solve several limitations. Among them, one has to mention poor photostability, UV radiation absorption limitation, contamination, low mechanical stability and problematic regeneration. Additionally, it has been found that immobilization of TiO_2 on AC surface significantly limits AC adsorption efficiency [52]. The recent research show, that adsorption obtained for AC/TiO_2 functionalized using diethylenetriamine (AC/TiO_2-DETA) is much higher than in case of AC/TiO_2 composite [53]. However, further research are required in order to improve adsorption and capacity of such hybrid composites.

4. Photocatalytic removal of contaminants from water and wastewater

Photocatalysis is widely applied to water and wastewater treatment to degrade contaminants to non-harmful products. It is mostly performed with the use of semi-conductive nanoparticles of metal oxides, mainly TiO_2 and ZnO

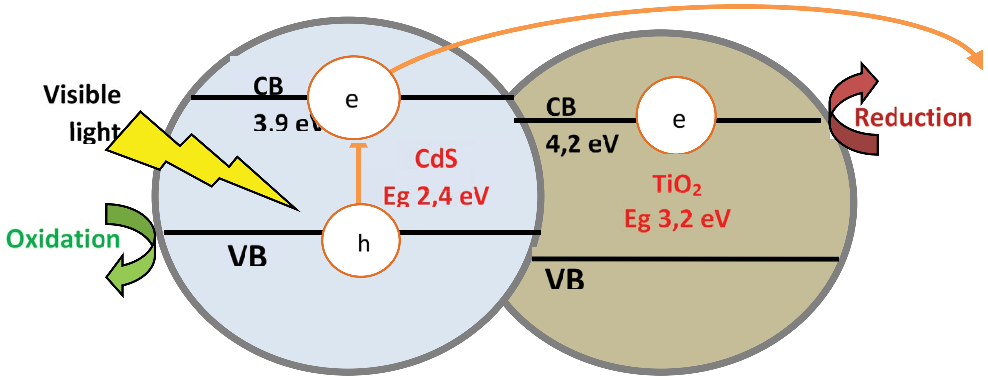

Fig. 5. The mechanism of charge transfer in CdS/TiO_2 composite photocatalyst.

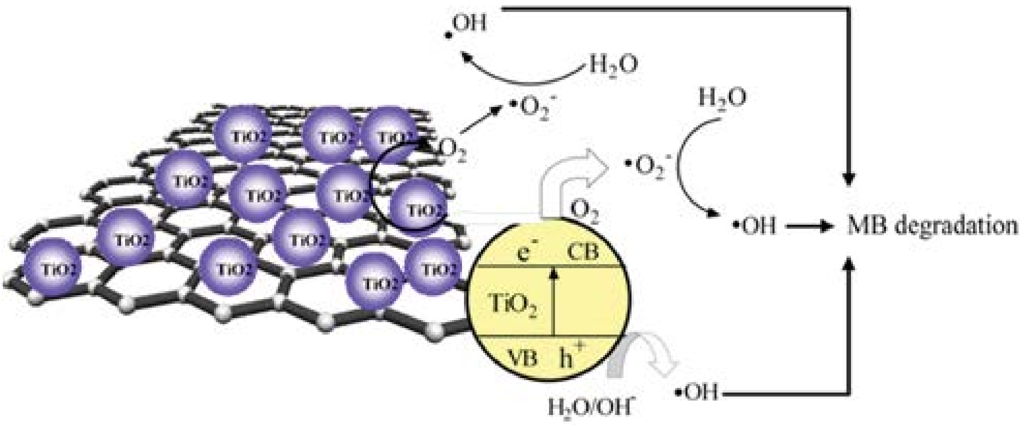

Fig. 6. The mechanism of exemplary degradation (MB dye) with the use of composite TiO_2/graphene photocatalyst.

[3,15,16,19]. Semi-conductive nanomaterials are active in mild reaction environments and very efficient even at low concentrations of contaminants. If reaction conditions favor formation of hydroxyl radicals ($^•OH$), which origin from water, complete degradation of contaminant to simple inorganic compounds (CO_2 and H_2O) is almost always obtained [12]. Photocatalysis is often applied as a preliminary method of removal of harmful compounds and as a process, which allows to improve affinity of refractory compounds to biodegradation. Moreover, the process may be applied as a tertiary/polishing water/wastewater treatment stage in water reclamation [3,4]. Photocatalysts may decompose and/or mineralize wide range of persistent contaminants present in water and wastewater, such as dyes, detergent, pesticides, chlorinated and halogenated derivatives, polymers, phenols, endocrine disruptive compounds, cyanotoxins, pharmaceuticals and other organic compounds as well as they may improve the removal of heavy metals and other contaminants [3,15,16,19,54–57]. Lately, photocatalysis has started to be regarded as efficient "green" method of disinfection. It has been observed that photocatalytic process is able to deactivate a wide range of microorganisms present in aquatic streams [10,16].

4.1. Removal of organic compounds

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 [58]. Photocatalysis performed with the use of such nanomaterials like metal oxides, that is, TiO_2, ZnO, WO_3, ZnS, SnO_2, Fe_2O_3, and Bi_2WO_6, is efficient in EDCs degradation [59–62]. In regard to final effectiveness, chemical and radiation stability, low cost, market availability and biocompatibility makes TiO_2 to be the most preferable and intensively investigated photocatalyst used to EDCs elimination [61].

Photocatalysis with the use of TiO_2 can be applied to degradation of organic and inorganic pesticides. Among representatives of these group of contaminants endosulfan (Rn), quinalphos (Qn), imidocloprid (Im) and chlorpyrifos (Ch) have been efficiently degraded in photocatalytic reactors operated with the use of nano-TiO_2 [63]. Rahman et al. [64] have investigated the kinetics of degradation of dichlorvos and phosphamidon (both pesticides) using Degussa 25 TiO_2 and they have found that addition of H_2O_2 improved the rate of contaminants removal. Solar photocatalysis has also been positively applied to degradation of aldrin and three byproducts of its transformation, that is, dieldrin, chlordane and 1,2-hydroxy-dieldrin [65]. Hybrid systems composed of TiO_2/zeolite matrices have also been used to efficient photodegradation and mineralization of dichlorvos due to lower energy of band split and larger surface of zeolite matrix of sufficient adsorption capacity. The composite catalysts can be also reused in dichlorvos degradation [66], while the compound may also be efficiently decomposed using zinc oxide ZnO [67].

Pesticides of carbamate type, soluble in water, such as cymoxanil, dimethoate, methomyl, oxamyl, pyrimethanil and 1,3-dichloropropene have completely been mineralized during heterogeneous photocatalysis with the use of solar UV radiation and TiO_2 nanoparticles in pilot scale process [68]. Pesticides are well adsorbed on TiO_2 surface and under radiation they are efficiently mineralized to CO_2, SO_4^{2-}, NH_4^+ and NO_3^-. Other pesticides like tiabendazole, enilconazole, acetamiprid, chlorpyrifos, lambda-cyhalothrine and diazinon have also been effectively removed in reactor with immobilized photocatalyst containing TiO_2 and under sunlight radiation [69]. The process has been compared with photo-Fenton (PhF) method and the rate of removal of COD (chemical oxygen demand) has been 90.7% for PhF and 79.6% for TiO_2 based photocatalysis [70]. The dedicated parabolic concentrators have been adapted to sunlight based photocatalytic degradation of carbaryl with the use of TiO_2. The performance of the process has been improved by addition of environmentally acceptable hydrogen peroxide [71].

TiO_2 materials doped with nitrogen, active under visible light radiation and immobilized on zinc sulphide phosphorescence (ZSP) has been applied to degradation of atrazine, which is a very persistent contaminants. By changing the amounts of N-TiO_2 on ZSP, the composite morphology has stepwise evolved to from pseudo-spherical shape, up to 30 wt.% of N-TiO_2, to elongated shape noted for final N-TiO_2 content equal 50 wt.%. It has been observed that capacity of ZSP immobilized catalyst is better than one revealed by N-TiO_2 or pure ZSP. The composite N-TiO_2/ZSP photocatalyst with 30 wt.% content of N-TiO_2 has characterized with the highest photocatalytic activity [72]. The pathways of photocatalytic degradation of atrazine are shown in Fig. 7.

pH of the solution and concentration of catalyst play an important role in final efficiency of the degradation process [72]. The analysis of byproduct indicates that dealkylation and oxidation of alkyl chain are crucial reactions occurring in the developed photocatalytic system. Cyanuric acid, resistant to $^•OH$ radicals action, is a common byproduct formed during atrazine photocatalysis. However, the use of TiO_2/ZSP photocatalyst does not lead to the appearance of the compound in the treated stream. These findings indicate on a unique mechanism of degradation of this novel photocatalytic system.

Novel magnetic photocatalytic system composed of $Fe_3O_4/SiO_2/TiO_2$ has been applied to degradation and mineralization of such pesticides as acephate, omethoate and methyl parathion [73]. Among investigated compounds acephate requires the longest action time (80 min) in regard to other compounds (50 min). Photocatalytic mechanism of degradation depends on pesticides structure. In case

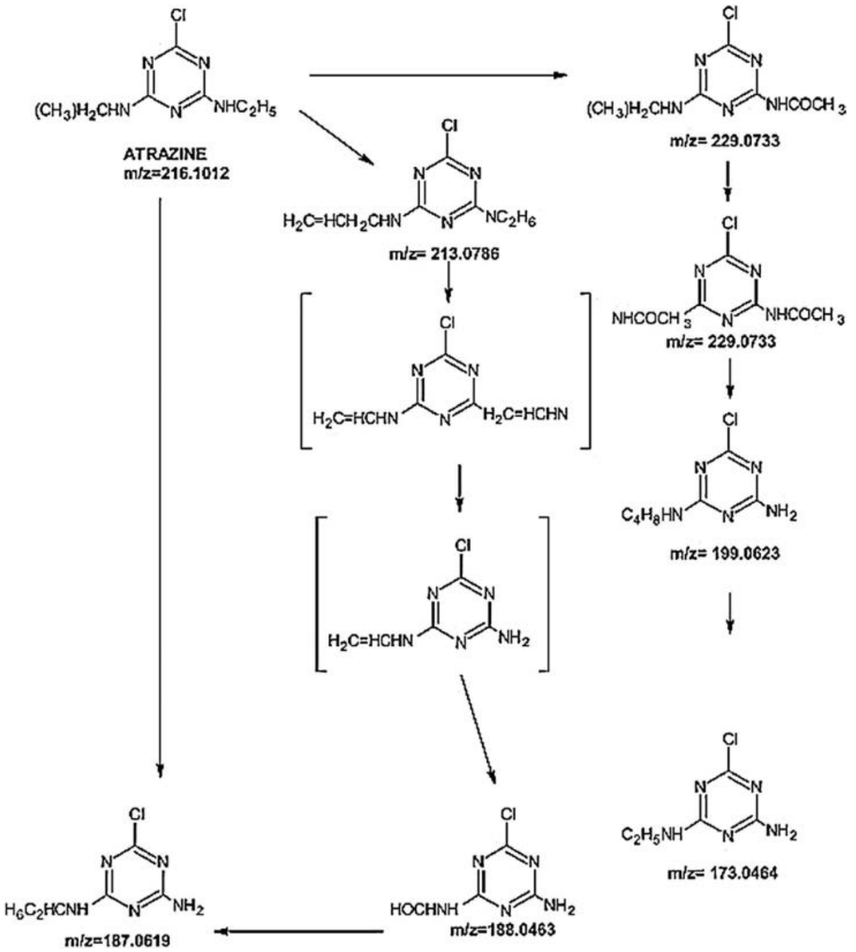

Fig. 7. Photocatalytic degradation of atrazine with the use of TiO_2 supported on zinc sulphide phosphorescence (ZSP) under UVA radiation [49].

of acephate, the first step is the oxidation of acetyl group, while in case of omethoate these are the destruction of P-S bond followed by destruction of S-C bond. On the other hand, three different pathways of methyl parathion are proposed, including preliminary destruction of nitrophenyl bond, P-S bond and P-O bond, which is related to aromatic ring [73]. As a result all byproducts of decomposition of these pesticides can be efficiently degraded to low-molecular compound and finally mineralized to inorganic compounds, what leads to complete elimination of organic carbon.

The presence of phthalates in environment mainly results from massive production of plastics, especially PCV, where there are used as plasticizers, and with the common use of plastics. Due to their harmful effects observed in living organisms, their concentration in different environmental species, especially in drinking water sources, should be monitored [58]. Hung et al. [74], by using hydrothermal and sol-gel method, have obtained immobilized photocatalysts modified with surfactants, that is, polyaniline-carbon nanotubes/TiO_2 (PANi-CNT/TiO_2) and they have used them to investigate the degradation of diethyl phthalate (DEP) under visible light of wavelength 410 nm. In order to improve nanoparticles dispersion and electrons transfer, TiO_2 surface has additionally been modified with sodium dodecylsulphate (SDS) as well as functionalized carbon nanotubes (CNT-COOH and CNT-COCl). Together with the addition of PANi, in the range from 1 to 5%, the adsorption of light revealed by such prepared photocatalysts increases. SDS binds PANi polymers, what enables to obtain thin film layers in the rage of 314–400 nm and 1301–1600 nm for photocatalysts obtained by sol-gel hydrolysis and synthesized hydrothermally, respectively. The sufficient thickness of the layer elongates the distance required for electron transfer and thus limits recombination of electron and electron gaps. The efficiency of DEP photodegradation observed for hydrothermally synthesized photocatalysts is better than degradation obtained for PhC produced by sol-gel hydrolysis. The research results have shown, that hydroxyl radicals are crucial oxidant in DEP degradation mechanism using hydrothermally synthesized PANi-CNT/TiO_2 photocatalysts.

Phenolic xenoestrogens (octylphenol, nonylphenol, bisphenol A and bisphenol F) are very problematic organic micropollutants due to their omnipresence and estrogenic activity [75]. Photocatalysis has already been proven to enable elimination of phenols from water and wastewater. Pino et al. [76] have investigated simultaneous degradation of two phenolic compounds, that is, 4-chlorophenol and

2,6-dichlorophenol. It has been found that the efficiency of the process is affected not only by a number of active sites on the photocatalyst surface but also by other factors like initial pH of a treated solution, contaminant concentration, radiation intensity, surface properties, phenolic particles structure and effect of adsorption of byproducts formed during the process. Rashid et al. [77] have examined the use of $InVO_4/TiO_2$ composite to degradation of 2-chlorophenol (2-CP) under visible light radiation carried out using synthetic wastewater. The degradation of 2-CP is influenced by solution pH, radiation intensity, photocatalyst dose and initial 2-CP concentration. $InVO_4/TiO_2$ composite reveals better 2-CP degradation effect than Degussa P-25 TiO_2 and the complete degradation can be obtained at optimized conditions defined as: 1 g/L of photocatalyst at contaminants concentration 50 mg/L, solution pH = 5 and radiation time 180 min, while the efficiency revealed by TiO_2 reaches 50.5%. Magnetic nanocomposite Fe_3O_4-Cr_2O_3 (MNC) has been found to be sufficient in photocatalytic degradation of 4-chlorophenol under UV radiation. Moreover, it can be magnetically separated, what improves its recycling [78].

The mechanisms and kinetics of photocatalytic degradation of 4-chlorophenol (4-CP and 2,4-dichlorophenol (2,4-DCP) with the use of TiO_2 under visible light radiation [79] have been investigated. The separated degradation of these phenolic compound have shown, that the rate of reaction may be described by pseudo-first-order reaction model. During photocatalytic degradation of both 4-Cp and 2,4-DCP at the same conditions (0.5 g/L TiO_2, irradiation 1000 m W/cm^2) different byproduct are detected, 3 derived from 4-CP (hydroquinone (HQ), phenol (Ph) and 4-clorocatechol (4-cCat)) and 2 related with 2,4-DCO (4-CP and Ph). The photocatalytic degradation of 4-CP and 2,4-DCP mixture has also been investigated at the same conditions, but at different initial concentrations of 2,4-DCP. The obtained results show that the rate of degradation of 4-CP decreases with the initial 2,4-DCP concentration increase and the detected decomposition byproducts are similar to ones, which are obtained during separate degradation of 4-CP and 2,4-DCP, but high concentration of Ph may be noted. In Fig. 8 exemplary pathways of chlorophenol photodegradation are presented. It can be noticed, that occurring processes may be quite complex [12].

Doong et al. [80] have developed the nanocomposite comprised of N-TiO_2 (anatase) nanotubes/titanate doped with Cu to bisphenol A (BPA) degradation under UV and visible light radiation. The research have indicated on the improved photocatalytic BPA degradation in comparison to commercial anatase P25 under both types of radiation applied. The results of roentgen analyses have revealed that Cu appears mainly as CuO, while N atoms in TiO_2 composite are bonded as O-Ti-N and Ti-O-N. The rate of BPA degradation is correlated with the mass load of Cu [80]. BPA degradation rate has also been investigated using conjugated anatase-rutile photocatalyst obtained via thermohydrolysis process at the presence of small amount (<1%) of Sn(IV), which acts as a promotor of rutile phase [81]. Additionally, the impact of conditions like initial BPA concentration, catalyst type, dose and reuse on the process efficiency has been checked. The obtained results have shown the high treatment effect of the use catalysts, even after 3rd reuse cycles.

4-Nitrophenol commonly appears in municipal and industrial wastewater and causes endocrine disruptions. The fact and very efficient photoreduction of p-Nitrophenol to chemically valuable p-aminophenol may be obtained at room temperature using TiO_2 with addition of silver at the presence of Na_2SO_3 as "mild" reducing agent [82]. Ag NPs deposited on TiO_2 P25 are able to increase the efficiency of photocatalytic process by 7 to 12 times and they act as both electrons scavengers and electron carriers, what in overall significantly improves the photocatalytic process. Kalarivalappil et al. [83] have investigated similar photocatalyst composition approach, but with the use of palladium (Pd) added to TiO_2 nanotubes, which has further been applied to photoreduction of 4-nitrophenol to 4-aminophenol. The photocatalyst with Pd content of 1.0mol% has shown the highest activity, while the catalysts with higher Pd content are not as efficient. It has also been observed that both morphology of nanotubes and higher anatase content play important

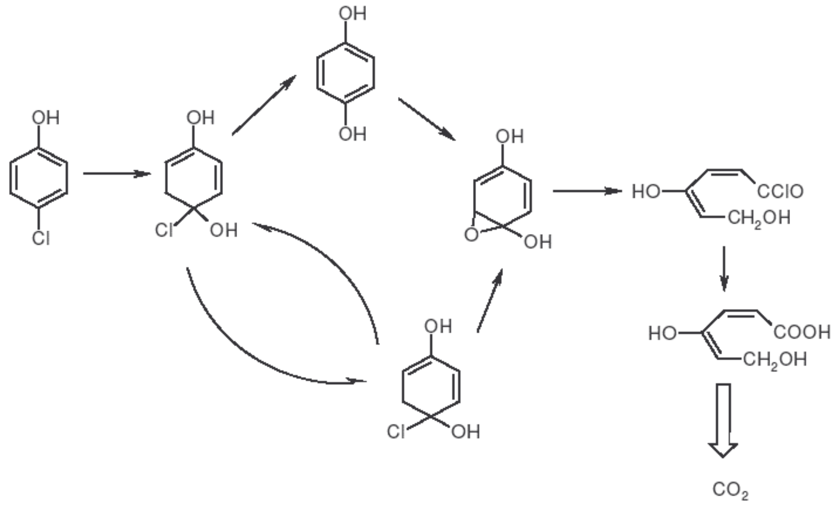

Fig. 8. The schematic presentation of reactions occurring during photocatalytic oxidation of 4-chlorophenol in the presence of TiO_2.

role in photocatalytic activity. Lee et al. [84] have investigated the nanocomposite comprised of graphene-palladium/TiO_2 (G-Pd@TiO_2-CNWs) to conversion of 4-nitrophenol under visible light radiation and they have observed 100% efficiency of the process. The content of graphene in TiO_2-graphene nanocomposites determines photocatalytic degradation of MB in water and benzene in air. Guo et al. [85] have applied hybrid material composed of graphene oxide-Fe_2O_3 (GO-Fe_2O_3) as heterogeneous catalyst used in photodegradation of rhodamine B and 4-nitrophenol under visible light radiation (>420 nm) and at the presence of H_2O_2.

Organic dyes are synthetic aromatic compounds of potential cancerogenic and mutagenic effects. They are common contaminants emitted by textile, plastic and paper industries. The main method dedicated to their removal from water is adsorption, however nanomaterials of high surface to volume ratio may also be applied to eliminate organic dyes from water [1]. Semi-conductive photocatalysts made of metals oxides like TiO_2, ZnO, etc. reveal high efficiency in degradation of many popular dyes present in water and wastewater [86–88]. For example, hybrid reactor containing nano-TiO_2 immobilized on regular glass balls and boron-modified glass balls has been used to degrade Congo red (CR) and methylene blue (MB) with the efficiency up to 98% [89]. Tian et al. [19] have shown that the rate of degradation of methyl orange (MO) with the use of ZnO is 4 times faster than one revealed by TiO_2 Degussa 25. ZnO nanowires have also been used to degradation of model dyes, that is, MB and MO, as representative chemical contaminants [87,90]. The comparison of photocatalytic activity of ZnO nanoparticles and nanowires of different sizes is shown in Fig. 9a [87]. Due to the larger surface of nanowires one may notice better degradation than it is observed in case of nanoparticles. In Fig. 9b, on the other hand, the efficiency of degradation of methylene blue and phenol with the use of ZnO/poly(methylene methacrylate) (PMMA) [91] is presented. The significant improvement of photocatalytic properties obtained due to combination of ZnO and PMMA may be observed.

Sathishkumar et al. [39] have synthesized nanocomposite photocatalyst comprised of CuO/ZnO, which enhances degradation of Acid Red 88 dye in wastewater under visible light radiation. The twice better efficiency of photocatalytic degradation is observed for CuO/ZnO than for non-modified ZnO. Eskizeybek et al. [40] have obtained modified polyaniline/ZnO nanocomposite, which enables 99% removal of methylene blues and malachite from wastewater, even at low catalysts dose equal 0.4g/L. Dutta et al. [92] have synthesized γ-Fe_2O_3 nanoparticles using thermal decomposition method, which reveal high photocatalytic activity during Bengal rose and methylene blue degradation under visible light radiation.

In Table 1 data on the possible use of photocatalysis with the use of various photocatalyst to different dyes degradation is collected [93].

One of the most important group of anthropogenic substances adversely affecting the environment are pharmaceutical compounds and personal care products (PPCPs). There are a number review papers discussing appearance, sources, migration pathways and methods of removal of PPCPs from water and wastewater. PPCPs containing various functional groups are more and more often in surface and ground waters, and their presence is also noted in drinking water. The most of PPCPs (similarly as EDCs) are polar, slightly or non-volatile, resistant to biodegradation and harmful to environment due to their negative effects on flora and fauna species [94,95]. Even in water dedicated to potable purpose, which is properly treated, 15 up to 25 pharmaceuticals are detected all over the world [96,97]. Photocatalysis seem to be proper

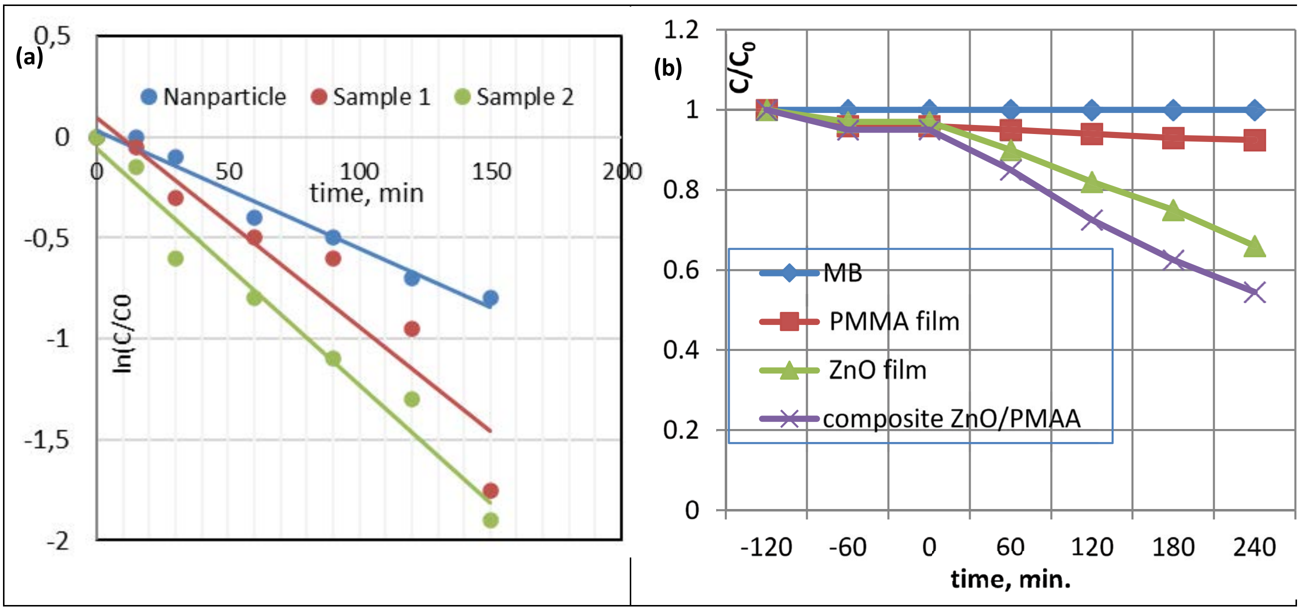

Fig. 9. Photocatalytic degradation of (a) methylene blue with the use of ZnO nanoparticles and nanowires immobilized on glass surface under radiation generated by halogen lamp made of tungsten and (b) methylene blue with the use of ZnO/PMMA nanocomposite as a function if irradiation time.

Table 1
Exemplary literature data on photocatalytic degradation of dyes

Photocatalyst	Dye/contaminant	Comment
Nanocrystalline anatase and rutile TiO_2	Acetophenone Nitrobenzene Methylene blue Malachite green	Anatase activity is better than rutile one, but no explanation of this fact is given.
Nano-TiO_2	Methylene blue Methyl orange Condo red	TiO_2 size and phase are important. Adsorption of dye on photocatalyst surface is crucial (Freundlich isotherm).
Nanostructured TiO_2	Mono-, di- and tri-azo dyes class	Degradation depends on chemical structure of a dye and the presence of nitrate group enhances degradation activity. Monoazo-dyes are decomposed fasted than anthraquinone dyes.
Nanosize TiO_2	Acid Orange 10 (AO10) Acid Red 14 (ARI14)	Factors influencing on degradation are azo and sulfonate group.
Nano-TiO_2 (anatase)	Reactive blue 4 (anthraquinone dye)	Dye degradation is improved at the presence of H_2O_2.
TiO_2 and TiO_2 doped with Cu	Reactive blue 4, Reactive orange 30, Reactive red 120 and Reactive black 5	TiO_2 nanoparticle doped with Cu are found to be very efficient in dyes degradation.
NanoTiO_2 (C-Fe doped)	C.I. Basic blue 9 C.I. Acid orange 52	Real wastewater treatment.
ZnO nanoflowers	Methyl orange Congo red Eosin B Chicago Sky Blue	Methyl orange is the most vulnerable to degradation in comparison with other dyes.
ZnO nanopowder	Rhodamine B	95% dye degradation is obtained under sunlight radiation.
In/ZnO nanoparticles	Methylene blue	Ind is well dispersed in ZnO
SiO_2 nanoparticles doped with Ag and Au	Methyl red	$^{\bullet}OH$ radical formed initiates and sustains dye degradation
Mn_3O_4 nanoparticles	Amido black 10B	Peroxymonosulfate (PMS), peroxydisulfate (PDS) and hydrogen peroxide (HP) enhance degradation.

solution for efficient PPCPs degradation. NPs TiO_2-anatase possess high efficiency of degradation of doxorubicin, highly toxic chemotherapeutic agent and antibiotic, which appears in water [98]. It is assigned to surface adsorption and oxidation by UV induced electron holes present in TiO_2 nanoparticles. Immobilized TiO_2 in the form of quartz fiber filters (QFT) and porous sheets (PTT) have been applied to treat wastewater containing pharmaceuticals like carbamazepine, wenphlaxin, fluoxetin, atenolol, sulfamethoxazole, ibuprofen, atorvastatin, naproxen, triclosan and triclocarban and their metabolites including carbamazepine-10,11-epoxide, norfluoxetine, p-hydroxy-atorvastatin, o-hydroxy-atorvastatin [99]. At pH 4.5–5, QFT are negatively charged, while PTT are positively charged. As a consequence, there appear interactions between charged contaminants and the catalyst, that is, QFT are efficient in removal of cationic contaminants, while PTT are sufficient for anionic contaminants. TiO_2 nanowires (anatase) of 10 μm length, under radiation of wavelength 30–100 nm, are also able to decompose pharmaceuticals (naproxen, carbamazepine) and personal care products (teophylline) [100]. TiO_2 nanocomposites modified with graphene allow for degradation of carbamazepine during drinking water treatment, whereas complete degradation may be obtained at photocatalyst dose 25.14 mg/L graphene-TiO_2 after 5 min UV irradiation of intensity 1.35 m W/cm^2 [101]. Moreover, photocatalytic removal of carbamazepine, diclofenac and sulfamethoxazole under sunlight radiation is much better in case of use of composite materials comprised of semi-conductor and carbon nanomaterial [102]. In general, it has been found that carbon materials induce absorption of light and allow for more efficient charge separation improving photoactivity of composites. Carbon may be introduced to a semi-conductor (usually TiO_2) as a supporting or a doping material, that is, nanoporous chars, carbon nanotubes (CNTs), graphene and its derivatives, carbon quantum dots (CQDs) and biochars. Specific role of carbon materials depends on their properties, but even more amorphous forms like nanoporous chars or biochars allow to develop composites of improved properties in comparison to a pure semi-conductor.

UV/TiO_2 photocatalysis have been evaluated in regard to degradation of gemfibrozil and 17β-estradiol [103]. At optimized conditions, that is, pH = 5 and TiO_2 dose 1.5 g/L, 95% of gemfibrozil and 93% of 17β-estradiol can be degraded within 30 min. Mboula et al. [104] have investigated photocatalytic degradation and toxicity of 17β-estradiol using three different TiO_2 containing materials, that is, nanocrystalline TiO_2, TiO_2 modified with nitrogen and reduced composite comprised of graphene oxide and TiO_2. They have observed that even after decomposition of 17β-estradiol below detection limit, the trace estrogenic activity is still detected, what complicates byproducts removal (Fig. 10) [104].

Methylparaben (methyl 4-hydroxybenzoate) (MEP) is a chemical, highly resistant EDC, which appears in many skin care products. Photocatalytic degradation of methylparaben using TiO_2 suspensions have been investigated under different types of radiation (UV-A, UV-C and Vis) [105]. Noticeably higher reaction rates and more efficient photodegradation have been obtained for systems involving UV-C radiation. The complete mineralization o methylparaben can be obtained after 60 min reaction at MEP concentration 30 mg/L, pH = 9 and TiO_2 dose 500 mg/L. The toxicity analyses of trace degradation byproducts performed with the use of Artemia franciscana crustacean show the significant decrease of the parameter after photocatalytic MEP degradation [105].

Foiled graphite carbon nitride (g-C3N4) and two commercial titanium dioxide materials (P25 and CG300) have been investigated to paracetamol, ibuprofen (IBU) and diclofenac (DOC) photocatalytic degradation [106]. Sizes and specific surface area (SSA) of TiO_2 nanoparticles have been equal to 6 nm and 300 m^2/g for CG300 and 21 nm and 50 m^2/g for P25, while SSA for g-C3N4 has been 140 m^2/g. All photocatalytic experiments have been carried out under UV (368 nm) and VIS (446 nm) radiation. TiO_2 P25 is the most effective photocatalyst under UV radiation, while g-C3N4 under VIS radiation. Paracetamol and ibuprofen may be completely mineralized, while diclofenac byproducts may be detected even after 6 h of irradiation. Among them one can find carbasol-2-acetic acid, 2,6-dichloroanilin and hydroxylated diclofenac derivatives. However, research show that g-C3N4 may be a very promising photochemical material.

Surface modified TiO_2 doped with mono- and bimetallic Au, Ag and Cu nanoparticles may be used to photocatalytic degradation of ciprofloxacin [107]. Mono- and bimetallic materials reveal better activity than non-modified TiO_2 in simulated sunlight radiation tests, while under UV-C radiation only bimetallic materials characterize with improved efficiency in comparison to pure TiO_2. The photocatalytic activity observed in experiments with UV-C may be assigned to effective separation of electron-electron holepair, and, to a lower extent, to improved adsorption of an antibiotic on a surface of modified materials. Photocatalysts modified with bimetals reveal the highest decomposition rate obtained at the end of an experiment under both UV-C and sunlight radiations. Even though the complete mineralization of investigated compounds under sunlight radiation cannot be obtained, treated wastewater turns out to be non-toxic, while antibiotic activity is completely eliminated.

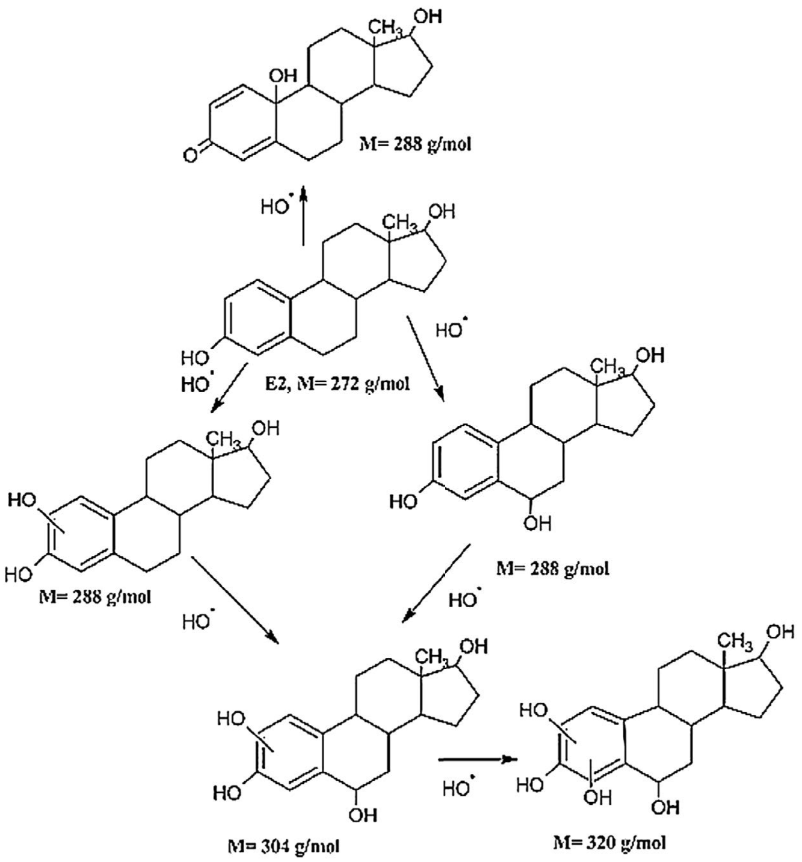

Fig. 10. The mechanism of photocatalytic degradation of 17β-estradiol.

Photocatalysis has also been used to decomposition of natural organic matter (NOM), including humic substances [108]. Eggins et al. [109] have observed almost 50% decrease of humic acid concentration in drinking water after its treatment with TiO_2 nanoparticles. The research reveal high photocatalytic activity toward humic acid in water resulting in 40% and 75% reduction of organic carbon and color, respectively. It has been shown, that NOM can be adsorbed on TiO_2 nanoparticles, what leads to agglomeration and reduces catalytic efficiency. NOM may also limit photocatalytic degradation of organic micropollutants (OMPs) by means of internal filter effect, reactive oxygen sweeping (ROS), and noticeable competition to adsorption and redox transformations occurring in the system [110].

4.2. Removal of inorganic contaminants

4.2.1. Anions

Inorganic contaminants, such as bromates, cyanides, thiocyanates, nitrites and nitrates may be efficiently degraded using photocatalytic reactions [11,15].

In recent years the use of heterogeneous photocatalysis to removal of bromates (BrO_3^-) has gained the wide attention [111,112]. Cunha et al. [111] have evaluated the rate of photoreduction of bromates present in aqueous solution in concentration of 200 μg/L in regard to following parameters: photocatalyst layer thickness, solution pH, mechanism of radiation of surface coated with photocatalyst and type and dose of protective substance. The possibility of photocatalyst layer reuse as well as matrix impact (ultrapure vs. freshwater) have also been checked. The obtained results show that (i) molar rate of bromates reduction is similar to molar rate of bromides formation, (ii) the use of formic acid ($[(BrO_3^-)]$:$[CH_2O_2]$ in molar ratio 1:3) as electrons scavenger reveal better reduction efficiency as use of humic acids (HA = 1 mg/L), (iii) photocatalyst layer is stable for min. 4 treatment cycles and keeps the initial efficiency. At the optimum operational conditions (2wt.% of TiO_2-P25 suspension, pH 3.0) the use of ultrapure water matrices leads to similar of higher reaction rates than ones observed for freshwater. Regardless of other process parameters, heterogeneous TiO_2 photocatalysis performed in NETmic reactor may be used to efficient reduction of BrO_3^- do Br^- and the concentration of former may be decreased to 10 μg/L after 2 h of treatment. Semi-conductive photocatalyst, platinized titanium dioxide, Pt-TiO_2 has also been used to reduction of bromates to bromide under UV light radiation [112]. First order kinetics of bromates removal slows down at the presence of competitive ions, including bromides and sulfates. Pt-TiO_2 photocatalyst may also be applied to reduction of bromates not only in the form of dispersed powder, but also as a thin layer placed in flow reactor.

Photocatalysis is also a promising method of removal of cyanides. During the process toxic cyanides CN^- are transformed to cyanates OCN^-, which may be further mineralized to N_2 and CO_2, that is, environmentally neutral compounds [113,114]. The use of TiO_2 in the form of suspension to degradation of free and complex cyanides under artificial UV radiation has also been widely investigated [113]. Lopez Munoz et al. [115] have performed research on photocatalytic removal of $[Ag(CN)_2]^-$ complex in the presence of oxygen using TiO_2. Both the reduction of Ag(I), which deposits om TiO_2 surface in the form of Ag(0) and oxidation of CN^- to cyanates can be run simultaneously. Karunakaran et al. [116] have compared the photocatalytic effectiveness of various TiO_2 crystalline forms (anatase, rutile, Degussa P25, Hombikat) to decomposition of cyanides present in alkaline solution radiated with sunlight. The final effect of the treatment depends on specific surface area and average size of TiO_2 crystals (except for rutile). Binary oxides are also applied in cyanides removal as the use of conjugated semi-conductors may improve photocatalytic process. There are research covering the use of various photocatalysts such as TiO_2/ZnO [117], TiO_2/CeO_2 [118] and TiO_2/SiO_2 [114], in which these materials are evaluated in regard to cyanides removal under UV or visible light radiation. The research show that photocatalytic of TiO_2/ZnO is much higher than one observed for TiO_2 under visible light radiation [117]. Hydroxyapatite (HAP) has also been combined with TiO_2 based photocatalysts in order to modify the photocatalytic process. Pd-TiO_2-hydroxyapatite (Pd-TiO_2-HAP) nanoparticles reveal better photocatalytic activity under visible light radiation and the highest photochemical stability in comparison with monocatalysts. The degradation rate constant of composite photocatalyst is 2.71 higher than one of Pd-TiO_2 and 12.2 times higher that one of Degussa P25 [119] and its photocatalytic activity is also better than ones of separately used Pd-TiO_2 and HAP. The removal of cyanides has also been examined with the use of ZnO and ZnO-based modified materials [113]. ZnO doped with Ce (2%) obtained using sonochemical wet impregnation catalysis cyanides oxidation under UV-A and natural sunlight radiation [118]. The presence of Ce improves photocatalytic activity of ZnO, as it limits recombination of photogenerated electron-electron hole pairs. Salinas-Guzman et al. [120] have evaluated photocatalytic activity of ZnO impregnated with cobalt phthalocyanine (CoPc) used as sensitizer in degradation of cyanides in visible light. In comparison with commercial catalyst, that is, ZnO and Degussa P25 TiO_2, ZnO sensitized with CoPc reveals the highest degradation activity toward potassium cyanide present in aqueous solution radiated with visible light.

High concentration of nitrates are harmful to living organisms due to the fact that during their metabolism they can be transformed to nitrites, which significantly increase the risk of digestive system cancer. Hence, limitation of nitrite consumptions is required. The permissible concentration of nitrates and nitrites in drinking water are usually established at 50 and 0.5 mg/L, respectively. The removal of nitrates from water gains the increasing interest, while photocatalysis is one of the most advanced methods used for this purpose.

TiO_2 nanoparticles and TiO_2/PAN nanofibers show maximum nitrates removal at the level of 88.2% and 74.67% at initial concentration equal 10 mg/L and solution pH equal 4 [121]. The average size and diameter of TiO_2 NPs and TiO_2/PAN NFs are equal 22 nm and 90 nm, respectively. In case of both photocatalysts the removal efficiency decreases with the initial nitrate concentration and solution pH increase, while TiO_2/PAN NFs reveal lower activity than TiO_2 NPs. On the other hand NFs can be more easily separated from water than NPs.

Another research have been focused on the use of polystyrene (PS) – TiO_2 (PS-TiO_2) catalyst to photocatalytical reduction of nitrates in aqueous solution at the presence of formic acid used as electron holes scavenger [122] and at various experimental conditions including solution pH, formic acid concentration and catalyst doses. The complete denitrification of water initially containing 40mgN-NO_3/L can be achieved after 135 min of radiation at initial solution pH 2.5, catalyst dose 15 g/L and formic acid concentration 16 mM. Floating character of photocatalyst particles enables their simple recovery ≥98% after 5 cycles of denitrification experiments.

Liu et al. [123] have discussed photocatalytic denitrification (PCDN) performed with the use of non-linear optical materials (NLO), that is, lithium niobate ($LiNbO_3$). The use of the material in the form of suspension reveals effective denitrification and nitrates removal rate reaches 98.4% during 120 min carried out in neutral pH. On the basis of 1st order PHDN kinetics, the reaction constant of $LiNbO_3$ is almost three times higher than reaction constant of conventional TiO_2 (P25) established for the same process conditions. The experiments suggest that photocatalytic nitrate reduction with the use of $LiNbO_3$ is performed by means of direct heterogeneous interaction with electrons present in $LiNbO_3$ conduction band. Another mechanism is established for P25 based photocatalysis, in which nitrates are reduced by radicals generated by electron holes present in valence band. In case of NLO based photocatalysis, the number of generated electrons is higher, while recombination of electron-electron hole pair is minimal, what improves capacity and stability of PCDN process.

Dharmagunawardhane et al. [124] have presented the novel method of photocatalytic nitrate reduction based on in-situ generation of Ti^{3+}/Ti^{2+} ion in TiO_2/Al catalyst. Ti^{3+}/Ti^{2+} ions present in the catalyst absorb wavelengths from UV to almost IR range and are spontaneously generated under visible and close to IR light radiation. The use of TiO_2/Al photocatalysts enables 95% removal of nitrates at their initial concentration equal to 100 mg/L. On the basis of XPS, FTIR and reaction product analyses the proposed reduction mechanisms relies on in-situ generation of Ti^{3+}/Ti^{2+} ions which collect visible and IR close photons, while these ions are also active sites of nitrates reduction.

In natural water sources, nitrites are often accompanied with ammonia. Hence, it is very important that photocatalysis process applied to nitrite removal also allow for simultaneous elimination of ammonia. Ye et al. [125] have synthesized and characterized zinc ferrite/activated carbon photocatalysts ($ZnFe_2O_4$/AC) used to simultaneous removal of nitrite and ammonia carried out at anaerobic conditions under UV radiation in the first stage of the process. The obtained result indicate on nitrite removal rate up to 92.7% and ammonia removal rate equal to 64% at initial contaminant concentration 50 mg/L, initial ammonia concentration equal 100 mg/L, solution pH = 9.5 and after 3 h of anaerobic treatment. In the second stage of the process gaseous oxygen is introduced to the reactor in order to remove the remaining ammonia at constant radiation conditions. Such the process configuration in overall, allows for removal of nitrite, ammonia and total nitrogen up to 92.0%, 90.0% and 90.2%, while the final product of photocatalytic degradation of these contaminants is gaseous nitrogen N_2.

Photocatalysts composites such as Cu_2O/TiO_2 (1–10 wt.% Cu_2O) and Cu_2O/TiO_2-AC (2.5–20 wt.% AC) have also been prepared to simultaneous removal of nitrates and oxalic acid [126]. Composite containing 2.5wt.% Cu_2O in Cu_2O/TiO_2 reveals the best photocatalytic capacity and allows to remove 57.6% of nitrates and 99.8% of oxalic acid after 3 h. Cu_2O/TiO_2-AC photocatalyst show the highest activity at AC content 2.5wt.% and enables the removal of 42.5% and 96.6% of nitrates and oxalic acid, respectively. Oxalic acid have also been used as electron holes scavenger in photocatalytic removal of nitrates [127] with the use of Au/TiO_2 photocatalyst.

The impact of pH and doping with 4 noble metals (0.1 mol% Au, Ag, Pd and Pt) on nitrates photoreduction using commercial nanostructural TiO_2 (P25) and TiO_2 nanograins obtained by means of flame spray pyrolysis (FSP) has also been checked [128]. Optimum pH of the reaction is either 11.4 or 5.1, whereas nitrates conversion reaches 8.8% and 10.4% for P25 and FSP, respectively, after 5 h treatment. The formation of different byproducts resulted from the change of pH may influence on nitrates reduction mechanisms. In general, selectivity toward ammonia formation increases in acidic pH, whereas it is significantly lower in alkaline pH. The catalysts doped with noble metals enhances reduction activity, probably by disfavoring competitive reactions and increasing selectivity toward ammonia formation. Ag reveals the best capacity, regardless of catalyst basis (P25 or FSP) and the conversion rates are 14.5% (FSP) and 10.7% (P25) after 5 h reaction. However, also in this case the dependence between conversion and selectivity has to be considered.

Selective photocatalytic oxidation of NH_3 to N_2 is proposed as a novel method of removal of ammonia from water. Photocatalytic oxidation of ammonia on non-coated, metallized TiO_2 from water saturated with air, nitrogen or N_2O [129] has been investigated. Above 80% photocatalytic conversion of ammonia to nitrogen under visible light radiation during 40 min process using Pt/TiO_2 saturated with N_2O may be obtained. N_2O possesses the ability to accept electron from generated in conduction band f Pt/TiO_2, what has been verified by photo-electrochemical measurements. The presence of Pt deposits on TiO_2 particles modifies photocatalytic pathway of ammonia conversion by means of increased generation of $^{\bullet}OH$ radical by N_2O as well as by stabilization of transition NH_x forms (where $x = 0,1,2$), what enhances their recombination to N_2.

CdS/TiO_2 tubular nanotubes (TNTs) has also been used to photocatalytic oxidation of ammonia [11]. CdS/TiO_2 TNTs have been successfully synthesized by means of simple, fast and reliable microwave hydrothermal method. CdS NPs synthesized using microwaves of power 140 W at temperature 423 K photodegrade 26% ammonia, while the efficiency noted for CdS/TNTs composite reaches up to 52.3%. The obtained results indicate that CdS/TNTs photocatalysts reveals better photoactivity than separately used CdS or TNTs materials.

4.2.2. Heavy metals

Heave metals are especially harmful to aquatic environment, as they do not undergo to biodegradation processes and they may be bioaccumulated in living organisms [113,130,131]. The expansion and growth of mining, fertilizers production, electronic, paper, tanning, galvanization, etc. industries result in direct or indirect deposition of heavy metals containing wastewater to environment. Hence, photocatalytic removal of heavy metals and metalloids become a subject of interest in regard to efficient wastewater treatment [130,131]. Photocatalytic treatment processes allow for transformation of heavy metals to their metallic forms, which are further deposited on semi-conductive photocatalyst surface or they may be transformed to less harmful soluble forms. Redox potential of metal/ion pair related with potential of conduction and valence bands is crucial parameter enabling to predict the efficiency of photodegradation of these contaminants.

Except for removal, some research also discuss the photocatalytic recovery of metals such as gold (Au(III)), platinum (Pt(IV)) and rhodium (Rh(III)) using dispersed TiO_2. It has been shown that at pH = 0 and sunlight radiation 90% of gold can be recovered from a mixture comprised of salts Au(III), Pt(IV) and rhodium chloride [11]. The metals' photorecovery may be also performed using cyanide solutions of metals at simultaneous degradation of CN^-, but it has to be done at the presence of peroxides like H_2O_2 and $S_2O_8^{2-}$.

Shyni et al. [132] have investigated the removal of heavy metals and degradation of pharmaceutical wastewater using ZnO/Se nanocomposite. The use of selenium doped ZnO nanoparticles increases photocatalytic capacity of the nanocomposite. Heavy metals present in pharmaceutical wastewater, such as Cu, Pb, Ni, Zn, Cd and Cr are efficiently reduced, while Ni and Zn are completely removed during treatment with the use of 0.5 g of nanocomposite introduced to 20mL of wastewater.

The removal of cadmium (Cd) from wastewater can be obtained using TiO2 nanoparticles of 4.5 nm diameter under radiation of wavelength 253.7 nm. TiO_2 nanoparticles may be modified with histidine (His) or alanine (Ala) [133]. Above 90% reduction and recovery of Cd n TiO_2 surface may be obtained. Rahimi et al. [134] have investigated photocatalytic removal of cadmium (Cd^{2+}) and lead (Pb^{2+}) in continuous flow and batch systems. The research have been carried out in laboratory scale in a reactor comprised of UV radiation source, reaction chamber and mixing chamber. Synthetic wastewater containing 25 mg/L of Cd^{2+} and Pb^{2+} have been used in both continuous flow and batch experiments and the impact of titanium dioxide (TiO_2) dose, pH and air dispersion on removal efficiency has been investigated. The research have revealed that the increase of TiO_2 dose and solution pH improves cadmium and lead removal. Maximum removal rates reach 99.8% (Cd) and 99.2% (Pb) at TiO_2 dose 0.9 g/L and pH = 11. Additionally, the photocatalyst may be separated from the reaction mixture and it can be easily recycled.

TiO_2 photocatalyst has also been used to removal of toxic mercury (Hg^{2+} ions) accompanied with reduction of lead to metallic state and simultaneous recovery [135] TiO_2 photoactivity has been investigated in regard to silver nitrate, mercury(Hg(II)) and methylmercury ($CH_3Hg(II)$) chloride in simulated sunlight (AM1.5) [11]. Waste derived activated carbon has also been applied after combination with TiO_2 to reduce of Hg^{2+} ions and recovery of metallic mercury. Above 70% removal of Hg(0) adsorbed on activated carbon and TiO_2 surface after photoreduction can be obtained with the use of the discussed method [136].

4.2.3. Arsenic and chromium

Contamination of natural water sources with arsenic, especially in regard to groundwaters, is a worldwide problem. The presence of arsenic in natural water usually results from geochemical conditions related with volcanic rocks, geothermal effluents, mine activities and waste landfilling. Uncontrolled anthropogenic activity, such as smelting of metals, use of arsenic-based pesticides and wood preservation compounds may also cause arsenic release to environment and water contamination. Inorganic and organic arsenic forms, such as As(V) and As(III) (former) and monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) (latter) are main contaminant forms, which appear in nature. As(III) is more toxic as As(V) and it is very difficult to remove this arsenic form using most of conventional water treatment methods. As(III) is usually removed from water by oxidation to As(V), which is next eliminated by means of adsorption, precipitation or ionic exchange processes.

Semi-conductive TiO_2 has been widely applied to remove inorganic and organic arsenic forms due to low cost and environmentally neutral character [137,138]. The final product of oxidation of different arsenic forms is As(V) [136]. Oxidation of As(III) [137,139] and phenylarsonic acid [138] has been investigated using heterogeneous photocatalysis with TiO_2 under UV radiation. Tsimas et al. [139] has examined simultaneous oxidation of As(III) and humic acid (HA) in aqueous suspensions of TiO_2 Degussa 25 under UV radiation of wavelength 350–400 nm. At initial As(III) concentration in the range of 3–20 mg/L the removal is obtained within 10–30 min using catalyst suspension of concentration 50 mg/L. However, the oxidation effect is lower at the presence of HA [139]. Zheng et al. [138] that phanylarsonic acid (PA), the compound commonly used in poultry farms as a feed additive can be easily degraded using TiO_2 Degussa P25. The final product of photocatalytic reactions is As(V) [138]. Nanocrystalline TiO_2 has also been used as both as adsorbent to removal of arsenates and arsenite and a photocatalyst oxidizing and transforming As(III) to As(V) [140].

Titanium dioxide nanoparticles modified with palladium and doped with nitrogen (TiON/PdO) have been evaluated in regard to removal of As(III) under visible light radiation [141]. In such the way, the concentration of As(III) can be reduced to the level below permissible concentration established by US EPA standards, that is, 10 μg/L. The efficient removal of As(III) results from strong adsorption and photocatalytic activity revealed by TiON/PdO, which is caused by strong optoelectric conjugation between PdO and TiON [141].

TiO_2 photocatalyst immobilized on porous support matrices, like polymeric [142] or activated carbon [143] ones has also been applied to As(III) removal. TiO_2 suspension of 10% concentration immobilized on PET (polyether phthalate ethylene) bottles exposed to sunlight radiation for 4 h and accompanied with arsenic co-precipitation on ferric oxide-hydroxides has been used to removal of As(III)

Table 2
Transformation and removal of various metal with the use of nano-TiO_2 based photocatalysis

Metal	Removal effect discussion
Lead(II)	Removal of lead(II) may be performed by photocatalysis, but pure TiO_2 reveals poor effect. However, the process may be improved by TiO_2 modification.
Arsenic	Arsenic may be transformed to less toxic species by means of photo-oxidation or photo-reduction.
Mercury(II)	Mercury(II) may be reduced to metallic Hg(0), Hg_2O or calomel (Hg_2Cl_2)by direct photo-reduction.
Chromium(VI)	Photocatalytic reduction may transform Cr(VI) to less toxic Cr(III), which can be next removed from the solution.
Silver	Silver photo-reduction may lead to deposition of metal on TiO_2 surface, even at low metal concentration in the treated solution.

from contaminated water [142]. Above 99% of As(III) and total As can be obtained, whereas water matrix does not affect the oxidation process. Yao et al. [143] have synthesized composite photocatalysts comprised of TiO_2 deposited on activated carbon fibers (TiO_2/ACF) and granulated carbon (GAC-TiO_2). Photocatalytic oxidation of As(III) with the use of TiO_2 enhanced with carbon materials occurs within several minutes and the removal mechanism corresponds to 1st order reaction kinetics. As(III) oxidation may be obtained within the wide range of pH from 2 to 10, but the oxidation efficiency increases with the pH increase.

Photocatalytic removal of arsenic(III) and monomethylarsonic acid (MMA(V)) has been investigated at the presence of UV light (350 nm) and aqueous suspensions of ZnO synthesized by means of sol-gel method [144]. Photocatalysis process results in effective and fast As(III) mineralization to significantly less toxic inorganic arsenate [As(V)]. The impact of ZnO dose and solution pH on photocatalytic UV/ZnO process are also recognized. The optimal removal of As(III) and MMA(V) from solution of their concentration 5 mg/L is observed at catalyst dose 0.25 and 0,50 g/L and pH equal 7 and 8, respectively. The research also show that at comparable process conditions photoactivity of ZnO sol-gel derived catalyst is much better in regard to arsenic removal from water in comparison to commercially available ZnO and TiO_2 Degussa P25 catalysts.

Nanocrystalline bismuth pyrostannate ($Bi_2Sn_2O_7$) (BiPyr) synthesized using hydrothermal method has also been evaluated in regard to removal of As(III) from water under visible light radiation [145]. BiPyr NPs reveal high photocatalytic activity under the applied radiation and allow for up to 96.8% oxidation of As(III) at its initial concentration equal 2 mg/L.

Chromium appear is aquatic environment mainly as Cr(VI) and Cr(III). Cr(VI) compounds are recognized as toxicants and carcinogens, while Cr(III) is less toxic and may be easily precipitated in the form of $Cr(OH)_3$ [146]. Chromium(VI) is a common contaminant of wastewater formed by such industrial branches like galvanization, leather tanning and paints production [113]. The most often detected forms of Cr(VI) are $Cr_2O_7^{2-}$, CrO_4^{2-}, H_2CrO_4, and its appearance depends on solution pH, chromium concentration and redox potential. Any of these forms, however, does not form insoluble precipitates, thus their separation by means of direct precipitation is not possible. The transfer of chromium(VI) to solid phase, which can be further separated from aqueous stream, requires the change of its oxidation state. Hence, the application of heterogeneous photocatalysis to Cr(VI) reduction is accepted to be an attractive option for removal of Cr(VI) from wastewater [113,146].

Degussa P25 is a semi-conductive photocatalyst commonly applied in photocatalytic removal of Cr(VI) and the process usually is run under UV radiation [147] or sunlight radiation [148]. Cr(VI) removal with the use of TiO_2 is beneficial at lower pH range due to increased potential difference between conduction band of TiO_2 and Cr(VI)/Cr(III) and anionic adsorption of Cr(VI) on TiO_2 surface [146]. The reaction may be speeded up by addition of organic compounds, which act as electron holes or $^{\bullet}OH$ radicals scavengers, for example citric acid [113,148]. Size and shape of external photocatalyst surface are very important factors considered in determining TiO_2 activity. Almost complete removal efficiency may be obtained for initial Cr concentration below 53.7 mg/L after 3 h of sunlight radiation.

Au doped TiO_2 has been used to reduction of Cr(VI) present in synthetic solution [149] and soil effluents [150]. Alternatively, Behnajady et al. [151] have immobilized commercial ZnO on a glass plate to remove 5 mg/L of Cr(VI) at pH 5.7 under UV 254 nm radiation (35 W/m^2). The change of ZnO morphology may have an influence on its activity and stability. Hence, ZnO synthesized by means of precipitation [152] have also been used to Cr(VI) removal. Catalysts of nanosize range have been evaluated at neutral or slightly alkaline pH using suspended ZnO and UV radiation, while the modification with reduced graphene oxide (RGO) [153] has been made to improve the removal effect. ZnO-RGO composite containing 1wt.% of RGO allows to remove Cr(VI) to the highest extent equal 96% during 240 min process, while the composite stability enables its reuse even after 3 treatment cycles.

In Table 2 the possible uses of TiO_2 nanocatalyst to transformation and/or removal of various metals from aquatic environment is presented [42].

4.3. Photocatalysis in water and wastewater disinfection

Water and wastewater treatment methods should assure not only the efficient removal of chemical contaminants, but also microbiological ones, such as bacteria, fungi, viruses and molds. Photocatalytic inactivation of microorganisms is a complex process, and its efficiency depends on kind, concentration and physiological state of microorganisms [16]. Additionally, type, morphology, concentration and form (suspended or immobilized ones) of a photocatalyst also influence on the process performance [16]. Among microorganisms commonly appearing in water and wastewater streams, *E. coli* has widely been rested to optimize photocatalysis conditions and preferable design of photo-reactors [15,16]. Other bacteria from coli group, that is, *Pseudomonas aeruginosa*, *Salmonella typhirium* and *Enterobacter cloacae* have also been undergone to photocatalytic inactivation [15].

TiO_2 nano-photocatalyst reveals efficient ability of inactivation of pathogenic microorganisms present in water and wastewater [154]. In literature there are a number of research papers discussing the use of TiO_2 nanoparticles (Degussa P25) activated with sunlight and applied in inactivation to bacteria (*E. coli*, *Pseudomonas aeruginosa*), fungi (*Candida albicans*, *Fusarium sloani*), protozoa (*Acanthamoeba polyphaga* trophozoite stadium), spores (*Bacillus subtilis*) and cysts [155] The use of powdered TiO_2 has one significant disadvantage which is a problematic separation from aquatic stream. Hence, in order to assure the efficient antibacterial treatment, nanoparticles are immobilized on supports [156]. Akhavan [157] has showed Ag particles introduced to TiO_2 foil (Ag/TiO_2) as well as mesoporous Ag/TiO_2 composites exhibit 6.9 higher antibacterial effect toward *E. coli* than conventional TiO_2 P25. It is due to the fact, that the formed composite characterizes with larger surface area, and thus possesses more active sites available to microorganisms deactivation [156]. TiO_2 films doped with palladium, tin dioxide (SnO_2), molybdenum (Mo), boron (B), cerium (Ce), iron (Fe) and nitrogen (N) have also been applied in deactivation of model microorganism (*E. coli*, *Staphylococcus aureus*, Saccharomyces cerevisiae and spores of *Aspergillus niger*) [16]. The novel achievement in photocatalytic disinfection is the use of polymeric nanocomposites. For example, TiO_2/PMMA nanocomposite have been successfully tested to inactivation of *E. coli* as an model microorganism [16].

Photocatalytic inactivation of gram-negative *E. coli* and gram-positive *Bacillus subtilis* in water using ZnO nanowires under visible light radiation in much better than disinfection effect exhibited by ZnO without light access [158,159]. The damage of cellular membrane and DNA degradation are main deactivation mechanisms. The high efficiency of pathogenic bacteria deactivation revealed by ZnO nanowires under visible light radiation indicates on possible ex situ water decontamination under sunlight radiation. Moreover, ZnO nanowires immobilized on cellulose sheet also reveal antibacterial properties under visible light radiation [158].

Other metallic compounds, mainly Fe_2O_3, CdS, GaP and ZnS may also be used to water disinfection [2,3]. The new type of photocatalyst is graphite carbon nitride $g\text{-}C_3N_4$, which characterizes with increased activity due to large adsorption surface area available for many toxic synthetic and microbial contaminants [160]. Hence, composites containing carbon nanosheets ate promising materials enabling the spreading of the use of semiconductive photocatalysts in water and water treatment. Many semi-conductors, such as BiOCl, $BiVO_4$, Bi_2MoO_6, Bi_2WO_6, In_2S_3, CuO_2, $SrTiO_3$, TiO_2, WO_3, ZnO and Ag/AgBr have been in involved in synthesis of nanocomposites comprised also of $g\text{-}C_3N_4$. Zeng et al. [161] have elaborated three component nanocomposite based of carbon dots and graphene rGo (CTR) to enhance charge separation in TiO_2. Under sunlight radiation, CTR suspension causes 1.03 log inactivation of *E. coli* within 60 min in comparison to 0.58 log inactivation exhibited by TiO_2-rGO. These results prove, that the increase activity of CTR composite results from the presence of carbon inclusions. Easier generation of reactive oxygen species (ROS), especially $^{\bullet}O_2^-$ and H_2O_2 accompanied with improved charge separation in CTR photocatalyst result in faster bacteria inactivation. The mechanism of photocatalysis performed with the use of CTR relies on the transfer of TiO_2 electrons to carbon particles via rGO nanosheets. These electrons trapped in carbon dots are transferred to O_2 particles forming $^{\bullet}O_2^-$ radicals, which are able to damage cellular membranes of microorganisms cells.

In Table 3 selected progress in the field of bi and three component graphene based photocatalysts used to water disinfection is presented [162].

ROS are crucial for efficient destruction of microorganisms cells using TiO_2/UV, and among available species the best antimicrobial effects are noted for hydroxy radicals ($^{\bullet}OH$) [163]. This radicals are formed on nano-TiO_2 surface during its contact with water, characterize with short lifespan and are able to penetrate cellular wall and membrane and damage DNA structure, similarly as H_2O_2, as well as cause lipids peroxidation [164]. Photocatalytic mechanisms, which inactivates microorganisms, starts with the breakage of cellular wall membrane, what causes leakage of intercellular substances, such as RNA and proteins, which is followed by complete cell damage and death [65,165].

5. Final remarks

Since the discovery of photocatalysis process, many researches on production and modification of photocatalysts as well as in the application of the process to water and wastewater treatment have been performed. Among available photocatalysts, titanium dioxide remains the most popular one and it is widely applied in processes carried out under UV and visible light radiation. It results from many factors, especially small losses during process, nontoxic properties and high efficiency of oxidation. In order to improve photocatalytic properties of TiO_2, many modification methods have been elaborated. They cover mainly formation of hetero-bonds (between different TiO_2 phases or between TiO_2 and another photocatalytic material) and use of chemical dopes/modifiers or additives, which allow to decrease the break in bandgap of TiO_2. Both of these modification methods are found to be sufficient. The increase of interest in the use of other photocatalytic material like ZnO, CdS, ZnS, WO_3 and Fe_2O_3. Moreover, modification of ZnO performed with the use of graphite-like C_3N_4, silver, chromium, aluminum, tin, cobalt and reduced graphene oxide. The doping of photocatalyst is also proposed in order to enable their activation by visible light. Hybrid materials like ZnS-CuS-CdS, carbon spheres/CdS, $g\text{-}C_3N_4$-Au-CdS, ZnS-WS_2-CdS, C_3N_4-CdS and Pd-Cr_2O_3-CdS

Table 3
Graphene based photocatalysts in water disinfection

Photocatalyst material	Radiation source	Process characteristics
rGO@ TiO_2 film	Sunlight	100% *Escherichia coli* inactivation.
GO-TiO_2 nanowires	Sunlight	100% *Escherichia coli* inactivation.
GO-ZnO-Ag	Visible light	99.99% *Escherichia coli* inactivation.
GO-CdS	Visible light	100% *Escherichia coli* and *B. subtilis* inactivation.
rGO-C_3N_2-S	Visible light	100 % *Escherichia coli* inactivation.
TiO_2-GO	UV and sunlight	Improved and faster photodegradation under UV and sunlight radiation.
TiO_2-C dots/rGO	Sunlight	1.03 log *Escherichia coli* inactivation within 60 min.

are formed for this purpose. However, despite intensive development of photocatalysts active in visible light (TiO_2 based or other ones), the standard reference data on the performance of the process in this radiation range is not available, and thus the comparative review of novel achievements cannot be sufficiently performed.

Photocatalysis is able to degrade and mineralize organic contaminants disrupting endocrine systems, including pesticides, pharmaceuticals, personal care products, dyes, detergents, phenolic contaminants, chlorinated-derivatives and non-halogenated organic compounds, but also heavy metals and other chemical compounds. Many of these substances is problematic in regard to their removal, as during commonly used treatment techniques they are transformed to more toxic byproducts or keep their disrupting properties even after oxidative processing. Even though there are many research indicating on degradation of endocrine disrupting compounds by TiO_2 or its composites, they do not usually cover the examination of final toxicity of the treated stream.

In recent years, efficient inactivation of microorganisms present in water and wastewater has become an important research field due to their harmful effect on living organisms and human health. TiO_2 has the ability to photocatalytical inactivation of pathogenic microorganisms, which is based on the damage of cellular wall followed by oxidation of intercellular substances. However, future research in this field should also be accompanied with examination of final toxicity, which allow for reliable evaluation of the process and its further development and improvement.

In general, photocatalytic treatment of water and wastewater strongly depends on configuration and operational conditions of photo-reactor. There are two basic configurations of photoreactors commonly used in practice, that is, suspended phase photoreactors and reactors based on immobilized photocatalysts [4]. Various techniques of either dispersion/recovery or immobilization of a photocatalyst focused on the maximization of its efficiency have been proposed. A numerous research on systems parameters have been carried out at laboratory and pilot scale and they result allow to determine the impact of water/wastewater quality, photocatalyst dose, pH, temperature, dissolved oxygen concentration, type and concentration of contaminants, wavelength and intensity of radiation of final process efficiency [9]. There are commercial photocatalytic systems dedicated to removal of organic compounds, for example, Purifics Photo-Cat™ (of treatment capacity 10^4 m^3/d, and photoactive surface – 62 m^2) [165] or SODIS system (Solar Water Disinfection Process) containing nano-TiO_2 used to potable water production in developing regions. Moreover, SODIS system may be used in a small scale (water production for 1 person) or it can be scaled up to average size parabolic sun collectors. There are also commercial systems dedicated to households, designed in "point-of-use" mode, such as Aquapure®, Kinetico® and QSI-Nano®, which assure the removal of 99.99% of pathogens using antibacterial compounds based on nano zinc oxide (ZnO) and involving membranes coated or impregnated with silver [166].

Photocatalysis reveals tremendous potential to become cheap, sustainable treatment technique dedicated to water and wastewater. There are still however several technical problems, which need to be solve before the common, industrial scale application of the process, that is, [4]: (1) optimization of a photocatalyst action toward the improvement of its quantum capacity and activation under visible light, (2) effective design of photocatalytic reactors, (3) efficient photocatalyst recovery or immobilization, (4) improvement of photocatalytic reactions selectivity.

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