Nanostructured Materials for the Photocatalytic Degradation of Organic Pollutants in Water

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Abstract The heterogeneous photocatalysis combined with the use of nanostructured materials has proven to be a viable and highly efficient technology in the degradation of numerous organic compounds. This chapter present the fundamental aspects of nanometric semiconductors related to photodegradation and their treatment conditions for effluents contaminated. The role of the predominant species involved in each process has been studied using radical scavengers. In photocatalytic studies, clay minerals have recently been used as supports for the anchoring of semiconductors, developing photocatalysts with appropriate crystalline structure, which are more ecologically compatible and also have a high surface area. Additionally, the operational devices and influence on the degradation effectiveness such as dyes, pesticides and drugs were discussed for environmental treatment.

Keywords Semicondutor · Oxide · Photodegradation · Clay minerals

1 Introduction

Uncontrolled growth of contamination and discharge of micropollutants in the natural environment is a current major global concern [1, 2]. The majority of these contaminants are derived from human activities, whether from industrial, agricultural and/or urban processes (e.g., pharmaceuticals, dyes, pesticides, plastics). They are a threat to all living beings in terms of toxicity, carcinogenic and mutagenic effects [2–4]. For this reason, the investigation of new methods and materials for effective wastewater treatment is extremely important.

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Efforts have been made to develop ecologically sound and economically viable technologies that guarantee good quality of water resources from the degradation or immobilization of organic pollutants in natural waters [5–9]. Among the various approaches to water treatment are biological (aerobic, anaerobic and enzymatic), physical (decantation, filtration and adsorption) and chemical processes (advanced oxidative processes, ozonation, photocatalysis, etc.) [4, 7, 10, 11]. Advanced oxidative processes (AOPs) have been shown to be an efficient technology for the removal and degradation of organic pollutants due to the production of hydroxyl radicals through different formation routes, generating strong oxidizing power, so effectively degrading toxic and/or recalcitrant compounds, which provides great versatility in the treatment of aquatic pollutants [9, 11, 12]. By definition, AOPs are based on the generation of highly reactive and oxidizing compounds, such as hydroxyl radicals ($^{\cdot}OH$), ozone (O_3), and hydrogen peroxide (H_2O_2), which react non-selectively, and rapidly, with the great majority of organic compounds, mineralizing them and producing carbon dioxide (CO_2), water (H_2O) and inorganic ions (SO_4^{2-}, NO_3^-, Cl^-) [3, 11–13]. Among the types of AOPs, photocatalysis was highlighted due to its heterogeneous nature that allows for the treatment of waters and industrial effluents over a wide range of pH [14–17]. Based on this context, the next section will describe the fundamental aspects of nanometric semiconductors related to photodegradation and their treatment conditions for effluents contaminated with defined species, such as synthetic dyes, drugs, and pesticides.

2 Nanosemiconductors Applied to Heterogeneous Photocatalysis

The phenomenon of heterogeneous photocatalysis has been studied since the 1970s, originating from the work of Fujishima and Honda that described the process of water splitting, using TiO_2 as a photocatalyst, in an electrochemical cell, that promoted its oxidation generating H_2 and O_2 [18–21]. Since then many researches have demonstrated new ideas and innovations in the field of photocatalysis, for example the oxidation of water and pollutant organic compounds [22–24] promoted by semiconductors, especially on a nanometric scale, due to their high surface area and size-induced effects. Figure 1 shows the accelerated growth in several areas, and countries, of the use of photocatalytic technology. The main advantages of this technology include, in particular, the ability to use solar energy to control the temperature and ambient pressure conditions, so favoring economically viable photoresistance and low waste production, i.e. "green treatment", allowing the reuse of the photocatalysts. Finally, this chapter discussed the degradation of a diverse variety of pollutant species [14–17, 19, 24, 25].

The excitation of a semiconductor (e.g., TiO_2, ZnO, CdS, WO_3, ZnS) involves, in principle, the absorption of photons of visible or ultraviolet light [26–28]. In the semiconductor there is a region of energy discontinuity between the electronic levels

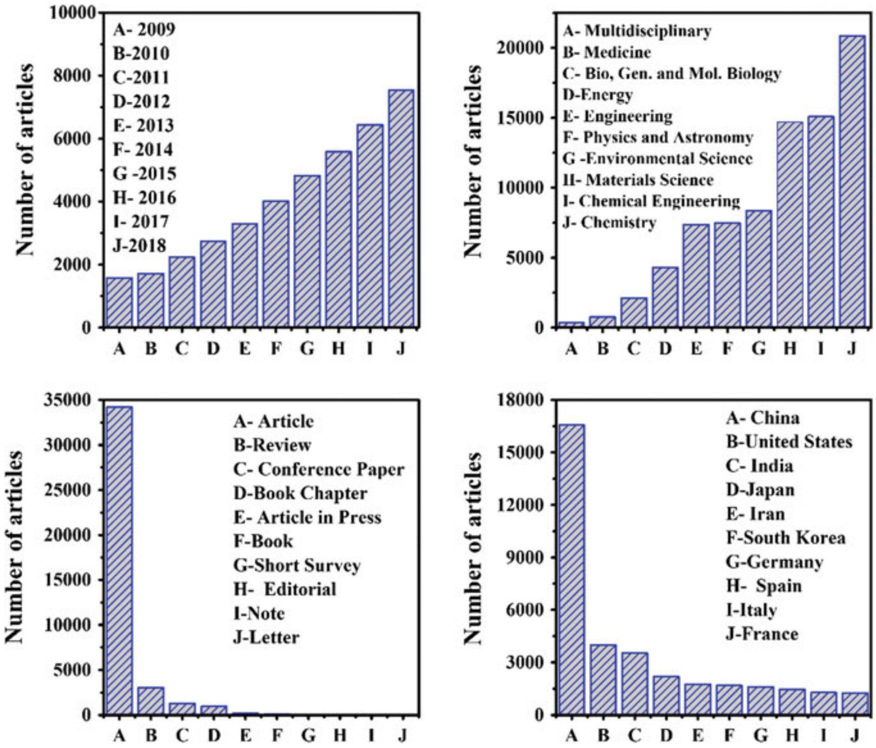

Fig. 1 Percentage related to the growing number of publications using heterogeneous photocatalysis as a technology for environmental remediation, in the last decade, by the Scopus database. Evolution of the number of articles over the years (**a**), areas of concentration involving the use of photocatalysis (**b**), the types of documents that are targeted (**c**), and the countries that concentrate articles on this technology (**d**)

called the band gap, this region being composed of two energy bands, the first called the valence band (VB—lower energy region), and the second, the conduction band (CB—energy), the band gap being the energy difference between the bands VB and CB [9, 19]. When the energy of the photon ($h\upsilon$) is equal to, or greater than, the band gap energy, the electrons (e) are promoted from VB to CB, leaving a positive hole (h^+) in VB, thus giving an electron/hole pair ($e^-{}_{CB}/h^+{}_{VB}$), the exciton [16, 24], the process of which is illustrated in Fig. 2, which showed the CdS photocatalytic scheme and the photodegradation of RR141 under the irradiation of natural sunlight [29].

These excitons can recombine directly, or indirectly, via surface defects, by radioactive or non-radiative processes, without causing a chemical reaction (recombination of charges), or by migrating to the surface of the semiconductor, so inducing oxidation-reduction reactions that subsequently degrade the organic contaminants [9, 14, 30–32]. Normally $h^+{}_{VB}$ readily reacts with H_2O from the surface and produces $^{\cdot}OH$ (oxidation reaction), whereas, $e^-{}_{CB}$ most often reacts with O_2 to produce

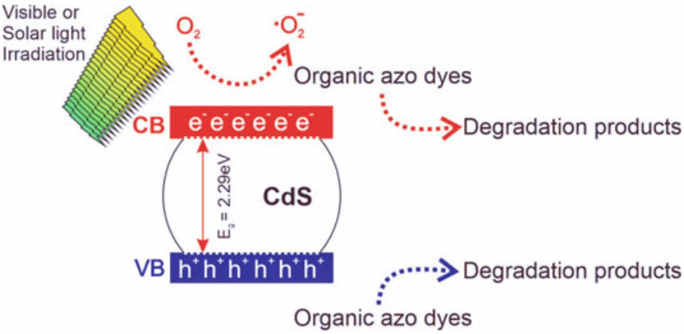

Fig. 2 Schematic diagram of a possible photodegradation mechanism of RR141 azo dye over a CdS photocatalyst under visible light, and natural solar light irradiation. Adapted from Senasu and Nanan [29]

O_2^- (superoxide anion), triggering reactions that lead to the generation of radicals (reduction reactions) [9, 30]. Rauf et al. [15, 33] in studies on the fundamentals and application of photocatalysis, showed that degradation does not necessarily occur exclusively through the hydroxyl radical, but also through other radical species, such as O_2, and $HO_2^{\cdot}$.

After excitation, photocatalytic efficiency is an alternative to the removal of energy at the surface of the semiconductor and a rapid recombination between the pairs e^-/h^+ [26, 34], releasing energy in the form of heat. Oxy-reduction reactions involving semiconductor excitation, load maintenance, and recombination of loads, are listed below [15, 26, 31].

$$\text{Photocatalyst} + hv \rightarrow e^-{}_{CB} + h^+{}_{VB} \tag{1}$$

$$H_2O_{(ads)} + h^+ \rightarrow {}^{\cdot}OH_{(ads)} + H^+{}_{(ads)} \tag{2}$$

$$h^+ + OH^- \rightarrow {}^{\cdot}OH_{(ads)} \tag{3}$$

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

$$O_2{}^{\cdot -}{}_{(ads)} + H^+ \rightarrow HO_2{}^{\cdot}{}_{(ads)} \tag{5}$$

$$HO_2{}^{\cdot}{}_{(ads)} \rightarrow O_2 + H_2O_{2(ads)} \tag{6}$$

$$H_2O_2 + {}^{\cdot}O_2{}^- \rightarrow OH^- + {}^{\cdot}OH + O_2 \tag{7}$$

$$H_2O_{2(ads)} + hv \rightarrow 2^{\cdot}OH_{(ads)} \tag{8}$$

$$\text{Pollutant } (h^+, {}^{\cdot}OH, HO_2{}^{\cdot} \text{ or } O_2{}^{\cdot-}) \rightarrow \text{pollutant degradation} \tag{9}$$

The efficiency of a photocatalyst is understood by indirect and direct mechanisms [14, 15, 19, 33, 35]. The indirect mechanism can be explained, based on the indirect oxidation photogenerated by the hole, on the surface of the semiconductor. In the case of direct mechanism, the action of the photogenerated holes occurs through the transfer of direct charge on the surface of the semiconductor, a fact explained by the adsorption (chemisorption) on the surface of the semiconductor [14, 15, 33]. Furthermore, it is known that the knowledge of these steps, in agreement with the kinetics and stoichiometry established for a given reaction, can generate a better understanding of the processes, facilitating the identification of the generated products, as well as facilitating the reactive phases and species important for the photocatalytic efficiency improvement [36].

3 Understanding the Role of Scavengers in Photocatalysis Using Nano-semiconductors

Not only is the efficiency of the degradation process important, but also the influence of each species on the degradation, and its interaction from the use of inhibitors and/or radical scavengers avoiding recombination between the charge. Because of this, the understanding and adjustment of the process efficiency are very important [26, 37], monitoring the mechanisms involved in photodegradation more reliable [37–40]. Recently, there have been several papers in the literature involving the use of radical scavengers to better understand the reactions involved. These works are distinguished by the wide variety of pollutants studied, and the structural modifications of different materials [38, 41, 42]. Some of these works are presented in chronological form as follows:

Samsudin et al. [43] synthesized $BiVO_4$ via the solid-liquid state reaction and evaluated its photocatalytic potential in the oxidation of MB dye (methylene blue). The study emphasized the role of scavengers of reactive species, such as hydrogen peroxide (H_2O_2), silver nitrate ($AgNO_3$), and methanol (CH_3OH), to elucidate the photocatalytic degradation. According to the authors, the presence of $AgNO_3$ generated an intensification in the photocatalytic activity, resulting in 100% degradation of MB in 120 min under visible light irradiation. This high activity is attributed to the action of the scavenger, its performance being strongly dependent on the surface area of the crystalline planes $\{010\}$ and $\{110\}$ of the synthesized $BiVO_4$.

Sanad et al. [38], synthesized ZnO, ZnS and ZnO-ZnS nanocomposites by the sol-gel method and evaluated the degradation of methylene blue, and eosin, dyes using electron scavenging agents ($AgNO_3$), holes (KI), hydroxyl radicals (isopropanol), and superoxides (benzoquinone), under UV light. They found that the incorporation of ZnO, on the surface of the ZnS, induces the stabilization of the oxide particles in order to reduce the recombination rate of the electron-hole pair, so causing the complete destruction of the organic pollutants. However, the hydroxyl radicals, and holes played predominant roles in the degradation of the dyes.

Liu et al. [42], by a simple solvothermic method, synthesized AgTiS from TiO_2/sepiolite for the photocatalytic system in the degradation of methyl orange. Specifically, the 5% AgTiS composite exhibited the best photocatalytic activity, with 100% of the dye degraded after 50 min UV light and 260 min visible light. For the entrapment of the active species, t-butanol (TBA, 1 mM), p-Benzoquinone (p-BQ, 1 mM) and ammonium oxalate (AO, 1 mM), were the scavengers of hydroxyl radicals ($^{\cdot}OH$), superoxide ($^{\cdot}O_2{}^{-}$), and holes (h^+), respectively. The degradation efficiency of methyl orange was slightly reduced by the addition of TBA, however the degradation was suppressed significantly in the presence of β-BQ and AO, indicating that $^{\cdot}O_2$ and h^+ play important roles in the degradation process. The results of this research highlighted the AgTiS composite as a promising catalyst for environmental protection applications.

Mohammadi et al. [44], when evaluating the degradation of MB dye using rGO-TiO_2 synthesized in a hydrothermal approach, pointed out how the electrons are the main active species in the photodegradation of MB by rGO-TiO_2. This behavior is taken into account, since, among the numerous reactive species scavengers evaluated, the addition of $AgNO_3$ considerably decreases the degradation efficiency, indicating that the electrons are the main active species during the degradation process, a result confirmed by the use of a electron scavenger. In addition, the oxygen rich species $^{\cdot}O_2{}^{-}$ also plays an important role in the photocatalytic process and contribute in the degradation of the molecule adsorbed on the surface of the TiO_2 nanocomposite.

Numerous semiconductors are applied in heterogeneous photocatalytic processes, with titanium dioxide (TiO_2–P25 from Degussa) being the most commonly employed. As already mentioned above, due to its excellent physico-chemical properties, such as chemical and photochemical sensitivity, high thermal stability, chemical stability over a wide range of pH, possibility of immobilization on solids, possibility of activation by sunlight, insolubility in water, non-toxic, and low cost, TiO_2 serves as reference material for the evaluation of other photocatalysts [26, 45–47]. However, due to the band gap of 3.2 eV (= 385 nm), its application is limited to the UV range, which represents only 4–5% of solar irradiation at sea level [23, 48]. In order to reverse this situation, different strategies, such as doping [48], chemical modification with transition metals [49], and nitridation [50], have been applied in order to modify the TiO_2 for use in the visible region [45, 46, 51, 52]. Among the classes of the alternative compounds are, for example, the titanates [52], the ferrites [53], the niobates [54], and stannates [55–57]. Another alternative is the combination of oxide-clays [58–61], used in the degradation of a variety of organic pollutants, which will be given a more specific approach in this work.

4 Nanosemiconductors Supported on Clays

Clays have a different, and interesting, set of characteristics and properties that make them promising in the catalytic processes [62]. In photocatalytic studies, the clay minerals have been used, recently, as support for the anchoring of semiconductors, developing more ecological photocatalysts with an appropriate crystalline structure and with a high surface area. Therefore, the combination of oxides with these clay substrates can improve the photo efficiency, compared to pure semiconductors, resulting in the presence of new energy levels favoring the occurrence of a greater number of photogenerated charges, so obtaining effective catalysts under sunlight, and decreasing the electron/hole recombination and the formation of toxic intermediates [59, 63].

The metallic oxide nanoparticles, such as TiO_2, are mainly studied for the photodecomposition of organic pollutants. However, it is difficult to recover them in solution which prevents adequate reuse, and there is the possibility of agglomeration in solution so reducing their active surface area. Thus, the immobilization of semiconductors in substrates can provide viable solutions to overcome these problems [64]. The intercalation of metal oxide nanoparticles in the interlamellar spacing of clay minerals could affect the photocatalytic activity of the semiconductor due to the difficulty of access to the surface of the intercalated semiconductor [65]. Thus, the incorporation of semiconductors in the structures of clay minerals is still a challenging alternative as a strategy to increase the photocatalytic activity of nanomaterials and their subsequent reuse [66]. However, these porous materials possess favorable properties for their substrate use, such as high adsorption capacity, non-corrosiveness, non-toxic, accessibility, availability, and good thermal and chemical stability [67], which make them an appropriate alternative in the field of environmental remediation. In recent years, different porous silicates such as montmorillonite [68], sepiolite [69], kaolinite [70], diatomita [71], and zeolites [72], have been used as a support to obtain photocatalytic composites.

Montmorillonite is a lamellar clay with a di-octahedral structure of type 2:1, expansivity, high surface area, and cation exchange capacity, being a material widely applied as a support for the dispersion of semiconductors in heterogeneous catalysis. Samples prepared by the precipitation of small crystals of TiO_2 on the montmorillonite surface were used in the photodegradation of the herbicide dimethachlor [65], and phenol [73], in aqueous solution, and exhibited remarkable catalytic efficiency by the mass of TiO_2 dispersed in the nanocomposites.

Among the lamellar clay minerals, vermiculite has a high load between the lamellae, and excellent physicochemical properties, such as high cation exchange capacity, interaction capacity with organic molecules, and variable interlamellar distance. Silicates, derived from the vermiculite form of materials are essentially exfoliated and chemically functionalized by an acid leaching process. TiO_2 nanoparticles were dispersed on the surface of the support to obtain highly efficient functional photocatalysts for the degradation of organic dyes in solution [74].

Functional compounds based on lamellar clay minerals still favor the separation of charges, after immobilization of the semiconductors, so favoring the non-recombination of the excitons. Zr-TiO_2/cloisite [63], and W-TiO_2/cloisite [75], were synthesized by the sol-gel method and their catalytic performance, under sunlight and visible light, was evaluated by the photodegradation of antipyrine and atrazine. The antipyrine photodegradation results, after six hours of testing, indicated the formation of small organic acids as intermediates that were finally decomposed into CO_2 so achieving a moderate mineralization of the drug. In the experiments for atrazine removal, the results showed that the nanocomposite has higher photocatalytic efficiency under sunlight than under visible light. TiO_2-cloisite heterostructures [59], and Ce-TiO_2/cloisite [58], made using the dispersion of semiconductor nanoparticles on the surface of exfoliated lamellar clay, were used as a photocatalyst in the degradation of rhodamine B and phenol under the irradiation of sunlight. The formed nanocomposites were shown to be promising for photodegradation of the dye and the phenolic compound. The results indicated that after 24 h of reaction, the total mineralization of the phenol, and the intermediate aromatic compounds formed, had been observed, thus reducing their initial toxicity. Figure 3 shows the nanostructured materials formed from the presence of the TiO_2 nanoparticles between the delaminated layers of the cloisite clay.

Different techniques of immobilization of semiconductors are used, such as the incorporation of species among the lamellar clay minerals, and subsequent calcination, that gives rise to thermally stable materials by the pillarization process, these materials being promising for the catalytic removal of organic pollutants dissolved in chains, due to the presence of acid sites and their permanent porosity [68, 76]. The thermal stability, adsorptive properties and catalytic activity of the clay minerals can be enhanced by their intercalation with precursor solutions of one or more metal cations. Generally, the most easily incorporated cation (e.g. Al^{3+}) may act alone as a pillarizing agent, or may be followed by the addition of a second cation forming a mixed pillar [77].

Abdennouri et al. [61] investigated the photocatalytic potential of a titanium oxide pillar clay for the decomposition of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP) pesticides in solution, which showed a high photocatalytic activity of the nanomaterial for the selective degradation of the pesticides. González et al. [68] investigated the photocatalytic activity for degradation of trimethoprim using titanium oxide doped with Cr^{3+} or Fe^{3+} doped clay. The Cr^{3+} doped solid presented better results in the degradation of the antibiotic in solution, reaching up to 76% of degradation in 180 min. Therefore, the pillar clays have a two-dimensional heterostructure that can prevent the agglomeration of oxide nanoparticles when incorporated in the interlamellar spacing, and exhibit high surface area and porosity, increasing the photocatalytic activity of the semiconductors [78].

Clays with fibrous morphology, such as sepiolite, have a structure consisting of blocks formed by an octahedral sheet of magnesium sandwiched between two tetrahedral silicon sheets, presenting cavities or tunnels along the c-axis, this structure being formed by channels of the zeolite type [69, 79]. Their structure, microporosity, high surface area, presence of silanol groups, and negative charge on the surface,

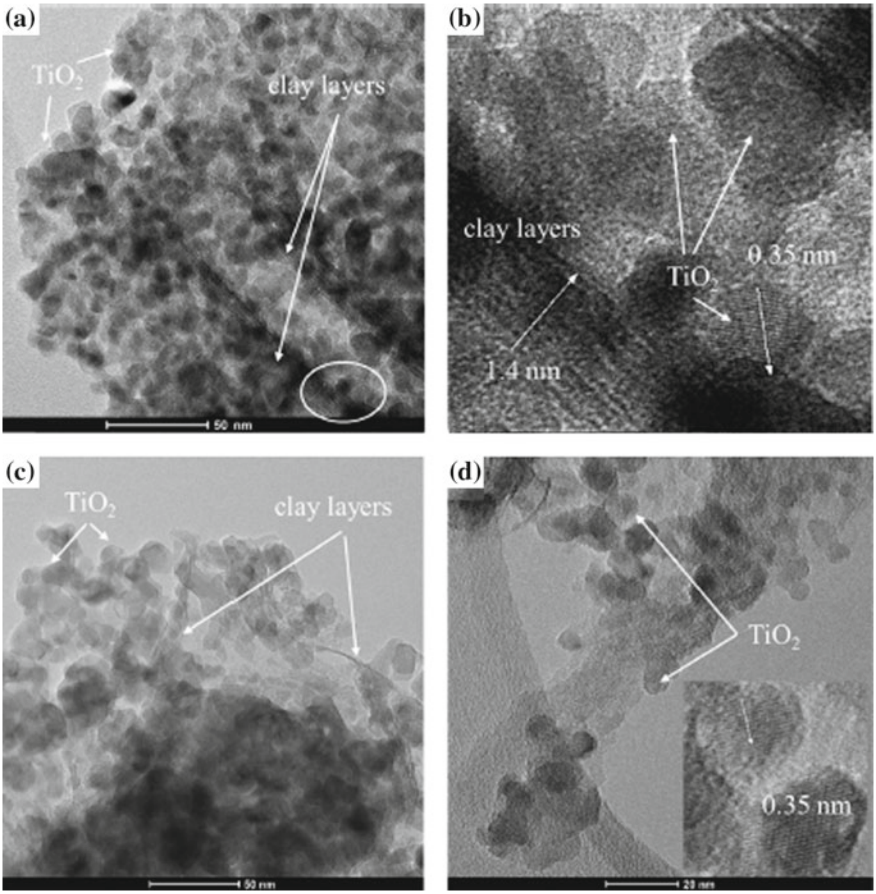

Fig. 3 Transmission electron micrographs (TEM) of the Zr-TiO_2/cloisite catalyst [63]

make the sepiolite materials attractive as supports for the anchoring of metallic oxides and applications in the photodegradation of organic pollutants. TiO_2/sepiolite photocatalysts show that sepiolite has a positive synergistic effect on TiO_2 photocatalytic activity for the degradation of phenolic compounds, which can be attributed to the high surface area obtained from the nanocomposite [69, 79].

Palygorskite is a fibrous silicate of magnesium, containing a significant presence of Al and Fe in its structure, with large crystals and a predominantly di-octahedral character. Nanostructured photocatalysts based on palygorskite were successfully prepared from the incorporation of different oxides in the microfibrous structure of this clay [80–82]. The studies showed the production of an inorganic-inorganic nanocomposite photocatalyst, in the visible spectrum, with high efficiency for the degradation of organic pollutants in aqueous solution.

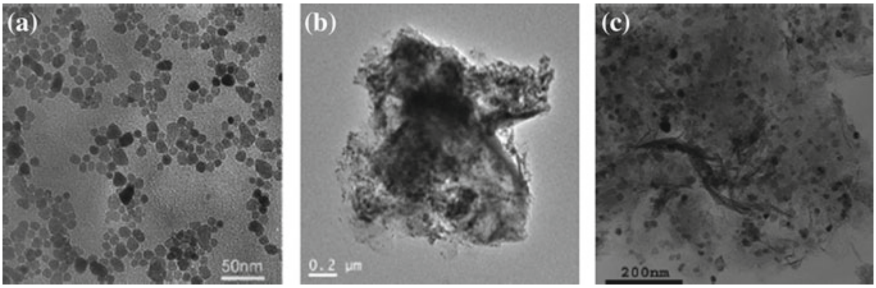

Fig. 4 TEM of the ZnO nanoparticles (**a**), ZnO/cloisite (**b**) and ZnO/Tunisian smectite (**c**) nanoarchitectures [85]

Nanocomposites based on ZnO anchored on the surface of clay minerals are widely reported in the literature for photocatalysis applications of organic compounds. Nanocomposites of ZnO/clays are highly reactive for the photodegradation of dyes in solution, showing good stability and activity, even after several cycles of reuse, with the ZnO: clay ratio being the determining factor of the photocatalysis potential [83, 84]. Figures 4 and 5 show the micrographs of the ZnO nanoparticles distribution on lamellar and fibrous clays, respectively.

Nanoparticles of TiO_2 and ZnO are generally the most used in the photocatalytic studies of nanomaterials based on clay minerals, but other nanocomposites based on different transition metals, for application in environmental remediation, can also be found in the literature [86–88]. Zhang and Yang [89] investigated the photocatalytic activity of cobalt oxide nanoparticles incorporated in halloysite nanotubes (HNTs). Figure 6 shows the scheme of the deposition of the nanoparticles on the clay surface and the proposed mechanism for the photodegradation of methylene blue dye. The authors investigated different oxide:clay ratios. The results indicated that the ratio by weight of 1:6 Co_3O_4 HNTs produced better results, reaching up to 97% of dye degradation. Hence, the combination of the catalytic properties of the cobalt oxide, with the adsorptive properties of the inorganic matrix, formed a nanomaterial with excellent properties for use in the environmental field for the removal of organic pollutants from aquatic effluents.

The various techniques applied for wastewater treatment have their advantages and disadvantages, such as cost, removal capacity, regeneration capacity, and reuse [90]. With advances in nanotechnology, the scientific community uses a lot of photocatalytic degradation to treat aquatic environments and this method has the main advantage, in relation to adsorption and other traditional methods, of the mineralization of the organic pollutant in CO_2 and water as complete photo-oxidation products [91–93]. But the formation of reaction intermediates may occur during the photocatalytic oxidation process, which, in many cases, may be even more harmful organic compounds than the initial pollutants themselves [94]. The TiO_2/zeolite photocatalyst promoted the rapid degradation, and made possible the elimination, of secondary pollution generated by the emission of harmful intermediates during the photocatalytic oxidation reactions of diethyl sulfate [94]. Zeolites are used as a strategy for the

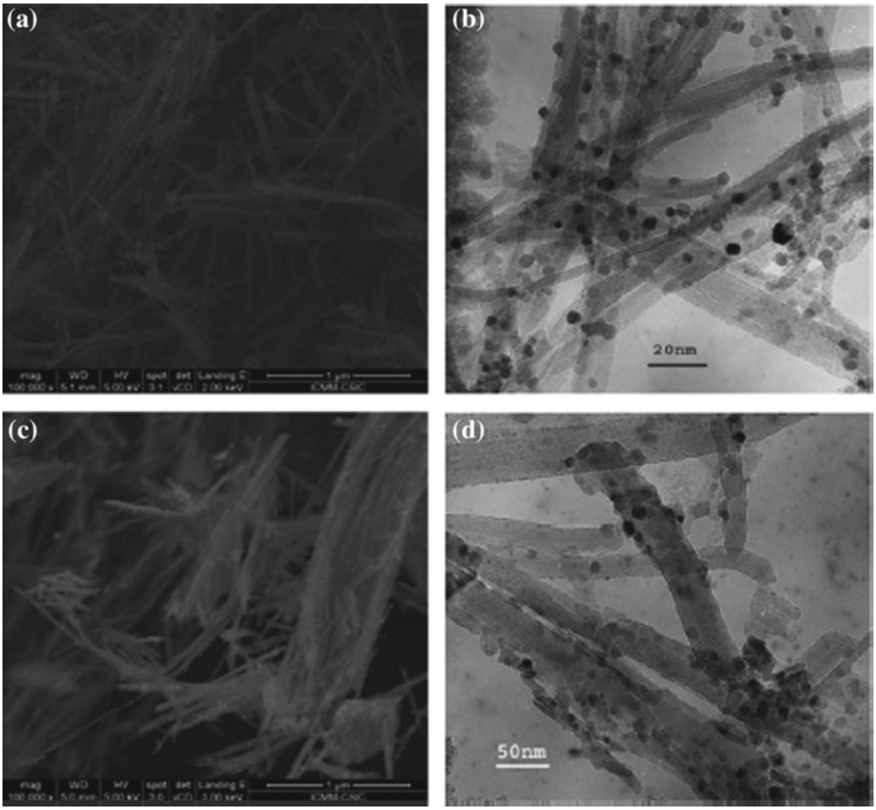

Fig. 5 SEM (**a** and **c**) and TEM (**b** and **d**) micrographs of the sepiolite based nanoarchitectures showing presence of ZnO nanoparticles covering the clay fibers [85]

development of greener catalysts, where the semiconductor, incorporated within the crystals of the zeolite, functions as an active site and the micropores of the support can be selective to diffuse the organic micropollutants in solution [95].

Therefore, the increased photocatalytic efficiency of the semiconductors incorporated in lamellar or fibrous clay minerals, and the zeolites, showed an excellent alternative material that can minimize the disadvantages such as rapid recombination of photoinduced electron-hole pairs, and the limited visible light absorption capacity semiconductors traditionally studied. Furthermore, they significantly improve the photo-efficiency of the functional materials, due to the increase of active sites, surface area, and a decrease in the formation of toxic intermediates during the photocatalysis process of organic pollutants, thus generating new selective and ecologically correct catalysts.

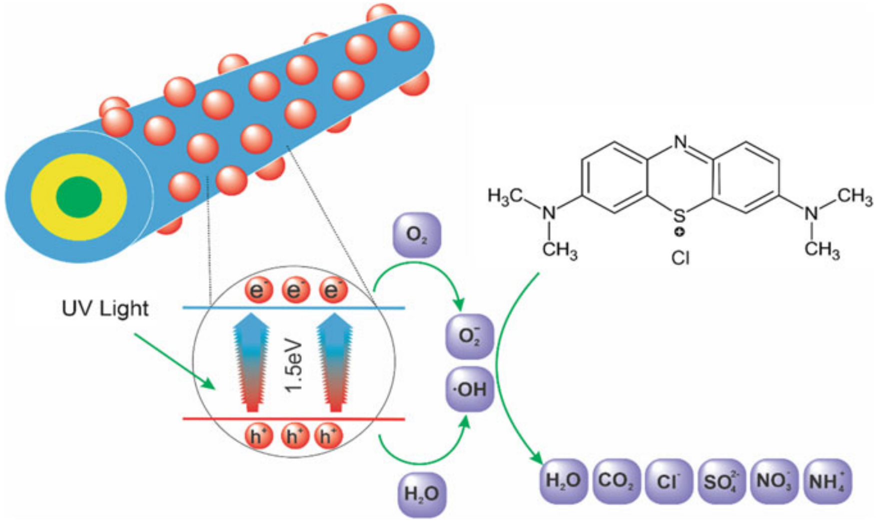

Fig. 6 Proposed mechanism for the photocatalytic activity of Co_3O_4 nanocomposite/HNTs in the photodegradation of MB under UV irradiation. Adapted from Zhang and Yang [89]

5 Operational Devices and Influence on the Degradation Effectiveness

The photocatalytic oxidation rates are highly dependent on several operational factors (photocatalyst concentration, pH of the solution to be degraded, concentration of pollutants, calcination temperature, intensity of light and irradiation time, dissolved oxygen, electrolyte effect and dopant) that affect the yield and efficiency of the process directed to the degradation of the organic compounds. In addition, another important factor is the structural characteristics of the materials and the potentials of the valence and conduction bands, which interfere directly in their performance [14, 15, 96–106]. In this sense, such parameters can be optimized in order to guarantee greater catalytic conversion and lower economic costs.

5.1 Effect of the Initial Concentration of the Organic Pollutant

The initial concentration of the organic contaminant is an important factor from the kinetic point of view, since, it interferes directly in the rate of photocatalytic oxidation. Initially, the rate of degradation is proportional to the increase in substrate concentration. As the oxidation proceeds, the rate of decomposition reaches a saturation that is related to the active surface of the semiconductor. In contrast, the photocatalytic rate is decreased with increasing irradiation time, while maintaining a fixed catalyst amount. The explanation for this decrease depends greatly on the semiconductor properties and the projected operating conditions [14, 15, 100, 104]. For Malato et al. [100], a series of tests, at different initial concentrations, were conducted to confirm whether or not the experimental results could be adjusted to the appropriate optimum pollutant concentration model.

5.2 Effect of the Amount of Catalyst

Normally the increase in the dosage of the photocatalyst gives the medium an increase of the active (OH, etc.), which in turn, react quickly, favoring the maximum of degradation and efficiency of the process. Although the direct ratio of efficiency and dosage guarantees maximum yields, after achieving the equilibrium of degradation at the optimized limit, the excess of particles of the photocatalyst decreases the rate of degradation as there is the dispersion and reduction of light penetration such that the solution blocks the radiation, so preventing the reaction from proceeding, and therefore, promotes a decreased effect of the photocatalytic performance [15, 101–103]. This behavior was also observed by Haque et al. [104] during the degradation of the antibiotic norfloxacin (0.25 mM), being investigated in different concentrations of Degussa P25, ranging from 0.5 to 3 g L^{-1}, in pH 6.8, for a duration 80 min.

5.3 Effect of pH

pH is a parameter that significantly affects the surface charge properties of the photocatalyst, so it is a very important variable in the photocatalytic processes. The analysis of the effects of pH on the efficiency in the photodegradation process is considered a complex assignment due to the numerous variables, such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate, and charged radicals, formed during the reaction process. These affect not only the particle charges, but also the size of the aggregates that can be produced, and still allow variations in the positions of the photocatalyst's electronic bands. Changes in pH tend to influence the rate of reaction as a function of the adsorption behavior between the organic molecules and the starting materials, ensuring an important step in the oxidation through simple, cheap, and efficient, optimization. Typically, the ionization state of the molecules can be protonated, or deprotonated, under acidic or alkaline conditions. In the literature, this concept is consolidated by TiO_2, taking into account its value of zero charge potential (PCZ), and its desired pH value, according to the written reactions $TiOH + H^+ - TiOH_2^+$//$TiOH + OH^- - TiO^- + H_2O$ [98, 100, 103, 104, 106, 107]. In the photocatalytic degradation of orange G dye, Sun et al. [108] showed that nitrogen doped TiO_2 (N: TiO_2) was responsible for the significant increase of dye degradation under visible light. In addition, it was found that lowering the pH of the solution from 6.5 to 2.0 increased the degradation efficiency from 32 to 99% during 150 min under visible light. In acidic conditions, the pH of the solution significantly influences the degradation, with 2.0 being the optimum pH studied.

Maddila et al. [109] reported the influence of pH on the degradation of the bromoxynil pesticide using CS-TiO_2 as a photocatalyst. The degradation experiments were performed at pH values of 3, 7 and 11. Their results indicated that the process efficiency was improved with increasing pH from 3 to 11. As the solution became alkaline, the decomposition rate for secondary oxidants, such as the hydroxyl radical, increased, thereby favoring the process. The optimum pH during these experiments was 11, the pH variation study being useful to understand the process mechanism with the highest degree of removal.

5.4 Intensity and Source of Irradiation

The effect of intensity of the light on the rate of degradation of the target molecule also depends on the type of photocatalyst, and it is expected that different behaviors will be observed according to the intensity. In this sense, at low intensities, the rate of degradation increases linearly, as its intensity increases gradually. This relationship is plausible if it is considered that in reactions involving low light intensity, the formation of electrons/holes are in the majority and avoid recombination between charges. However, in increasing light intensity, there is a competition between the separation of the charge carriers and their recombination, thus generating a negative effect on the rate of the photocatalytic reaction [14, 15, 98, 105, 110]. Also in this context, the increase of the irradiation time is expected to favor degradation kinetics, otherwise, there is competition between the substrate and the photogenerated intermediates making the process difficult.

There are other parameters that directly, and/or indirectly, affect the photocatalytic efficiency. When using interfering substances such as chlorides (Cl^-), carbonates (CO_3^{2-}), nitrates (NO_3^-), and phosphates (PO_4^{3-}), they may act by blocking or deactivating the oxidative rate during the photocatalytic process due to the interaction and/or adsorption of the ions with the sites of the photocatalysts [96, 97, 105, 106]. Depending on the pH of the solution, these species can compete directly with the model pollutant and influence the overall rate of photocatalytic oxidation. Other substances and parameters may also interfere positively, or negatively, with photocatalytic efficiency (H_2O_2, Ag^+), depending on the reaction medium. The velocity kinetics provides the real interpretation regarding the removal and mineralization of the contaminants. In the same way, parameters derived from the form and type of reactor, such as geometry, light distribution, and flow type, play an important role in the photocatalytic reactions involved.

The literature reports several works involving the variation of these parameters to evaluate the degradation of compounds (pesticide dyes and drugs) [38, 97, 111–115].

These works bring wide versatility and the possibility of their uses against different materials used as photocatalysts.

6 Photocatalytic Degradation of Organic Contaminants for Environmental Treatment

In agreement with the photocatalytic treatment and the use of semiconductive nanoparticles, the photocatalytic degradation of toxic compounds depends on several factors that have already been mentioned in the previous section, and help in the comprehension and interpretation of the photogenerated mechanisms after the process [116].

The most common pollutants in wastewater comprise mainly dyes, pesticides, pharmaceuticals, heavy metal ions, radioactive substances, and polyaromatic hydrocarbons, among many others [117, 118]. These contaminants classed as organic and inorganic, depending on their chemical composition [117, 118]. Table 1 shows the schematic representation of pollutant publications via photocatalytic treatments tested in the last decade. The search only pertains to articles such as the type of document evaluated in the databases.

In analyzing the presented values as showed in Table 1, it was noted how many studies on dyes have been expressly discussed in the past ten years. Considering the articles found, followed by the expressions: (1) dyes, (2) dyes and photocatalytic application, and (3) dyes and photocatalytic treatment, it was verified that the dyes are presented in a number of publications three times greater than that for pesticides,

Table 1 Number of articles found in the Web of Science, and Scopus databases, related to the mentioned pollutants and their usual combinations involved in the photocatalytic process

Description	Web of Science	Scopus
Organic contaminants	15,876	12,776
Organic contaminants and photocatalytic treatment	529	255
Organic contaminants and photocatalytic application	399	196
Pesticides	42,985	45,479
Dyes	119,589	156,005
Pharmaceuticals	78,139	134345
Pesticides and photocatalytic application	110	55
Dyes and photocatalytic application	2,627	2,758
Pharmaceuticals and photocatalytic application	211	118
Pesticides and photocatalytic treatment	237	117
Dyes and photocatalytic treatment	2,559	2,682
Pharmaceuticals and photocatalytic treatment	561	234

Obviously, the number found corresponds to articles concerning diverse applications, not only photocatalytic degradation. The same was observed for the two other pollutants. However, when taken into account for photocatalytic applications, this ratio is larger according to the information from both databases.

Dyes are substances soluble in the medium in which they are present, and are used to attribute permanent color to other materials, absorb light in the visible region of the electromagnetic spectrum, and have a chromophore group in their structure [119]. Synthetic dyes are generally used to color fabrics and textile fibers, and dyes are most commonly found in environmental remediation studies from industrial effluents. Dyes can be classified according to their structure, such as anthraquinones and azo dyes, or they can be classified according to the type of interaction with the textile fiber. From the different interactions, the synthetic dyes can be classified according to Salleh et al. [120]. Reactive dyes have in their structure a reactive group capable of forming a covalent bond with cellulose. They are usually represented by anthraquinones and azo dyes. Direct dyes have interactions with the fiber through Van der Waals forces. A dye class consisting of compounds having more than one azo group in their structure (diazo, triazo), Azo dyes are usually are synthesized on the fiber through a coupling agent. Acid dyes are a group of anion dyes that have three sulfonic groups [2, 14, 120, 121]. Dispersive dyes are generally stabilized in the fibers with the aid of long chain dispersing agents. Several works are found in the literature with the purpose of investigating the removal of these dyes in solution through photochemical reaction using semiconductors as photocatalysts [122–125].

The kinetics of photocatalytic degradation of methylene blue (MB) cationic dye has been reported in the literature. Dariani et al. [126] investigated the photodegradation and mineralization of this dye using TiO_2 under UV light irradiation. The results showed that photocatalysis is an excellent technique for discoloration of the MB dye in solution, reaching up to 90% of complete degradation in 2 h of reaction.

Rhodamine B cationic dye is also present in several studies that address dyes as polluting wastewater models. Fu et al. [127] investigated the photodegradation of Rhodamine B under visible light irradiation using Bi_2WO_6 nanoparticles. The results indicate that the decomposition of the RB by the semiconductor probably does not involve the $^{\cdot}OH$ radicals, and in this case, it may be due to the reaction between the directly photogenerated hole with the RB.

An azo dye used in the literature, in research involving photocatalysis for the degradation of emergent pollutants, is methyl orange (MO). Kulkarni et al. [111] used $ZnFe_2O_4$@ZnO nanoparticles to investigate the photodegradation of MO under visible and UV irradiation. The band gap of the material makes it a good photocatalyst in the visible region, leading to complete degradation of MO in 9 h.

For years, various pesticides are continually being released into the environment via processes from agriculture that, when left untreated, pose risks to biodiversity, terrestrial ecosystems, as well as the life of all living beings [128, 129]. Since then, compliance with strict quality standards is required in the case of toxic substances [130], such as pesticides, which are assessed by international and governmental bodies as to their physicochemical, toxicological and ecotoxicological properties, ensuring compliance with requirements and corrective measures for their use and safety [131, 132].

Pesticides are essential chemical compounds and they are effective tools to control agricultural pests, and/or weeds and insects, that would adversely affect agricultural productivity [132, 133]. Currently, most of the pesticides used are based on semi-volatile organic matter and can react strongly with species such as hydroxyl (OH), ozone (O_3), and nitrate (NO_3) [134]. As these contaminants are non-biodegradable, toxic, and strongly persistent in the environment [130, 135, 136], they become a cumulative problem in the long run. In this sense, treatment by efficient purification technologies is recommended, as well as for the other contaminants highlighted in this chapter, with photocatalytic degradation being the target of studies for the scientific community due to its uses, benefits, and adverse potential.

Contamination by chlorine compounds such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP), in aqueous solution, were evaluated against photocatalytic activity using purified and pounded clays with TiO_2 [61]. According to the authors, the photocatalysts effectively degrade the selected pesticides, where the activity of the TiO_2 pillarized clay sample is lower than pure TiO_2 due to poor surface accessibility of TiO_2 is the amorphous phase of the TiO_2 pillars. Nevertheless, a titanium intercalation, in the intermediate layer of clays, is one of the most promising methods to improve the photocatalysis, varying the percentages of the oxide present [61].

Atrazine is a herbicide, and/or triazine pesticide, widely used in pest control in agriculture, although it is of great concern because of its persistence and toxicity [133, 137]. Xue et al. [137], visible light-sensitive BiOBr/UiO-66 was synthesized and applied to the degradation of atrazine. Operational parameters, such as pH, presence of anions, inorganic cations, and water type, were investigated extensively in this study. The results showed that BiOBr/UiO-66 exhibited higher and better photocatalytic performance over pure BiOBr. Atrazine was rapidly degraded under acidic conditions ($pH = 3.1$) and strongly inhibited by HCO_3^- and the SO_4^{2-}, being the inorganic cations few influential in the degradation. Finally, atrazine degradation pathways were investigated via LC-MS/MS [137].

In the case of pharmaceutical micropollutants in the environment, they are seen as a hazard to health, water quality and, above all, food safety, due to the formation of metabolites of unknown nature [138, 139]. The concentrations of drugs released into the sewage system are affected by numerous conditions ranging from their manufacture to the seasons, climate, pH, temperature, the type of sewage involved, and other factors [140]. Drugs are substances absorbed by the body. Moreover, they are developed to be persistent, maintaining their chemical properties enough to guarantee their desired purpose [141–143].

On the issue of water decontamination, Bayan et al. [144] synthesized spheres composed of CdS by the simple hydrothermal method and they used them to evaluate the photocatalytic degradation of the drugs, acetaminophen and levofloxacin, under irradiation of visible light. Both drugs were degraded to more than 95% after 4 h of visible light irradiation. Stability was also evaluated by reusing the sample, after four cycles, indicating the high stability of the synthesized sample. Thus, CdS beads are useful, reusable, materials for the photocatalytic degradation of pharmaceuticals.

Ibuprofen is one of the most harmful drugs found in wastewater effluents [145]. In this study, its degradation was evaluated using TiO_2 nanoparticles with different ratios of the anatase/brookite phases. As for the degradation, 100% was achieved with a mixture containing TiO_2 61.8% of anatase and 38.2% of brookite. For the authors, this high oxidation rate is due to the mixture's synergistic effect, high surface area, and mesoporous structure. The photocatalyst, prepared under specific conditions, was considered very stable after eight cycles of reuse, without presenting significant losses to its photocatalytic performance [145].

7 Final Considerations

Due to the growing concern about the presence of these organic contaminants in the environment and their possible effects, researchers are increasingly investigating ways to minimize the disposal of these pollutants, because despite the numerous technologies for their remediation, there is still a deficit about their real effects and affinities in the environment and in the lives of all human beings. In addition, an assessment of the possibility of reducing, minimizing or treating at a lower cost is essential, thus ensuring the required acceptance by environmental standards and requirements. Another persistent approach is the complexity of effluents from which the treatment is discarded in isolation, i.e., if there are no standardized treatment procedures, it is feasible to handle it in isolation or in combination when possible. Tests of treatability, identification, ecotoxicity, antibacterials and others are extremely important in monitoring removal efficiency. Therefore, to know the impacts, establishing concentration standards and acceptable limits for the dismissal of unemployment insurance actions upon payment and maintenance of their health, well-being, health and quality of life for future.

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References

1. Giannakis, S., Gamarra Vives, F.A., Grandjean, D., Magnet, A., De Alencastro, L.F., Pulgarin, C.: Effect of advanced oxidation processes on the micropollutants and the effluent organic matter contained in municipal wastewater previously treated by three different secondary methods. Water Res. **84**, 295–306 (2015)
2. Brillas, E., Martínez-Huitle, C.A.: Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. Appl. Catal. B: Environ. **166–167**, 603–643 (2015)

3. Moreira, F.C., Boaventura, R.A.R., Brillas, E., Vilar, V.J.P.: Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. Appl. Catal. B: Environ. **202**, 217–261 (2017)
4. Babuponnusami, A., Muthukumar, K.: A review on Fenton and improvements to the Fenton process for wastewater treatment. J. Environ. Chem. Eng. **2**, 557–572 (2014)
5. Bel Hadjltaief, H., Ben Ameur, S., Da Costa, P., Ben Zina, M., Elena Galvez, M.: Photocatalytic decolorization of cationic and anionic dyes over ZnO nanoparticle immobilized on natural Tunisian clay. Appl. Clay Sci. **152**, 148–157 (2018)
6. Bel Hadjltaief, H., Da Costa, P., Galvez, M.E., Ben Zina, M.: Influence of operational parameters in the heterogeneous photo-Fenton discoloration of wastewaters in the presence of an iron-pillared clay. Ind. Eng. Chem. Res. **52**, 16656–16665 (2013)
7. Puangpetch, T., Sreethawong, T., Yoshikawa, S., Chavadej, S.: Synthesis and photocatalytic activity in methyl orange degradation of mesoporous-assembled $SrTiO_3$ nanocrystals prepared by sol–gel method with the aid of structure-directing surfactant. J. Mol. Catal. A: Chem. **287**, 70–79 (2008)
8. Augugliaro, V., Litter, M., Palmisano, L., Soria, J.: The combination of heterogeneous photocatalysis with chemical and physical operations: a tool for improving the photoprocess performance. J. Photochem. Photobiol. C: Photochem. Rev. **7**, 127–144 (2006)
9. De Araújo, K.S., Antonelli, R., Gaydeczka, B., Granato, A.C., Malpass, G.R.P.: Advanced oxidation processes: a review regarding the fundamentals and applications in wastewater treatment and industrial wastewater. Ambient. Agua – Interdiscip. J. Appl. Sci. **11**, 387 (2016)
10. Ghiasi, M., Malekzadeh, A.: Solar photocatalytic degradation of methyl orange over $La_{0.7}Sr_{0.3}MnO_3$ nano-perovskite. Sep. Purif. Technol. **134**, 12–19 (2014)
11. Bethi, B., Sonawane, S.H., Bhanvase, B.A., Gumfekar, S.P.: Nanomaterials-based advanced oxidation processes for wastewater treatment: a review. Chem. Eng. Process. Process Intensif. **109**, 178–189 (2016)
12. Cheng, M., Zeng, G., Huang, D., Lai, C., Xu, P., Zhang, C., Liu, Y.: Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: a review. Chem. Eng. J. **284**, 582–598 (2016)
13. Ribeiro, A.R., Nunes, O.C., Pereira, M.F.R., Silva, A.M.T.: An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. Environ. Int. **75**, 33–51 (2015)
14. Rauf, M.A., Meetani, M.A., Hisaindee, S.: An overview on the photocatalytic degradation of azo dyes in the presence of TiO_2 doped with selective transition metals. Desalination **276**, 13–27 (2011)
15. Rauf, M.A., Ashraf, S.S.: Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution. Chem. Eng. J. **151**, 10–18 (2009)
16. Byrne, C., Subramanian, G., Pillai, S.C.: Recent advances in photocatalysis for environmental applications. J. Environ. Chem. Eng. **6**, 3531–3555 (2017)
17. Wetchakun, K., Wetchakun, N., Sakulsermsuk, S.: An overview of solar/visible light-driven heterogeneous photocatalysis for water purification: TiO_2-and ZnO-based photocatalysts used in suspension photoreactors. J. Ind. Eng. Chem. **71**, 19–49 (2019)
18. Fujishima, A., Honda, K.: Electrochemical photolysis of water at a semiconductor electrode. Nature **238**, 37–38 (1972)
19. Kabra, K., Chaudhary, R., Sawhney, R.L.: Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: a review. Ind. Eng. Chem. Res. **43**, 7683–7696 (2004)
20. Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., Bahnemann, D.W.: Understanding TiO_2 photocatalysis: mechanisms and materials. Chem. Rev. **114**, 9919–9986 (2014)
21. Serpone, N., Emeline, A.V., Horikoshi, S., Kuznetsov, V.N., Ryabchuk, V.K.: On the genesis of heterogeneous photocatalysis: a brief historical perspective in the period 1910 to the mid-1980s. Photochem. Photobiol. Sci. **11**, 1121–1150 (2012)

22. Bora, L.V., Mewada, R.K.: Visible/solar light active photocatalysts for organic effluent treatment: fundamentals, mechanisms and parametric review. Renew. Sustain. Energy Rev. **76**, 1393–1421 (2017)
23. Athanasekou, C.P., Likodimos, V., Falaras, P.: Recent developments of TiO_2 photocatalysis involving advanced oxidation and reduction reactions in water. J. Environ. Chem. Eng. **6**, 7386–7394 (2018)
24. Shen, S., Kronawitter, C., Kiriakidis, G.: An overview of photocatalytic materials. J. Mater. **3**, 1–2 (2017)
25. Yasmina, M., Mourad, K., Mohammed, S.H., Khaoula, C.: Treatment heterogeneous photocatalysis; factors influencing the photocatalytic degradation by TiO_2. Energy Procedia **50**, 559–566 (2014)
26. Qian, R., Zong, H., Schneider, J., Zhou, G., Zhao, T., Li, Y., Yang, J., Bahnemann, D.W., Pan, J.H.: Charge carrier trapping, recombination and transfer during TiO_2 photocatalysis: an overview. Catal. Today **335**, 78–90 (2018)
27. Kumar, S.G., Rao, K.S.R.K.: Comparison of modification strategies towards enhanced charge carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO_2, WO_3 and ZnO). Appl. Surf. Sci. **391**, 124–148 (2017)
28. Hitkari, G., Singh, S., Pandey, G.: Photoluminescence behavior and visible light photocatalytic activity of ZnO, ZnO/ZnS and ZnO/ZnS/α-Fe_2O_3 nanocomposites. Trans. Nonferrous Met. Soc. China **28**, 1386–1396 (2018)
29. Senasu, T., Nanan, S.: Photocatalytic performance of CdS nanomaterials for photodegradation of organic azo dyes under artificial visible light and natural solar light irradiation. J. Mater. Sci.: Mater. Electron. **28**, 17421–17441 (2017)
30. Ângelo, J., Andrade, L., Madeira, L.M., Mendes, A.: An overview of photocatalysis phenomena applied to NOx abatement. J. Environ. Manag. **129**, 522–539 (2013)
31. Pawar, R.C., Lee, C.S.: Basics of photocatalysis. In: Heterogeneous Nanocomposite-Photocatalysis for Water Purification, pp. 1–23. Elsevier (2015)
32. Molinari, R., Lavorato, C., Argurio, P.: Recent progress of photocatalytic membrane reactors in water treatment and in synthesis of organic compounds. A review. Catal. Today **281**, 144–164 (2017)
33. Ajmal, A., Majeed, I., Malik, R.N., Idriss, H., Nadeem, M.A.: Principles and mechanisms of photocatalytic dye degradation on TiO_2 based photocatalysts: a comparative overview. RSC Adv. **4**, 37003–37026 (2014)
34. Zhang, L., Mohamed, H.H., Dillert, R., Bahnemann, D.: Kinetics and mechanisms of charge transfer processes in photocatalytic systems: a review. J. Photochem. Photobiol. C: Photochem. Rev. **13**, 263–276 (2012)
35. Kumar, P.S., Lakshmi Prabavathi, S., Indurani, P., Karuthapandian, S., Muthuraj, V.: Light assisted synthesis of hierarchically structured Cu/CdS nanorods with superior photocatalytic activity, stability and photocatalytic mechanism. Sep. Purif. Technol. **172**, 192–201 (2017)
36. Turchi, C., Ollis, D.F.: Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack. J. Catal. **122**, 178–192 (1990)
37. Palominos, R., Freer, J., Mondaca, M.A., Mansilla, H.D.: Evidence for hole participation during the photocatalytic oxidation of the antibiotic flumequine. J. Photochem. Photobiol. A: Chem. **193**, 139–145 (2008)
38. Sanad, M.F., Shalan, A.E., Bazid, S.M., Abdelbasir, S.M.: Pollutant degradation of different organic dyes using the photocatalytic activity of ZnO@ZnS nanocomposite materials. J. Environ. Chem. Eng. **6**, 3981–3990 (2018)
39. Pastrana-Martínez, L.M., Morales-Torres, S., Likodimos, V., Figueiredo, J.L., Faria, J.L., Falaras, P., Silva, A.M.T.: Advanced nanostructured photocatalysts based on reduced graphene oxide-TiO_2 composites for degradation of diphenhydramine pharmaceutical and methyl orange dye. Appl. Catal. B: Environ. **123–124**, 241–256 (2012)
40. Chen, F., Yang, Q., Niu, C., Li, X., Zhang, C., Zhao, J., Xu, Q., Zhong, Y., Deng, Y., Zeng, G.: Enhanced visible light photocatalytic activity and mechanism of $ZnSn(OH)_6$ nanocubes modified with AgI nanoparticles. Catal. Commun. **73**, 1–6 (2016)

41. Chen, F., Yang, Q., Li, X., Zeng, G., Wang, D., Niu, C., Zhao, J., An, H., Xie, T., Deng, Y.: Hierarchical assembly of graphene-bridged $Ag_3PO_4/Ag/BiVO_4(040)$ Z-scheme photocatalyst: an efficient, sustainable and heterogeneous catalyst with enhanced visible-light photoactivity towards tetracycline degradation under visible light irradiation. Appl. Catal. B: Environ. **200**, 330–342 (2017)
42. Liu, R., Ji, Z., Wang, J., Zhang, J.: Solvothermal synthesized Ag-decorated TiO_2/sepiolite composite with enhanced UV–vis and visible light photocatalytic activity. Microporous Mesoporous Mater. **266**, 268–275 (2018)
43. Samsudin, M.F.R., Siang, L.T., Sufian, S., Bashiri, R., Mohamed, N.M., Ramli, R.M.: Exploring the role of electron-hole scavengers on optimizing the photocatalytic performance of $BiVO_4$. Mater. Today Proc. **5**, 21703–21709 (2018)
44. Mohammadi, M., Rezaee Roknabadi, M., Behdani, M., Kompany, A.: Enhancement of visible and UV light photocatalytic activity of rGO-TiO_2 nanocomposites: the effect of TiO_2/graphene oxide weight ratio. Ceram. Int. **45**, 12625–12634 (2019)
45. Baeissa, E.S.: Environmental remediation of aqueous methyl orange dye solution via photocatalytic oxidation using Ag-$GdFeO_3$ nanoparticles. J. Alloys Compd. **678**, 267–272 (2016)
46. Inagaki, C.S., Reis, A.E. da S., Oliveira, N.M., Paschoal, V.H., Mazali, Í.O., Alfaya, A.A.S.: Use of SiO_2/TiO_2 nanostructured composited in textiles dyes and their photodegradation. Quim. Nova **38**, 1037–1043 (2015)
47. George, R., Bahadur, N., Singh, N., Singh, R., Verma, A., Shukla, A.K.: Environmentally benign TiO_2 nanomaterials for removal of heavy metal ions with interfering ions present in tap water. Mater. Today Proc. **3**, 162–166 (2016)
48. Sanzone, G., Zimbone, M., Cacciato, G., Ruffino, F., Carles, R., Privitera, V., Grimaldi, M.G.: Ag/TiO_2 nanocomposite for visible light-driven photocatalysis. Superlattices Microstruct. **123**, 394–402 (2018)
49. Litter, M.I.: Heterogeneous photocatalysis: transition metal ions in photocatalytic systems. Appl. Catal. B: Environ. **23**, 89–114 (1999)
50. Ansari, S.A., Khan, M., Ansari, O.: Nitrogen-doped titanium dioxide (N-doped TiO_2) for visible light photocatalysis. New J. Chem. **40**, 3000–3009 (2016)
51. Grabowska, E.: Selected perovskite oxides: characterization, preparation and photocatalytic properties—a review. Appl. Catal. B: Environ. **186**, 97–126 (2016)
52. Song, S., Xu, L., He, Z., Ying, H., Chen, J., Xiao, X., Yan, B.: Photocatalytic degradation of C.I. Direct Red 23 in aqueous solutions under UV irradiation using $SrTiO_3/CeO_2$ composite as the catalyst. J. Hazard. Mater. **152**, 1301–1308 (2008)
53. Hu, R., Li, C., Wang, X., Sun, Y., Jia, H., Su, H., Zhang, Y.: Photocatalytic activities of $LaFeO_3$ and La_2FeTiO_6 in p-chlorophenol degradation under visible light. Catal. Commun. **29**, 35–39 (2012)
54. de Souza, J.K.D., Honório, L.M.C., Ferreira, J.M., Torres, S.M., Santos, I.M.G., Maia, A.S.: Layered niobate KNb_3O_8 synthesized by the polymeric precursor method. Cerâmica **64**, 104–108 (2018)
55. Lucena, G.L., De Lima, L.C., Honório, L.M.C., De Oliveira, A.L.M., Tranquilim, R.L., Longo, E., De Souza, A.G., Maia, A. da S., dos Santos, I.M.G.: $CaSnO_3$ obtained by modified Pechini method applied in the photocatalytic degradation of an azo dye. Ceramica. **63**, 536–541 (2017)
56. Honorio, L.M.C., Santos, M.V.B., da Silva Filho, E.C., Osajima, J.A., Maia, A.S., dos Santos, I.M.G.: Alkaline earth stannates applied in photocatalysis: prospection and review of literature. Cerâmica **64**, 559–569 (2018)
57. Teixeira, A.R.F.A., de Meireles Neris, A., Longo, E., de Carvalho Filho, J.R., Hakki, A., Macphee, D., dos Santos, I.M.G.: $SrSnO_3$ perovskite obtained by the modified Pechini method—insights about its photocatalytic activity. J. Photochem. Photobiol. A: Chem. **369**, 181–188 (2019)
58. Belver, C., Bedia, J., Álvarez-Montero, M.A., Rodriguez, J.J.: Solar photocatalytic purification of water with Ce-doped TiO_2/clay heterostructures. Catal. Today **266**, 36–45 (2016)

59. Belver, C., Bedia, J., Rodriguez, J.J.: Titania–clay heterostructures with solar photocatalytic applications. Appl. Catal. B: Environ. **176–177**, 278–287 (2015)
60. Szczepanik, B.: Photocatalytic degradation of organic contaminants over clay-TiO_2 nanocomposites: a review. Appl. Clay Sci. **141**, 227–239 (2017)
61. Abdennouri, M., Baâlala, M., Galadi, A., El Makhfouk, M., Bensitel, M., Nohair, K., Sadiq, M., Boussaoud, A., Barka, N.: Photocatalytic degradation of pesticides by titanium dioxide and titanium pillared purified clays. Arab. J. Chem. **9**, S313–S318 (2016)
62. Mccabe, R.W., Adams, J.M.: Clay minerals as catalysts. In: Developments in Clay Science, vol. 5, pp. 491–538. Elsevier (2013)
63. Belver, C., Bedia, J., Rodriguez, J.J.: Zr-doped TiO_2 supported on delaminated clay materials for solar photocatalytic treatment of emerging pollutants. J. Hazard. Mater. **322**, 233–242 (2017)
64. Hassani, A., Khataee, A., Karaca, S.: Photocatalytic degradation of ciprofloxacin by synthesized TiO_2 nanoparticles on montmorillonite: effect of operation parameters and artificial neural network modeling. J. Mol. Catal. A: Chem. **409**, 149–161 (2015)
65. Belessi, V., Lambropoulou, D., Konstantinou, I., Katsoulidis, A., Pomonis, P., Petridis, D., Albanis, T.: Structure and photocatalytic performance of TiO_2/clay nanocomposites for the degradation of dimethachlor. Appl. Catal. B: Environ. **73**, 292–299 (2007)
66. Meng, X., Qian, Z., Wang, H., Gao, X., Zhang, S., Yang, M.: Sol-gel immobilization of SiO_2/TiO_2 on hydrophobic clay and its removal of methyl orange from water. J. Sol-Gel Sci. Technol. **46**, 195–200 (2008)
67. Bel Hadjltaief, H., Galvez, M.E., Ben Zina, M., Da Costa, P.: TiO_2/clay as a heterogeneous catalyst in photocatalytic/photochemical oxidation of anionic reactive blue 19. Arab. J. Chem. (2014)
68. González, B., Trujillano, R., Vicente, M.A., Rives, V., Korili, S.A., Gil, A.: Photocatalytic degradation of trimethoprim on doped Ti-pillared montmorillonite. Appl. Clay Sci. **167**, 43–49 (2019)
69. Zhang, Y., Wang, D., Zhang, G.: Photocatalytic degradation of organic contaminants by TiO_2/sepiolite composites prepared at low temperature. Chem. Eng. J. **173**, 1–10 (2011)
70. Lopes, J. da S., Rodrigues, W.V., Oliveira, V.V., Braga, A. do N.S., da Silva, R.T., França, A.A.C., da Paz, E.C., Osajima, J.A., da Silva Filho, E.C.: Modification of kaolinite from Pará/Brazil region applied in the anionic dye photocatalytic discoloration. Appl. Clay Sci. **168**, 295–303 (2019)
71. Wang, B., Zhang, G., Leng, X., Sun, Z., Zheng, S.: Characterization and improved solar light activity of vanadium doped TiO_2/diatomite hybrid catalysts. J. Hazard. Mater. **285**, 212–220 (2015)
72. Sun, Q., Hu, X., Zheng, S., Sun, Z., Liu, S., Li, H.: Influence of calcination temperature on the structural, adsorption and photocatalytic properties of TiO_2 nanoparticles supported on natural zeolite. Powder Technol. **274**, 88–97 (2015)
73. Kun, R., Mogyorósi, K., Dékány, I.: Synthesis and structural and photocatalytic properties of TiO_2/montmorillonite nanocomposites. Appl. Clay Sci. **32**, 99–110 (2006)
74. Wang, L., Wang, X., Cui, S., Fan, X., Zu, B., Wang, C.: TiO_2 supported on silica nanolayers derived from vermiculite for efficient photocatalysis. Catal. Today **216**, 95–103 (2013). https://doi.org/10.1016/j.cattod.2013.06.026
75. Belver, C., Han, C., Rodriguez, J.J., Dionysiou, D.D.: Innovative W-doped titanium dioxide anchored on clay for photocatalytic removal of atrazine. Catal. Today **280**, 21–28 (2017)
76. Vicente, M.A., Gil, A., Bergaya, F.: Pillared clays and clay minerals. Handb. Clay Sci. **10**(5), 523–557 (2013)
77. Galeano, L.A., Vicente, M.Á., Gil, A.: Catalytic degradation of organic pollutants in aqueous streams by mixed Al/M-pillared clays (M = Fe, Cu, Mn). Catal. Rev. Sci. Eng. **56**, 239–287 (2014)
78. Yang, J.-H., Piao, H., Vinu, A., Elzatahry, A.A., Paek, S.-M., Choy, J.-H.: TiO_2-pillared clays with well-ordered porous structure and excellent photocatalytic activity. RSC Adv. **5**, 8210–8215 (2015)

79. Aranda, P., Kun, R., Martín-Luengo, M.A., Letaïef, S., Dékány, I., Ruiz-Hitzky, E.: Titania-sepiolite nanocomposites prepared by a surfactant templating colloidal route. Chem. Mater. **20**, 84–91 (2008)
80. Chen, D., Du, Y., Zhu, H., Deng, Y.: Synthesis and characterization of a microfibrous TiO_2-CdS/palygorskite nanostructured material with enhanced visible-light photocatalytic activity. Appl. Clay Sci. **87**, 285–291 (2014)
81. Bouna, L., Rhouta, B., Amjoud, M., Maury, F., Lafont, M.C., Jada, A., Senocq, F., Daoudi, L.: Synthesis, characterization and photocatalytic activity of TiO_2 supported natural palygorskite microfibers. Appl. Clay Sci. **52**, 301–311 (2011)
82. Shi, Y., Yang, Z., Wang, B., An, H., Chen, Z., Cui, H.: Adsorption and photocatalytic degradation of tetracycline hydrochloride using a palygorskite-supported Cu_2O-TiO_2 composite. Appl. Clay Sci. **119**, 311–320 (2016)
83. Mamulová Kutláková, K., Tokarský, J., Peikertová, P.: Functional and eco-friendly nanocomposite kaolinite/ZnO with high photocatalytic activity. Appl. Catal. B: Environ. **162**, 392–400 (2015)
84. Xu, H., Yu, T., Liu, J.: Photo-degradation of Acid Yellow 11 in aqueous on nano-ZnO/Bentonite under ultraviolet and visible light irradiation. Mater. Lett. **117**, 263–265 (2014)
85. Akkari, M., Aranda, P., Ben Rhaiem, H., Ben Haj Amara, A., Ruiz-Hitzky, E.: ZnO/clay nanoarchitectures: synthesis, characterization and evaluation as photocatalysts. Appl. Clay Sci. **131**, 131–139 (2016)
86. Xiao, J., Peng, T., Ke, D., Zan, L., Peng, Z.: Synthesis, characterization of CdS/rectorite nanocomposites and its photocatalytic activity. Phys. Chem. Miner. **34**, 275–285 (2007)
87. Wu, S., Fang, J., Xu, W., Cen, C.: Bismuth-modified rectorite with high visible light photocatalytic activity. J. Mol. Catal. A: Chem. **373**, 114–120 (2013)
88. Zhang, G., Gao, Y., Zhang, Y., Guo, Y.: Fe_2O_3-pillared rectorite as an efficient and stable fenton-like heterogeneous catalyst for photodegradation of organic contaminants. Environ. Sci. Technol. **44**, 6384–6389 (2010)
89. Zhang, Y., Yang, H.: Co_3O_4 nanoparticles on the surface of halloysite nanotubes. Phys. Chem. Miner. **39**, 789–795 (2012)
90. Kataria, N., Garg, V.K., Jain, M., Kadirvelu, K.: Preparation, characterization and potential use of flower shaped Zinc oxide nanoparticles (ZON) for the adsorption of Victoria Blue B dye from aqueous solution. Adv. Powder Technol. **27**, 1180–1188 (2016)
91. Kaplan, R., Erjavec, B., Dražić, G., Grdadolnik, J., Pintar, A.: Simple synthesis of anatase/rutile/brookite TiO_2 nanocomposite with superior mineralization potential for photocatalytic degradation of water pollutants. Appl. Catal. B: Environ. **181**, 465–474 (2016)
92. Wen, X.J., Niu, C.G., Huang, D.W., Zhang, L., Liang, C., Zeng, G.M.: Study of the photocatalytic degradation pathway of norfloxacin and mineralization activity using a novel ternary Ag/AgCl-CeO_2 photocatalyst. J. Catal. **355**, 73–86 (2017)
93. Wen, X.J., Niu, C.G., Zhang, L., Liang, C., Zeng, G.M.: A novel Ag_2O/CeO_2 heterojunction photocatalysts for photocatalytic degradation of enrofloxacin: possible degradation pathways, mineralization activity and an in depth mechanism insight. Appl. Catal. B: Environ. **221**, 701–714 (2018)
94. Kovalevskiy, N.S., Lyulyukin, M.N., Selishchev, D.S., Kozlov, D.V.: Analysis of air photocatalytic purification using a total hazard index: effect of the composite TiO_2/zeolite photocatalyst. J. Hazard. Mater. **358**, 302–309 (2018)
95. Ma, R., Wang, L., Wang, S., Wang, C., Xiao, F.S.: Eco-friendly photocatalysts achieved by zeolite fixing. Appl. Catal. B: Environ. **212**, 193–200 (2017)
96. Carbonaro, S., Sugihara, M.N., Strathmann, T.J.: Continuous-flow photocatalytic treatment of pharmaceutical micropollutants: activity, inhibition, and deactivation of TiO_2 photocatalysts in wastewater effluent. Appl. Catal. B: Environ. **129**, 1–12 (2013)
97. Wang, C., Xue, Y., Wang, P., Ao, Y.: Effects of water environmental factors on the photocatalytic degradation of sulfamethoxazole by AgI/UiO-66 composite under visible light irradiation. J. Alloys Compd. **748**, 314–322 (2018)

98. Konstantinou, I.K., Albanis, T.A.: TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: a review. Appl. Catal. B: Environ. **49**, 1–14 (2004)
99. Greco, E., Ciliberto, E., Cirino, A.M.E., Capitani, D., Di Tullio, V.: A new preparation of doped photocatalytic TiO_2 anatase nanoparticles: a preliminary study for the removal of pollutants in confined museum areas. Appl. Phys. A: Mater. Sci. Process. **122** (2016)
100. Malato, S., Fernández-Ibáñez, P., Maldonado, M.I., Blanco, J., Gernjak, W.: Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. Catal. Today **147**, 1–59 (2009)
101. Rezaei, M., Habibi-Yangjeh, A.: Simple and large scale refluxing method for preparation of Ce-doped ZnO nanostructures as highly efficient photocatalyst. Appl. Surf. Sci. **265**, 591–596 (2013)
102. Gaya, U.I., Abdullah, A.H.: Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. J. Photochem. Photobiol. C: Photochem. Rev. **9**, 1–12 (2008)
103. Akpan, U.G., Hameed, B.H.: Parameters affecting the photocatalytic degradation of dyes using TiO_2-based photocatalysts: a review. J. Hazard. Mater. **170**, 520–529 (2009)
104. Haque, M.M., Muneer, M.: Photodegradation of norfloxacin in aqueous suspensions of titanium dioxide. J. Hazard. Mater. **145**, 51–57 (2007)
105. Ahmed, S., Rasul, M.G., Brown, R., Hashib, M.A.: Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review. J. Environ. Manag. **92**, 311–330 (2011)
106. Guillard, C., Lachheb, H., Houas, A., Ksibi, M., Elaloui, E., Herrmann, J.-M.: Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO_2 comparison of the efficiency of powder and supported TiO_2. J. Photochem. Photobiol. A: Chem. **158**, 27–36 (2003)
107. M.A.Fox, M.T. Dulay, Heterogeneous photocatalysis. In: Chemical Reviews, pp. 341–357. Elsevier (1993)
108. Sun, J., Qiao, L., Sun, S., Wang, G.: Photocatalytic degradation of Orange G on nitrogen-doped TiO_2 catalysts under visible light and sunlight irradiation. J. Hazard. Mater. **155**, 312–319 (2008)
109. Maddila, S., Lavanya, P., Jonnalagadda, S.B.: Degradation, mineralization of bromoxynil pesticide by heterogeneous photocatalytic ozonation. J. Ind. Eng. Chem. **24**, 333–341 (2015)
110. Sakthivel, S., Neppolian, B., Shankar, M.V., Arabindoo, B., Palanichamy, M., Murugesan, V.: Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2. Sol. Energy Mater. Sol. Cells **77**, 65–82 (2003)
111. Kulkarni, S.D.D., Kumbar, S., Menon, S.G.G., Choudhari, K.S.S., Santhosh, C.: Magnetically separable core-shell $ZnFe_2O_4$@ZnO nanoparticles for visible light photodegradation of methyl orange. Mater. Res. Bull. **77**, 70–77 (2016)
112. Chen, H., Liu, X.Y., Hao, X.D., Zhang, Y.X.: Facile biphasic synthesis of TiO_2–MnO_2 nanocomposites for photocatalysis. Ceram. Int. **42**, 19425–19428 (2016)
113. Papoulis, D., Panagiotaras, D., Tsigrou, P., Christoforidis, K.C., Petit, C., Apostolopoulou, A., Stathatos, E., Komarneni, S., Koukouvelas, I.: Halloysite and sepiolite –TiO_2 nanocomposites: synthesis characterization and photocatalytic activity in three aquatic wastes. Mater. Sci. Semicond. Process. **85**, 1–8 (2018)
114. Szczepanik, B., Rogala, P., Słomkiewicz, P.M., Banaś, D., Kubala-Kukuś, A., Stabrawa, I.: Synthesis, characterization and photocatalytic activity of TiO_2-halloysite and Fe_2O_3-halloysite nanocomposites for photodegradation of chloroanilines in water. Appl. Clay Sci. **149**, 118–126 (2017)
115. Srikanth, B., Goutham, R., Badri Narayan, R., Ramprasath, A., Gopinath, K.P., Sankaranarayanan, A.R.: Recent advancements in supporting materials for immobilised photocatalytic applications in waste water treatment. J. Environ. Manag. **200**, 60–78 (2017)
116. Ayodhya, D., Veerabhadram, G.: A review on recent advances in photodegradation of dyes using doped and heterojunction based semiconductor metal sulfide nanostructures for environmental protection. Mater. Today Energy. **9**, 83–113 (2018)

117. Iranpour, R., Stenstrom, M., Tchobanoglous, G., Miller, D., Wright, J., Vossoughi, M.: Environmental engineering: energy value of replacing waste disposal with resource recovery. Science (80-) **285**, 706–711 (1999)
118. Gao, Q., Xu, J., Bu, X.H.: Recent advances about metal–organic frameworks in the removal of pollutants from wastewater. Coord. Chem. Rev. **378**, 17–31 (2019)
119. Guillermin, D., Debroise, T., Trigueiro, P., de Viguerie, L., Rigaud, B., Morlet-savary, F., Balme, S., Janot, J.-M., Tielens, F., Michot, L., Lalevee, J., Walter, P., Jaber, M., De Viguerie, L., Morlet-savary, F., Balme, S., Tielens, F., Michot, L., Lalevee, J., Walter, P., Jaber, M.: New pigments based on carminic acid and smectites: a molecular investigation. Dye Pigment. **160**, 971–982 (2018)
120. Salleh, M.A.M., Mahmoud, D.K., Karim, W.A.W.A., Idris, A.: Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review. Desalination **280**, 1–13 (2011)
121. Zhou, Y., Lu, J., Zhou, Y., Liu, Y.: Recent advances for dyes removal using novel adsorbents: a review. Environ. Pollut. **252**, 352–365 (2019)
122. Fatimah, I., Wang, S., Wulandari, D.: ZnO/montmorillonite for photocatalytic and photochemical degradation of methylene blue. Appl. Clay Sci. **53**, 553–560 (2011)
123. Djellabi, R., Ghorab, M.F., Cerrato, G., Morandi, S., Gatto, S., Oldani, V., Di Michele, A., Bianchi, C.L.: Photoactive TiO_2-montmorillonite composite for degradation of organic dyes in water. J. Photochem. Photobiol. A: Chem. **295**, 57–63 (2015)
124. Khataee, A.R., Kasiri, M.B.: Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide: influence of the chemical structure of dyes. J. Mol. Catal. A: Chem. **328**, 8–26 (2010)
125. Manohar, D.M., Noeline, B.F., Anirudhan, T.S.: Adsorption performance of Al-pillared bentonite clay for the removal of cobalt(II) from aqueous phase. Appl. Clay Sci. **31**, 194–206 (2006)
126. Dariani, R.S., Esmaeili, A., Mortezaali, A., Dehghanpour, S.: Photocatalytic reaction and degradation of methylene blue on TiO_2 nano-sized particles. Optik (Stuttg) **127**, 7143–7154 (2016)
127. Fu, H., Pan, C., Yao, W., Zhu, Y.: Visible-light-induced degradation of rhodamine B by nanosized Bi_2WO_6. J. Phys. Chem. B. **109**, 22432–22439 (2005)
128. Damalas, C.A., Koutroubas, S.D.: Farmers' behaviour in pesticide use: a key concept for improving environmental safety. Curr. Opin. Environ. Sci. Health **4**, 27–30 (2018)
129. Gibbons, D., Morrissey, C., Mineau, P.: A review of the direct and indirect effects of neonicotinoids and fipronil on vertebrate wildlife. Environ. Sci. Pollut. Res. **22**, 103–118 (2015). https://doi.org/10.1007/s11356-014-3180-5
130. Fernández-Alba, A., Hernando, D., Agüera, A., Cáceres, J., Malato, S.: Toxicity assays: a way for evaluating AOPs efficiency. Water Res. **36**, 4255–4262 (2002)
131. Bolognesi, C., Merlo, F.D.: Pesticides: human health effects. Encycl. Environ. Health 438–453 (2011)
132. Jørgensen, L.N., Kudsk, P., Ørum, J.E.: Links between pesticide use pattern and crop production in Denmark with special reference to winter wheat. Crop Prot. **119**, 147–157 (2019)
133. Fernández-Domene, R.M., Sánchez-Tovar, R., Lucas-granados, B., Muñoz-Portero, M.J., García-Antón, J.: Elimination of pesticide atrazine by photoelectrocatalysis using a photoanode based on WO_3 nanosheets. Chem. Eng. J. **350**, 1114–1124 (2018)
134. Mattei, C., Wortham, H., Quivet, E.: Heterogeneous degradation of pesticides by OH radicals in the atmosphere: influence of humidity and particle type on the kinetics. Sci. Total Environ. **664**, 1084–1094 (2019)
135. Evgenidou, E., Fytianos, K., Poulios, I.: Semiconductor-sensitized photodegradation of dichlorvos in water using TiO_2 and ZnO as catalysts. Appl. Catal. B: Environ. **59**, 81–89 (2005)
136. Van der Werf, H.M.G.: Assessing the impact of pesticides on the environment. Agric. Ecosyst. Environ. **60**, 81–96 (1996)

137. Xue, Y., Wang, P., Wang, C., Ao, Y.: Efficient degradation of atrazine by BiOBr/UiO-66 composite photocatalyst under visible light irradiation: environmental factors, mechanisms and degradation pathways. Chemosphere **203**, 497–505 (2018)
138. Mackuľak, T., Marton, M., Radičová, M., Staňová, A.V., Grabic, R., Bírošová, L., Nagyová, K., Vojs, M., Bodík, I., Brandeburová, P., Gál, M.: Monitoring of micropollutants and resistant bacteria in wastewater and their effective removal by boron doped diamond electrode. Mon. Chem. **148**, 539–548 (2017)
139. Rastogi, T., Mahmoud, W.M.M., Kümmerer, K.: Human and veterinary drugs in the environment. In: Encyclopedia of Anthropology, pp. 263–268. Elsevier (2018)
140. Mackuľak, T., Černanský, S., Fehér, M., Birošová, L., Gál, M.: Pharmaceuticals, drugs and resistant microorganisms – environmental impact on population health. Curr. Opin. Environ. Sci., Heal (2019)
141. Stumpf, M., Ternes, T.A., Wilken, R.-D., Rodrigues, Silvana Vianna, Baumann, W.: Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil. Sci. Total Environ. **225**, 135–141 (1999)
142. Ankley, G.T., Brooks, B.W., Huggett, D.B., Sumpter, J.P.: Repeating history: pharmaceuticals in the environment. Environ. Sci. Technol. **41**, 8211–8217 (2007)
143. López-Serna, R., Pérez, S., Ginebreda, A., Petrović, M., Barceló, D.: Fully automated determination of 74 pharmaceuticals in environmental and waste waters by online solid phase extraction-liquid chromatography-electrospray-tandem mass spectrometry. Talanta **83**, 410–424 (2010)
144. Al Balushi, A.S.M., Al Marzouqi, F., Al Wahaibi, B., Kuvarega, A.T., Al Kindy, S.M.Z., Kim, Y.: Hydrothermal synthesis of CdS sub-microspheres for photocatalytic degradation of pharmaceuticals. Appl. Surf. Sci. **457**, 559–565 (2018)
145. Khedr, T.M., El-Sheikh, S.M., Ismail, A.A., Bahnemann, D.W.: Highly efficient solar light-assisted TiO_2 nanocrystalline for photodegradation of ibuprofen drug. Opt. Mater. (Amst) **88**, 117–127 (2019)