

## Review Article

# Heavy Metal Removal from Aqueous Effluents by TiO<sub>2</sub> and ZnO Nanomaterials

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The presence of heavy metals in wastewater, such as Ni, Pb, Cd, V, Cr, and Cu, is a serious environmental problem. This kind of inorganic pollutant is not biodegradable for several years, and its harmful effect is cumulative. Recently, semiconductor nanomaterials based on metal oxides have gained interest due to their efficiency in the removal of heavy metals from contaminated water, by inducing photocatalytic ion reduction when they absorb light of the appropriate wavelength. The most commonly applied semiconductor oxides for these purposes are titanium oxide (TiO<sub>2</sub>), zinc oxide (ZnO), and binary nanomaterials composed of both types of oxides. The main purpose of this work is to critically analyse the existent literature concerning this topic focusing specially in the most important factors affecting the adsorption or photocatalytic capacities of this type of nanomaterials. In particular, photocatalytic activity is altered by various factors, such as proportion of polymorphs, synthesis method, surface area, concentration of defects and particle size, among others. After a survey of the actual literature, it was found that, although these metal oxides have low absorption capacity for visible light, it is possible to obtain an acceptable heavy metal reduction performance by sensitization with dyes, doping with metallic or nonmetallic atoms, introduction of defects, or the coupling of two or more semiconductors.

## 1. Introduction

Owing to their unique properties, nanomaterials nowadays have found different practical applications involving a wide range of sectors, such as the transportation industry, construction materials, energy storage, electronic devices, environment, medicine, cosmetics, etc. These exceptional properties compared to bulk phases result from the small size and high specific surface area of the nanomaterials, which have at least one dimension on the nanometer scale. Medical and pharmacological applications are one of the most relevant uses of nanotechnology. In recent years, nanomaterials have been employed to develop both miniaturized high-sensitivity biosensors to detect biological molecules

from smaller samples, and also optimized drug delivery systems, contributing to the development of innovative preventive therapies. For example, several polymeric nanomaterials have been applied to drug transporting, optimizing medication management systems, and offering greater bioavailability of the drug at the DIANA site [1]. Moreover, nitric oxide releasing nanoparticles have received wide attention due to their promising wound healing and antimicrobial actions.

Currently, the application of Nanotechnology for sustainable development of several industrial sectors has increased notoriously, helping to moderate serious global problems caused by a growing population, such as rising energy demand, sustained increase in food consumption, and contamination of arable land, air, and drinking water.

For example, the growing global demand for food has found in nanotechnology a very promising tool to maximize crop production through the use of nanofertilizers and nanopesticides without causing an imbalance in micronutrients or long-term damage of the soil, preserving thus the ecosystem health. This type of nanobased agrochemicals are characterized by a controlled delivery of functional ingredients directly to the site of application, which improves their effectiveness to increase growth promotion, soil improvement or pest management with a very low residual toxicity [2]. Furthermore, in the case of food and agroindustry, the manufacture of packaging based on nanomaterials could help to replace conventional non-biodegradable plastic materials, allowing food to be transported more safely, preserving their quality and properties. In this way, the creation of nanocomposites formed by a matrix of biodegradable natural polymeric materials (proteins, polynucleotides, polysaccharides, etc.) reinforced by nanomaterials such as carbon nanotubes, silicates, nanoclays, etc., is currently under intensive research [3]. The development of this type of nanotechnologies could significantly reduce the generation of nonbiodegradable waste in food industry.

On the other hand, as a result of the increasing energy demand, more advanced nanomaterials are being developed for sustainable applications in energy storage. For example, lithium-sulfur (Li-S) batteries are being considered as promising candidates for the gradual replacement of traditional lithium-ion batteries due to their low cost and high specific theoretical capacity (1675 mAh/g, 2600 Wh/kg). Industrial application of these batteries still presents some obstacles, such as poor sulfur conductivity, large volume change, and dissolution of lithium polysulfides. However, it has been proposed that these difficulties could be solved by applying monolayers or multiple layers of metal-based two-dimensional (2D) nanocomposites with lightweight, high conductivity, and large surface area, in order to achieve more reaction sites to restrict the diffusion of lithium polysulfides and thus enhance the electrochemical properties of the resulting batteries. Currently, Fe and Cobased 2D nanomaterials, such as hydroxides, sulfides, nitrides, and oxides, have attracted great attention as potential host materials to mitigate the polysulfide shuttling effect [4].

In particular, a large number of materials have shown in the nanoscale high efficiency for removing and detecting toxic organic and inorganic compounds, so the environmental applications of nanomaterials are also very varied. Heavy metal ions, which we will refer to in this work, are extremely important pollutants in wastewater, water for human and animal consumption, and rivers and seas. In effect, due to the growing rate of production of different industries, such as mining, steel, textiles, petrochemicals, paper, etc., the concentration of this type of inorganic pollutants in wastewater has worryingly increased in recent years [5, 6]. Cadmium (Cd), zinc (Zn), chromium (Cr), lead (Pb), copper (Cu), and nickel (Ni), are the most common heavy metals causing pollution in the aquatic environment [7–9]. They are dangerous because of their ability to bioaccumulate along the food chain, their high stability and toxicity [10–13]. Cr (III) and Cr (VI) ions are the most abundant

chromium species found in aqueous effluents. Although both ions are toxic, Cr (VI) is the most dangerous and harmful given its higher solubility in water. For example, a high dose of chromium can cause irritation at the contact site, irritation of the nasal mucosa, and skin ulcers even during brief exposure [7, 14, 15]. Moreover, Cr (III) can be oxidised to the most damaging form Cr (VI). Cr (III) causes skin eruptions and, in the cases of higher exposure doses, it accumulates in cells, being carcinogenic to the lungs and stomach [5, 7]. In the case of nickel (Ni) and its ions, despite being essential in the nutrition of several species of animals, plants, and microorganisms, its application in metallurgy has caused a higher concentration in the environment, which results in negative effects like human carcinogen, chronic asthma, reduction of lung function, etc. [7, 9, 16]. The major proportion of lead (Pb) in water arises from hydrocarbon, steel, and battery industry wastes. Pb can accumulate in muscles, brain, bones, and kidney, causing hypertension, kidney, and brain damage [17, 18]. Cadmium (Cd) is mainly produced by the cement and ceramic production, battery industries, metallurgy, and pigments. In low doses it can cause cancer, chronic lung disorders, liver destruction, bone and kidney damage, etc. [10, 19]. Besides, a high level of copper (Cu) in the environment can cause gastrointestinal effects, Wilson disease, or metabolic disorder [20]. The effect of metallic zinc (Zn) on human health can be beneficial as a micronutrient but when its concentration overpasses the recommended limit in the human body, a series of worse effects follows in most of the processes. It was found that the recommended limit for the Zn concentration level in domestic water is 3 mg/L [21]. In addition to those mentioned, the presence of precious metals (PMs) in aqueous effluents, such as gold (Au), platinum (Pt), osmium (Os), and iridium (Ir), has also become a serious environmental problem. These pollutants are originated mainly from the jewellery, mining, electronics, ceramic, and glass industries and their harmful effects on human health include dermatological, allergic, blood diseases, or also alteration of the normal metabolism of carbohydrates or lipids [22]. In this way, it is needed to ensure effective procedures for of heavy metals removal from waste effluents before being released into the environment. In this regard, the traditional methods of treatment, such as reverse osmosis [23, 24], membrane filtration [25], chemical precipitation [26], ion exchange [23, 26], chemical coagulation [27], adsorption [7], flotation [25], electrochemical [28], oxidation [29], etc., are expensive, have high energy demand, and are poor in terms of their efficiency. Nowadays, new technologies based on physically and chemically stable adsorbent materials and/or heterogeneous photocatalysts are being developed for mitigating the serious problems caused by heavy metals in wastewater. Indeed, two main removal mechanisms stand out above the rest for the treatment of effluents containing heavy metals: adsorption and ion reduction, which are briefly described below.

Adsorption-based technologies are widely used in environmental remediation in a way to decrease pollution of industry, for example in the purification of wastewater, water for human and animal consumption, and other aqueous effluents. In general, this surface phenomenon consists

of heavy metal atoms or ions may establish chemical or physical interactions with the adsorbent's surface, in which the atoms have higher energy than those located in the bulk since they are not totally surrounded by neighbouring atoms, as it can be seen in Figure 1 [30]. This fact makes the adsorption of heavy metal ions possible and the phenomenon is more intense as the adsorption surface active sites increases [7]. In this way, a thin layer of the adsorbed material (adsorbate) is created on the active surface of the adsorbent.

Examples of suitable adsorbents for this application are zeolites, metal oxides, clay minerals, chelating materials, activated carbon, etc. [31]. The main advantages associated with this technique are the operational simplicity, versatility, low-time consuming, and low cost (depending on the chosen adsorbent), the possibility of recovering the adsorbent material to reuse it after a certain number of cycles, and high capacity to capture heavy metal ions. However, it is highly selective for certain metal ions and despite the ability to recover adsorbent materials. Moreover, toxic residues can be generated after regeneration [7, 32]. Several factors affect the efficiency of heavy metal adsorption. The initial concentration of adsorbate influences so that in the initial stage of the adsorption process the rate, in general, is high, decreasing until steady state is reached [33]. The adsorption time affects the process in different ways depending on the adsorbate particles size, the amount of active preferential sites on the surface, as well as changes in the chemical composition on the surface of the adsorbent material [34]. It emerges from this that adsorption is a function of the rate of diffusion of the adsorbate particles from the outside into the adsorbent material. The pH is important in the adsorption of heavy metal ions, as it modifies the rate of the process. An increase in the pH value of the aqueous effluents in which heavy metals are present, promotes their adsorption by semiconductor metal oxides such as ZnO and TiO<sub>2</sub>, as well as influencing the number of active sites on the surface of the adsorbent material, increasing the selectivity for adsorbing several heavy metal ions [35]. Temperature is another important variable, since if the adsorption process is exothermic the adsorption efficiency will be lower as temperature increase, due to a decrease in the intensity of attractive forces between surface-active sites and adsorbate particles [36]. On the contrary, if the adsorption process is endothermic, the adsorption efficiency will be improved as temperature increases [37]. The adsorbent dose is also very significant on the adsorption performance since the amount of heavy metal ions that can be adsorbed increases with the concentration of the adsorbent material in an aqueous solution, which occurs continuously up to a certain concentration value from which it becomes constant with the concentration [38, 39]. This limit value is different for each metal ion, keeping the other parameters of the system unchanged [7, 40]. Additionally, nanomaterials based on semiconductor oxides are also suitable for heavy metal decontamination of water because they may lead to the removal by advanced oxidation processes. The ionic reduction of heavy metals is based on the phenomenon of photocatalysis, typical of metal oxides such as TiO<sub>2</sub>, ZnO, ZrO,

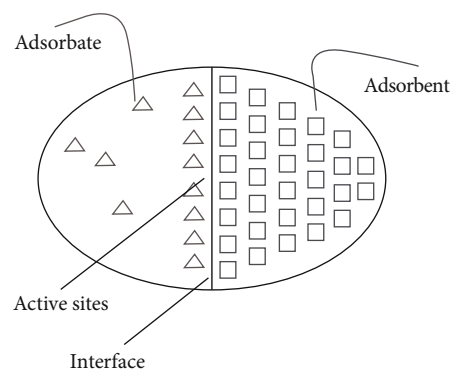


FIGURE 1: Simplified scheme of adsorption process.

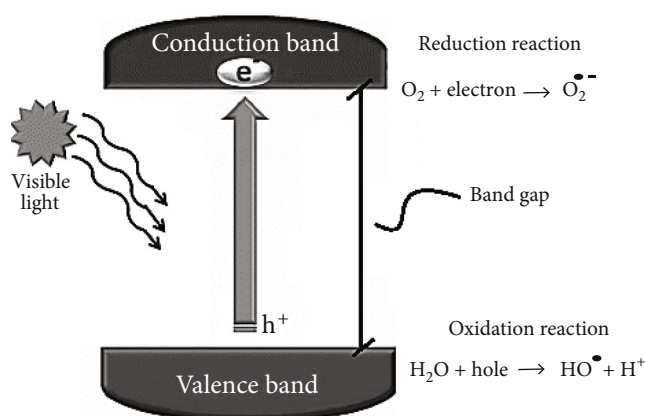


FIGURE 2: Photocatalysis mechanism of metal oxides semiconductors.

Fe<sub>3</sub>O<sub>4</sub>, etc. [41]. These heterogeneous photocatalysts have a relatively narrow band gap width between the conduction band (CB) and the valence band (VB), whose value is a very important factor to guarantee a good performance in the reduction of heavy metal ions [42, 43]. As it can be seen in Figure 2, in the presence of light of the appropriate wavelength (usually <370 nm) the photons are absorbed by the oxide, exciting the electrons from the VB towards the CB. This phenomenon, in turn, creates a positive charge in the VB, which is known as a hole. The existence of the electron-hole (e<sup>-</sup>/h<sup>+</sup>) pair enables redox-type reactions [44]. During photocatalysis, two reactions occur simultaneously, originating reactive chemical species that combine with the pollutant. First, the hole generated in the VB interacts with water or with free hydroxyl ions (HO<sup>•</sup>) in an oxidation reaction, generating a free hydroxyl radical (HO<sup>•</sup>) that is highly oxidizing. Therefore, it can participate in the oxidation of organic pollutants. In turn, in the CB, the electron that has migrated from the VB reacts with the molecular oxygen that is adsorbed by the metal oxide in a reduction reaction, thus generating a superoxide radical (O<sub>2</sub><sup>•-</sup>). This radical can reduce the heavy metals to ions with a lower oxidation state, which usually are less aggressive for the environment; such is the case of Cr (VI) to Cr (III) ion [45–48]. In fact, it has been shown that the reduction of heavy metal ions is more effective when it is carried out

simultaneously with the removal of organic contaminants [40, 49]. The reduction process is influenced by a series of factors, similar to those influencing on adsorption process: the pH of the solution, the size of the photocatalyst particles, temperature, and the mass ratio pollutants/photocatalyst, in addition to the modifications that may be implemented in the structure of the semiconductor oxide (oxygen vacancies, dopants such as transition metals, etc.). Photocatalytic activity is also strongly affected by the intensity of light radiation fed and irradiation time. The most commonly used semiconductor oxides in water remediation by advanced oxidation processes are  $\text{TiO}_2$  and  $\text{ZnO}$ , among others such as  $\text{ZrO}_2$ ,  $\text{CuO}$ , etc. [41, 45, 50, 51].

## 2. Removal of Heavy Metal Ions from Wastewater by Semiconductor Oxides

**2.1.  $\text{TiO}_2$  Nanomaterials.**  $\text{TiO}_2$  is a semiconductor material extensively used due to its low toxicity, high abundance, low cost, high stability, and redox potential [52, 53]. Figure 3 shows the three crystallographic structures that this oxide can be found in nature: the metastable anatase (tetragonal) and brookite (orthorhombic) phases, and in the rutile (tetragonal) phase, which is thermodynamically stable. Due to its potential applications in lithium batteries, in recent years, the polymorph  $\text{TiO}_2$ -B, with a monoclinic structure, has received special attention [54–56]. Owing to its greater reactivity and high mobility of  $e^-/h^+$  pairs, anatase has greater photocatalytic activity than rutile, while brookite and  $\text{TiO}_2$ -B have not yet been systematically explored for heavy metal removal applications.

As noted above, adsorption and photocatalytic capabilities can be affected by various factors, such as synthesis method, particle size, proportion of polymorphs, surface area, and numbers of defects, among others [9, 42, 57]. In particular, numerous modifications have been implemented to improve photocatalytic performance. This is due to the fact that the oxide has a significant bandwidth (3.2 eV for anatase), whose high energy does not allow the development of photocatalytic reactions using visible light, requiring use of ultraviolet light (UV) [43, 58, 59], which is extremely impractical. Also, the recombination of  $e^-/h^+$  pairs is a serious problem in materials for reduction of heavy metal ions as the excited electron that has migrated to CB returns to the VB and no reaction with the pollutant occurs [43, 60, 61]. In effect, when the electron–hole recombination takes place, a photo-excited electron in the CB returns to the VB without reacting with the adsorbed species, occupying the position of a hole in the VB. As a result, the photo-generated electron–hole pair disappears and the number of free charge carries available for reaction with heavy metal ions decrease. Therefore, the recombination process reduces the overall photocatalytic activity, and becomes one of the major limitations for reductive water treatment. Several alternatives have been proposed in order to promote separation of the electron–hole pair and thus reduce recombination, including doping and heterojunction coupling [38]. It is possible to obtain an acceptable performance with visible

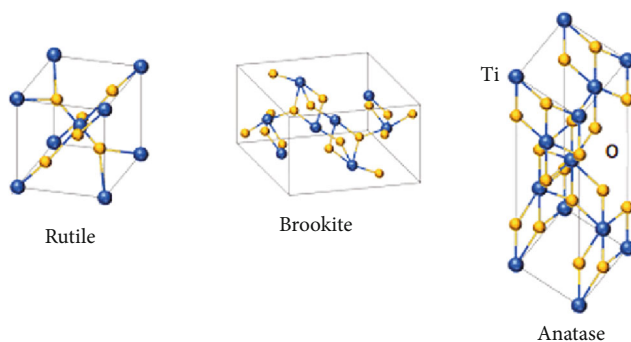


FIGURE 3: Crystal structures of rutile, brookite, and anatase.

light by applying various strategies; some of them are presented in Table 1.

In principle, the existing modifications for improving the remediation capacity of  $\text{TiO}_2$  are physical and chemical. Those included in the first group are based on the morphology of the semiconductor material and include the increase in the specific surface or porosity of the oxide, and its morphology, which results in a greater quantity of active sites to initiate redox reactions [42, 43, 58]. The most used morphologies in this sense are monodisperse nanoparticles in which the diameter is kept limited to reduce the recombination of  $e^-/h^+$  pairs increasing the specific surface for the chemical reactions responsible for remediation [43, 62]. Nanotubes, nanowires, and other  $\text{TiO}_2$ -based nanostructures are also used, achieving a high transfer of charges, greater porosity, and low recombination of pairs [43, 62–64]. In this way, theoretical-experimental studies have been carried out on the influence of the active face of  $\text{TiO}_2$  with anatase structure on the adsorption of certain heavy metal ions. Thus, density functional theory (DFT) calculations suggested that face (001) exhibited a relatively higher adsorption energy and better diffusion of metal ions with respect to face (101). The experimental analysis indicated that increasing the exposed (001) facets, the adsorption capacity was higher. In effect, when the percentage of exposed (001) facets was increased to 80%, the detection sensitivity reached a maximum of 190% for  $\text{Pb}$  (II) and 93% for  $\text{Cd}$  (II) [65]. Another method to increase the photocatalytic activity, as found in recent research, consists in deforming the crystalline lattice of the material. Indeed, a theoretical study applying the DFT method suggests that by applying strain up to 10%, the band gap is about decrease from 3.48 to 2.82 eV, so the absorption of visible light would be made possible [66]. A recently developed research indicates that cellulose- $\text{TiO}_2$ /rectorite composite in a natural polymer support has shown interesting results in  $\text{Pb}$  (II),  $\text{Cu}$  (II), and  $\text{Cd}$  (II) removal from acidic aqueous effluents. Rectorite (REC) strengthens the bond between  $\text{TiO}_2$  nanoparticles and cellulose hindering the agglomeration effects, enabling a better distribution of the nanoparticles. The multiple adsorptions of  $\text{Pb}$  (II),  $\text{Cu}$  (II), and  $\text{Cd}$  (II) were determined by the solution pH, reaching an adsorption capacity of 69.81 mg/g by using cellulose- $\text{TiO}_2$ /REC 2:1 in a pH = 6 solution [67]. Chemical-based methods to improve photocatalytic reactivity of  $\text{TiO}_2$  involve several strategies. Most common chemical

TABLE 1: Modifications of TiO<sub>2</sub> for improving remediation capacity [52].

Technique	Examples of application materials	Effects of modification on TiO <sub>2</sub> removal performance
Doping	Graphite, graphene oxide, semiconducting metal oxides (ZnO), metals (Cu, Zr).	Band gap between VB and CB is difficult to overcome by UV and visible light. Doping introduces midgap states and decreases the band gap energy.
Composites	Carbon nanotubes, metallic oxides, graphene oxides.	Combination of favourable properties for photocatalysis of all constituents.
Complexes	Porphyrin-TiO <sub>2</sub>	Absorption of UV and visible light.
Nanorods	Anatase/rutile/titanate rods	Increases specific area and mesoporosity.
Nanosheets	TiO <sub>2</sub> , graphene	High specific surface area, large number of active sites/facets. Increased separation and delayed recombination of holes.

modifications are sensitization with dyes [42], doped with metallic [59, 68, 69] or nonmetallic [70] elements, or the coupling of TiO<sub>2</sub> with another semiconductor metal oxide [71–73], carbon nanomaterials [52] or adequate polymers [61, 74] in order to obtain functional nanocomposites. Dye sensitization is based on the fact that electrons that have been excited during the irradiation of light, are transferred directly to the CB of TiO<sub>2</sub>, increasing the photocatalytic reactivity. This injection of electrons into the semiconductor material occurs in much shorter periods of time than recombination of e<sup>-</sup>/h<sup>+</sup> pairs (femtoseconds versus nanoseconds) [42, 75]. By other hand, doping of TiO<sub>2</sub> with noble metals such as Ag, Pt, Au, etc., results in an electronic transfer between the CB towards the doping atom, reducing the recombination of e<sup>-</sup>/h<sup>+</sup> pairs, which increases the reactivity of the photocatalyst oxide [53]. In this sense, Ag-doped TiO<sub>2</sub> presents higher photocatalytic activity when visible and UV-light irradiates the nanomaterial [76]. In general, the photocatalytic activity of TiO<sub>2</sub> doped with noble metals improves depending on the synthesis method such as photodeposition, impregnation, hydrothermal, and sol-gel. However, Au-TiO<sub>2</sub> and Pt-TiO<sub>2</sub> seem to be less susceptible to the manufacturing method, and in both cases the photocatalytic activity increases up to a limit concentration in the TiO<sub>2</sub> structure [77]. The TiO<sub>2</sub> doped with transition metals also presents a higher photocatalytic reactivity [42, 43, 48, 63, 78]. Thus, impurity energy levels are created in the band gap, resulting in the absorption of visible light and the highest electron transfer between the TiO<sub>2</sub> and the dopant [78]. Implanting metal ions also increases the photoreactivity of TiO<sub>2</sub> under visible light, for example, bombarding the oxide semiconductor with the ions so that they penetrate its crystalline structure and thus create additional energy levels [42, 43]. Doping modification is illustrated in Figure 4. The effects on the photocatalytic properties of TiO<sub>2</sub> after metal doping were also studied by means of first-principles and other theoretical methods, such as DFT. For example, DFT + U (U = 10 eV) calculations using the VASP package with GGA-PBE functional were recently performed to study photocatalytic properties of Sn/Pb-doped (101) TiO<sub>2</sub> anatase surface. It was found that the substitution of Ti atoms with Sn atoms on the surface or Pb atoms within the bulk phase can form an unoccupied local energy level below CB minimum, which could act as electron trap and inhibit the recombination of e<sup>-</sup>/h<sup>+</sup> pairs, promoting the photocatalytic activity. However, results also suggest that

the presence of the Sn impurity in the bulk leads to an increase in the anatase band gap, so in this case a lessening of the yield of e<sup>-</sup>/h<sup>+</sup> pairs and the photocatalytic performance can be expected [79]. Another study based on LDA + U (U = 8 eV) functional calculations have been carried out using the CASTEP code to evaluate the electronic and optical properties of Ce-doped anatase with various impurity concentrations. It was found that the increase in Ce concentration leads to a decrease in Ti 3d states and enhancement of 4f states in the bottom of CB, which provokes a gradual reduction of the band gap. In effect, the obtained energy band gap values of Ti<sub>1-x</sub>Ce<sub>x</sub>O<sub>2</sub> are 2.40, 2.34, 2.28, and 2.17 eV for x = 0.0625, 0.125, and 0.25, respectively, resulting in an optical absorption decrease in the range of 180–600 nm [80]. By the other hand, the combined effect of the presence of oxygen vacancies and interstitial Sn<sup>4+</sup> ions in TiO<sub>2</sub> rutile and anatase phases was analysed by GGA + U (U = 3.2 eV) calculations performed with the CASTEP package, adopting the PBE exchange-correlation functional. It was found that the oxygen vacancies promote the migration of the dopant ion from the interstitial to the substitution sites, especially in the case of the rutile phase. Furthermore, calculations suggest a reduction in bandwidth to 2.35 eV in the Sn-doped O-defected anatase due to the introduction of a defect level into the forbidden band. As a consequence, the presence of oxygen vacancies could tune the electronic excitation from the valence to the CB, helping to obtain well-separated e<sup>-</sup>/h<sup>+</sup> pairs and thus enhancing the photocatalytic performance of TiO<sub>2</sub> under visible-light irradiation [81].

In general, heavy metal ions are combined with other dangerous pollutants in aqueous effluents such as the polycyclic aromatic hydrocarbons (PAHs). Therefore, a simultaneous removal mechanism is extremely useful and efficient, such as the one developed using a phenanthroline/TiO<sub>2</sub> nanocomposite with rich oxygen vacancy defects for pollutant detection, adsorption, and degradation [82]. This material adsorbs Cr (III) ion, enhancing the photocatalytic degradation of methyl orange under visible light. Phenanthroline/TiO<sub>2</sub> was preadsorbed with 1, 20, 50, and 100 mg/L of Cr (III) ion and used to photocatalytically degrade this organic pollutant, showing higher photocatalytic capacity than TiO<sub>2</sub>. It was found that photocatalytic degradation of methyl orange increased as Cr (III) ion concentration increased from 1 mg/L to 50 mg/L [82]. Recently, TiO<sub>2</sub> nanofibers on a porous ceramic support of fly ash

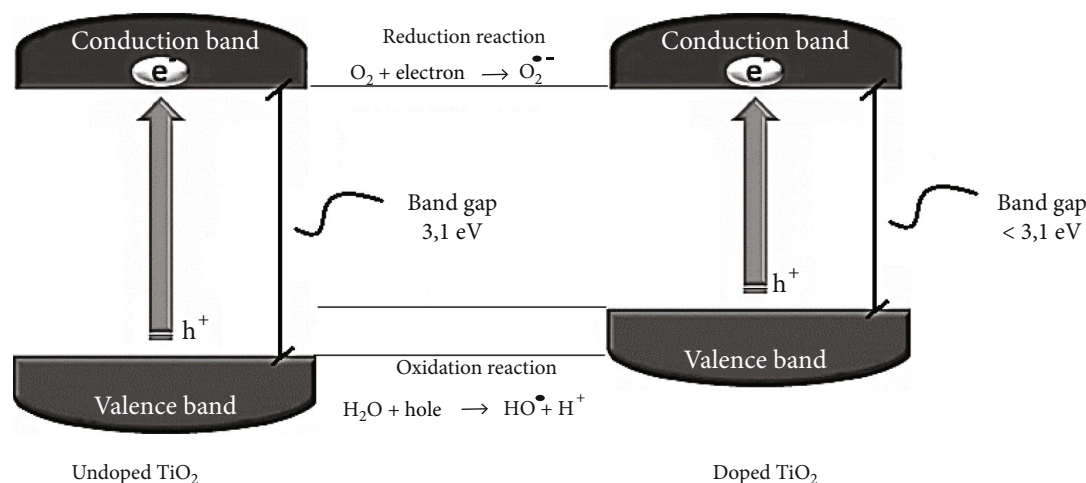


FIGURE 4: Comparison between the performance of  $\text{TiO}_2$  and doped  $\text{TiO}_2$ .

(TNM-PFACS), manufactured using the hydrothermal technique, showed the simultaneous elimination of the rhodamine B (RhB) dye and Cu (II), Cd (II), and Cr (VI) heavy metal ions through synergism and antagonism between the adsorption and photodegradation process [83]. A high elimination rate (90.15%) was found and the adsorption capacity (9.56 mg/g) of Cu (II) was maintained while the adsorption of the Cd (II) ion was disabled. The photodegradation of RhB creates an acidic environment that promotes the reduction of Cr (VI) to Cr (III) ion, showing a high efficiency of almost 97% [83]. Another research work analysed by experimental and theoretical methods the Cu (II) ion adsorption and phenanthrene reduction by an anatase/titanate ( $\text{TiO}_2/\text{TiNT}$ ) nanotube composite [84]. This nanomaterial has a large surface area and more active groups  $^-\text{ONa}/\text{H}$ , improving Cu (II) adsorption and photocatalytic degradation of phenanthrene. The maximum adsorption capacity of Cu (II) was 115.0 mg/g at pH = 5.  $\text{TiO}_2/\text{TiNT}$  showed higher reaction rate than unmodified TiNTs for phenanthrene photodegradation. Furthermore, the coexistence of Cu (II) promoted the photocatalytic degradation of phenanthrene, since Cu (II) adsorbed by the TiNT network acts as an electron receptor reducing the recombination rate of  $e^-/h^+$  pairs [84]. Another  $\text{TiO}_2$ -based nanomaterial for the simultaneous removal of several pollutants was obtained using Rh-Sb codoped  $\text{TiO}_2$  nanorods (RS-TONR) coupled with titanate nanotubes (TiNT) [85], in an attempt to reduce the level of pollution in aqueous effluents with more than one type of pollutant. Under visible light, it was found that RS-TONR/TiNT showed a high adsorption capacity for Zn (II), Cu (II), Pb (II), and Cd (II), while the photocatalytic degradation of the dye orange (II) and bisphenol A (BPA) was enhanced in solution containing these heavy metal ions [85]. Recently, the simultaneous removal of BPA and Cr (VI) ions by photodegradation under visible light irradiation was reported. It was found that under visible light, electrons are excited and migrated to the CB of anatase, were received by the Cr (VI) ion to reduce it to the Cr (III) ion, less harmful to the environment. In turn, superoxide radicals ( $\text{O}_2^{\bullet-}$ ) are produced, which can degrade the organic compound

BPA [86–88]. Nonmetal doping also can be applied to enhance the visible-light photocatalytic activity of a semiconductor oxide, using for example dopants as N, F, C, S, etc. This technique is more efficient than metal doping because of the lower recombination of  $e^-/h^+$  pairs [42, 43]. Several researches indicate that N-doped  $\text{TiO}_2$  turns out to be more efficient than the other dopants mentioned above, which makes it a more widespread resource. For example, it was found that an N-doped  $\text{TiO}_2$  photocatalyst synthesized by hydrothermal method showed a narrow band gap making this nanomaterial suitable for operation under visible light. This N-doped  $\text{TiO}_2$  (1.0 g of N- $\text{TiO}_2$ ) was added in a 3 mg/L Cr (VI)-containing solution, and after 120 min, the concentration of Cr (VI) and total chromium was 0.42 and 0.82 mg/L, respectively, which shows the reduction of Cr (VI) to Cr (III) [89]. Moreover, it was found by means of DFT methods that N atoms can occupy O-sites on the anatase bulk structure, with the consequent overlap of the  $\text{O}_{2p}$  and  $\text{N}_{2p}$  states and thus a lower energy bandwidth [90]. Also, the technique of codoping with different nonmetal atoms can be applied in order to improve the adsorption capacity of  $\text{TiO}_2$  nanomaterials. For example, mesoporous anatase codoped with S and N atoms shows a higher photocatalytic efficiency than anatase doped with S and N atoms separately [91, 92]. It has been proposed that the improved photocatalytic activity of anatase (001) nanosheets codoped with S and N is due to the narrowing of the forbidden energy band [91]. Significant improvement of the visible-light photoactivity of N-F codoped  $\text{TiO}_2$  films has been observed using a silica colloidal crystal for liquid phase deposition of the doped oxide, achieving macroporous structures with high photocatalytic activity by tuned morphology and photon multiple scattering effects [93]. Finally, coupling  $\text{TiO}_2$  with carbon nanostructures or polymers has also been used in order to obtain more active photocatalysis for heavy metal removal. In particular, reduced graphene oxide (rGO) has received great attention because it can act as an electron acceptor, promoting the transfer of photoexcited electrons from  $\text{TiO}_2$  and thus reducing the electron-hole recombination rate [94].  $\text{TiO}_2/$

rGO nanocomposites have been studied with different mass ratios synthesized by hydrothermal method. Those materials demonstrate improving adsorption capacity of Cd (II), Pb (II), and Cu (II) [95]. Similarly, TiO<sub>2</sub>/rGO synthesized by sol-gel method was studied finding an improved reduction capability of Cr (VI) to Cr (III) from an acidic aqueous solution in comparison with pure TiO<sub>2</sub>, with a maximum removal of 86.5% under visible-light illumination. The adsorption and reduction of Cr (VI) weakened with a rise in pH, due to the electrostatic attraction among cationic Cr (VI) and TiO<sub>2</sub>/rGO and the decline in the thermodynamic driving force of Cr (VI) reduction to Cr (III) [94, 96]. In a similar line, a recent study is based on the reduction of the Cr (VI) ion by a TiO<sub>2-x</sub>/rGO nanocomposite modified with carbon quantum dots (CQDs), synthesized by the hydrothermal calcination method. The presence of CQDs and rGO leads to a synergistic effect that promotes the separation of e<sup>-</sup>/h<sup>+</sup> pairs, increasing the photocatalytic activity of the CQDs-TiO<sub>2-x</sub>/rGO nanocomposite to reduce the contaminating ion to the Cr (III) form, even under irradiation with visible light [97]. Other authors have explored composites formed by TiO<sub>2</sub> and polymers that can enable doping-doping process, such as polypyrrole, polythiophene, or polyaniline, with the aim to reach a selective adsorption of heavy metal ions. For example, the coupled structure of polypyrrole (PPy), in its oxidised p-type doping state, and TiO<sub>2</sub> in n-type state, allows to achieve a high selectivity to Zn (II) ion, which is strongly dependant of TiO<sub>2</sub> mass fraction in the composite material, with a 77.81 mg/g adsorption capacity, disabling Cu (II) remotion [98]. Nonstoichiometric imperfections in the crystal lattice also influence the photocatalytic activity of TiO<sub>2</sub> by reducing the energy between CB and VB [70]. In this way, introduction of defects, especially oxygen vacancies (V<sub>O</sub>), can be a successful strategy for the remediation of heavy metals and other pollutants through metal oxides. For example, phenanthroline/TiO<sub>2</sub> nanocomposite (Phen/TiO<sub>2</sub>) with rich V<sub>O</sub> defects were synthesized to integrate the functions of pollutant detection, adsorption, and photocatalytic degradation. The results showed that the nanocomposite could adsorb Cr (III) ion, enhancing photocatalytic degradation of methyl orange pollutant under visible light [82]. Excess of oxygen also reduces the band gap by VB shift, higher electron receptivity, and lower e<sup>-</sup>/h<sup>+</sup> pairs recombination rate compared to TiO<sub>2</sub> with anatase morphology [70].

**2.2. ZnO Nanomaterials.** Zinc oxide (ZnO) is a semiconductor with a band gap of 3.37 eV, which has received extensive attention due to its high chemical stability and excellent photoelectric properties [46, 99–102]. Doped impurity in ZnO material could change its geometrical structures producing unusual electromagnetic properties. Compared to TiO<sub>2</sub>, it has lower production cost and greater tendency to generate oxygen vacancies, which allows a higher production of hydroxyl radicals and a higher reaction speed. ZnO is biodegradable and biocompatible in suitable doses. It exists in nature in three crystalline structures: wurtzite, blende, and salt rock (see Figure 5). Wurtzite (hexagonal cell with lattice parameters  $a = 3.2495 \text{ \AA}$  and  $c = 5.2069 \text{ \AA}$ ; Point group =

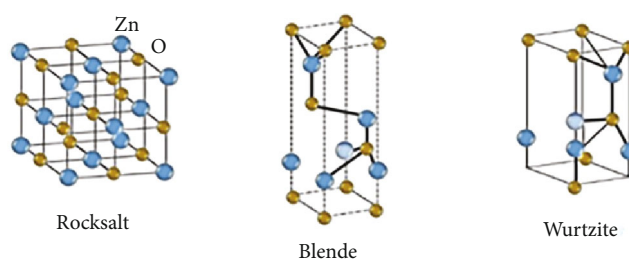


FIGURE 5: Crystal structures of rock salt, zinc blende, and wurtzite.

TABLE 2: Removal performance of ZnO for common heavy metals pollutants [5, 46].

Ion	Removal performance		Removal mechanism
	Visible light	UV light	
Ag (I)	Inadequate	Acceptable	Adsorption and redox
Cr (VI)	Medium	Inadequate	Adsorption and redox
Pb (II)	Medium	Acceptable	Adsorption and redox
Mn (II)	Inadequate	Inadequate	Adsorption
Cu (II)	Acceptable	Acceptable	Adsorption
Cd (II)	Inadequate	Inadequate	Adsorption
Ni (II)	Inadequate	Inadequate	Adsorption

6 mm; Space group = P63 mc) is the most stable form, while the rock salt structure occurs at high pressures and blende is synthesized only on cubic substrates [57]. It can be obtained in the form of nanostructured material, such as nanorods, nanowires, nanobelts, or nanotubes by means of spray pyrolysis, sol-gel method, physical and chemical deposition method, and hydrothermal method [103]. However, ZnO has a series of drawbacks associated with its dissolution in acids and corrosion in alkalis under UV radiation, high rate of recombination of e<sup>-</sup>/h<sup>+</sup> pairs, and low absorption capacity for visible light [57]. Table 2 shows ZnO performance on removing different heavy metal ions under visible and UV light, indicating that irradiation source strongly affects its removal capacity. A scheme for the heavy metal reduction process based on the photocatalytic mechanism on ZnO hexagonal nanorods is shown in Figure 6.

The strategies to increase the photocatalytic activity of ZnO are similar to those already described for TiO<sub>2</sub>, and include physical modifications, hybridization in different proportions with materials with comparable bandwidths, sensitization with dyes, and doping with noble and nonnoble metals [57]. In this way, by changing the morphology of ZnO adsorbent, it is possible to obtain better results using visible-light radiation [104]. For instance, it was found that using mesoporous ZnO with specific surface area of 15.75 m<sup>2</sup>/g and pore volume of 0.038 cm<sup>3</sup>/g, shows adsorption capacities of 160.7 mg/g and 147.25 mg/g in the adsorption of Pb (II) and Cd (II), respectively. Similarly, ZnO nanoparticles of 40 nm size and specific surface area of 80.42 m<sup>2</sup>/g prepared by gel combustion method were analysed as Pb (II) adsorbent, resulting in a maximum rate of 26.109 mg/g at optimum pH = 4 [105]. In another research,

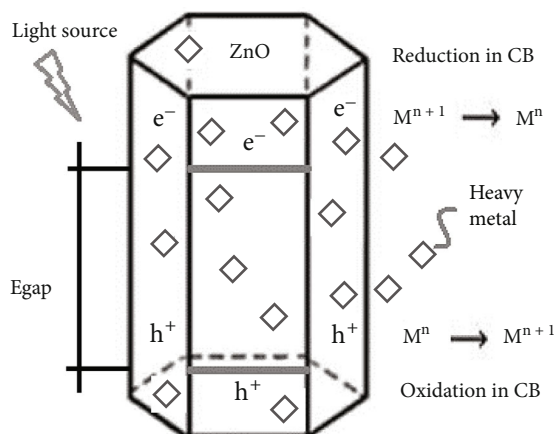


FIGURE 6: Reduction process on ZnO hexagonal nanorods.

ZnO nanosheets were evaluated for selective adsorption of Cd (II) in aqueous solution, showing an adsorption capacity of 97.36 mg/g in the presence of other metal ions such as Cu<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup>, and Y<sup>2+</sup> [106]. As it was previously explained, another effective method for improving the adsorption performance in the visible-light region consists on incorporate metallic and/or a nonmetallic atom in the metal oxide structure, in order to decrease the band gap energy and prevent the recombination of e<sup>+</sup>/h<sup>-</sup> pairs. Different transition metals such as Ag, Ni, Mn, Fe, and Cu have been used as ZnO dopants, concluding that the amount of doping exists where only the optimal concentrations show an increase in photocatalytic activity [107]. For example, in recent research an activated carbon loaded with biosynthesized Ag-doped ZnO nanocomposite was considered for Cr (VI) removal, showing that the optimum conditions for adsorption was at pH = 2.5 after 60 h of remediation treatment, for a heavy metal ion concentration of 40 ppm [108]. Another work has demonstrated that La and Ti-doped ZnO synthesized by sol-gel method show better capacity for Cd (II) adsorption than pure ZnO. A high adsorption efficiency of 93 mg/g was achieved at initial concentration of 300 mg/L by 8% of Ti-doped ZnO. In the same way, the adsorption capacity of undoped ZnO increased from 32 mg/g to 62 and 94 mg/g after La and Ti-monodoping, respectively [109]. Similarly, Ga-doped and Ca-doped ZnO nanopowders were tested for Pb (II) adsorption from wastewater. Results show that the incorporation of 3% of Ga or Ca in ZnO led to maximum adsorption capacity of lead of about: 458 and 449 mg/g for Ga-ZnO (at pH = 4 and 298 K) and Ca-ZnO (at pH = 5.4 and 328 K), respectively [110]. By other hand, a theoretical and experimental study shows that the UV and visible-light absorption and the photocatalytic degradation efficiency are significantly improved by means of Fe-Ce-codoping of ZnO. The degradation rate of pure ZnO is 72.6%, which increased to 98.5% with the addition of 3% of Fe and Ce. A DFT analysis performed with the VASP package at GGA-PBE level has demonstrated that ZnO band gap is reduced after doping with Fe and Ce at Zn sites, and e<sup>-</sup>/h<sup>+</sup> recombination is obstructed by the impurity donor levels, improving the photocatalytic activity. It was

also found that the band gap becomes narrower increasing dopant concentration to 4% [111]. In the same way, DFT models performed with CASTEP code show that by introducing Ni in wurtzite-ZnO structure, the higher the concentration of Ni, the more the forbidden band gap narrows. The obtained band gaps of Zn<sub>0.9583</sub>Ni<sub>0.0417</sub>O and Zn<sub>0.9722</sub>Ni<sub>0.0278</sub>O are 0.395 and 0.448 eV, respectively, both of which are smaller than those band gap calculated for pure ZnO (0.726 eV). Simultaneously, a shift in the light absorption range towards wavelengths close to red colour was obtained [112]. Other researchers have evaluated the capacity of ZnO nanotubes and ZnO-graphene like sheets for the adsorption of Ni, Cu, Ag, and Cd. For ZnO nanotubes, DFT calculations with SIESTA code and GGA-PBE functional show that calculated maximum and minimum values for adsorption energy were 3.45 and 1.3 eV, respectively, suggesting that this nanostructure is capable of adsorbing all of those heavy metals. On the contrary, ZnO nanosheets present maximum and minimum adsorption energy values of 2.19 and 0.24 eV, respectively, so this nanomaterial could act as an efficient adsorbent only for Cd and Ag [113].

Regarding doping of ZnO nanomaterials with nonmetallic elements, N-doping is commonly chosen to improve the photocatalytic properties. For example, ZnO nanorods doped using the ion implantation method shows a reduction from 3.2 to 2.18 eV in band gap because of the generation of localised energy states near the VB. Moreover, ZnO nanoparticles were synthesised, doped with N atoms and integrated to a multilayer polyethersulfone/chitosan adsorptive membrane in order to improve the removal efficiency for Cr (VI) depletion. This material, showed an increase from 12.9% to 31.48% under visible-light irradiation after doping. Under UV light, the removal efficiency was increased from 31.48% to 47.73% after N-doping of the membrane [114]. Likewise, ZnO doping with carbon, sulphur, and fluorine also generates localised energy states near the VB of ZnO, increasing the visible-light absorption property of modified ZnO photocatalysts [115]. On the other hand, oxygen (V<sub>O</sub>) or zinc (V<sub>Zn</sub>) vacancies into ZnO induces local defective states within the band gap, decreasing the bandwidth and improving visible-light adsorption. Therefore, the electron is photoexcited from the VB to an intermediate level state provided by V<sub>O</sub> near the CB or by V<sub>Zn</sub> near the VB, and finally reaches the CB. V<sub>O</sub>-rich ZnO, was found to present an energy band gap of 3.05 eV, in spite of 3.37 eV that is the band gap of pristine ZnO. In a similar way, V<sub>Zn</sub>-rich ZnO shows a slight narrowing of the band gap from 3.23 to 3.16 eV, but UV-light absorption capacity is lower than that corresponding to unmodified-ZnO structure [116].

**2.3. Binary ZnO/TiO<sub>2</sub> Systems.** Coupling of two or more semiconductor oxides promotes photocatalytic efficiency since recombination time of charge carriers is longer than if a single semiconductor oxide is used. Based on this principle, several hybrid compounds that have allowed to achieve satisfactory results in water remediation, such as those formed by metal oxide, metal nitride, metal sulphide, and ternary compounds such as Ag<sub>2</sub>O/ZnO/CuO. In these



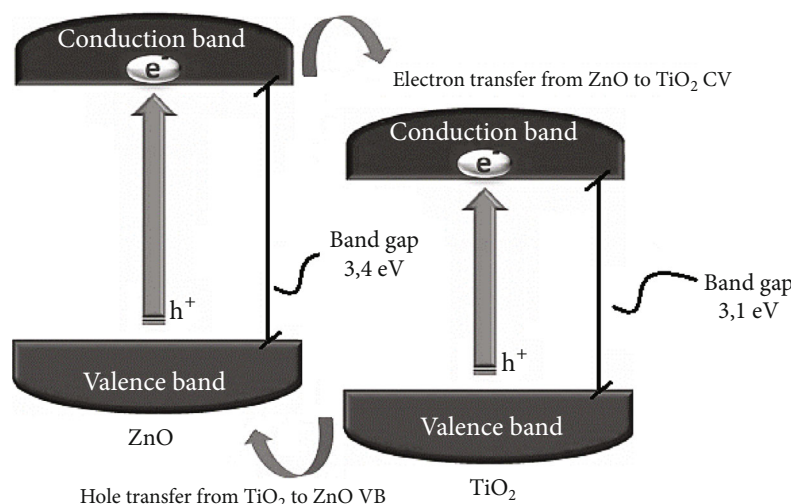


FIGURE 7: Charge transfer process on binary ZnO/TiO<sub>2</sub> system.

cases, the hybrid material has a more extensive range for visible-light absorption due to the different band gaps of each oxide and an increased potential for reduction of pollutants. In this way, it is possible to extend the useful life of the charge carriers, accelerate the reactions and increase the efficiency for removal of contaminants [72, 117]. In particular, ZnO/TiO<sub>2</sub> nanocomposites have been widely used in removal of various pollutants such as heavy metal ions like Cr (VI), dyes, drugs, Bisphenol A (BPA), and phenol. Coupling ZnO and TiO<sub>2</sub> leads to a lower recombination rate of charge carriers, improving heterogeneous photocatalytic performance, as shown in Figure 7. In this image, it can be seen that e<sup>-</sup> in the CB of TiO<sub>2</sub> are allowed to transfer to the CB of ZnO, since the energy level of the CB for TiO<sub>2</sub> is higher than that of ZnO. In the same way, h<sup>+</sup> in the VB of ZnO can move to VB of TiO<sub>2</sub> due to the energy level of VB of ZnO is below the energy of VB of TiO<sub>2</sub> [118, 119].

Several applications of this couple of oxides were developed concerning water treatments, and a great number of modifications were improved on the resulting composite materials for still increasing remediation performance. For example, heavy metal adsorption efficiency is also enhanced by TiO<sub>2</sub>/ZnO nanocomposite formed by a ZnO core and TiO<sub>2</sub> shell monolithic system having both mesoporous and microporous nature, synthesized via nanocasting method, with a high surface area between 120 and 332 m<sup>2</sup>/g. Pb (II) and Cd (II) ions from aqueous water were adsorbed by this nanocomposite under a pH = 6 aqueous solution, showing that maximum adsorption efficacy of Pb (II) was 790 and 978 mg/L for ZnO and TiO<sub>2</sub>/ZnO monoliths, respectively. Also, the maximum adsorption efficacy of Cd (II) was found to be 643 and 786 mg/L for ZnO and TiO<sub>2</sub>/ZnO monoliths, respectively, [71]. Similarly, TiO<sub>2</sub> and ZnO nanoparticles have been coated on a sewage sludge carbon (SSC) surface in order to obtain an efficient adsorbent for removal of Ni (II) and Cu (II) ions from aqueous solutions and wastewater. It was investigated, the effect of adsorption parameters such as TiO<sub>2</sub>/ZnO mass ratio, TiO<sub>2</sub>/ZnO concentration, pH, adsorbent dosage, contact time, ionic strength, temperature,

and initial concentrations of Ni (II) and Cu (II) as adsorbates. The maximum monolayer sorption capacities of Ni (II) and Cu (II) were found to be 62.3 and 75.1 mg/g, respectively, under a pH = 6 solution, TiO<sub>2</sub>:ZnO mass ratio of 3 : 1, TiO<sub>2</sub>/ZnO concentration of 10 wt.%, adsorbent dosage of 1 g/L, and equilibrium time of 120 min [120]. A hybrid TiO<sub>2</sub>/ZnO nanocomposite has also been used as a dopant for a matrix of synthetic materials with high stability, such as polyacrylonitrile (PAN) polymer nanofibers. The obtained PAN/ZnO/TiO<sub>2</sub> nanocomposite presents high efficiency to remove Cr (VI) ions from aqueous effluents after an exposure time of 240 min while this time was of 360 min when using only PAN nanocomposites. Moreover, adsorption capacities were also enhanced since they were found to be of 153.85 mg/g, 234.52 mg/g, and 333.43 mg/g for PAN nanofibers, PAN/ZnO, and PAN/ZnO/TiO<sub>2</sub>, respectively [121].

### 3. Conclusion

As mentioned, the application of nanoparticulate semiconductor oxides for the remediation of aqueous effluents has many advantages and results in significant decreases in the concentration of several transition or noble metals and other pollutants. Semiconductor oxide-based photocatalysts has received considerable attention for its diversified potential applications in environmental issues due to nontoxicity, excellent photochemical stability, great oxidizing power, chemical inertness, high abundance, low cost, and environmentally friendly nature [122]. These nanomaterials have also many exceptional properties for removal of heavy metals from water by adsorption processes, like high reactivity, strong mechanical property, nanosize, porosity characters, large surface area, hydrophobicity, dispersibility, and strong solution mobility [123]. They not only can efficiently adsorb heavy metals, but also have favourable redox properties that are beneficial for the ionic reduction of heavy metals and simultaneous degradation of redox-sensitive organic pollutants via photocatalytic mechanisms [124]. However,

there is scarce information available about the reuse of nanoparticulate materials or, when this is not possible, their final disposal. Since adsorption process is reversible, in many cases nanoparticulated adsorbents could be regenerated by desorption [71]. Investigating this aspect is particularly important given that the adsorption capacity of pollutants must be maintained at acceptable values throughout the cycles of use of the adsorbent material. In addition, once its useful life is over, it must be treated so that it does not become a toxic and dangerous waste. For instance, TiO<sub>2</sub> and ZnO nanoparticles were supported in poly(vinylidene difluoride)-co-trifluoroethylene (P(VDF-TrFE)) porous membrane, in order to produce nanocomposites of ZnO (15 wt. %) and TiO<sub>2</sub> (5, 10, and 15 wt. %) nanoparticles. To test its reusability, each nanocomposite was applied several times to the degradation of methylene blue under UV light during 5 h, showing higher photocatalytic efficiencies as photocatalyst concentration increases and even presenting low decrease throughout three cycles of use. The degradation rates of 15 wt. % TiO<sub>2</sub> and ZnO systems are similar, and the photoactivity decreases 6, 16, and 13% for 5, 10, and 15 wt. % TiO<sub>2</sub>, respectively, and 11% for 15 wt. % ZnO, in all cases after three cycles, showing thus the suitable reusability of the obtained nanocomposites [125].

There is another series of contaminants, commonly known as emerging pollutants, that nowadays are not included in water quality monitoring programs and that do not necessarily refer to new substances, but to compounds whose presence has been recently detected, so its environmental impact is not always known [126]. For example, pharmaceutical and personal care products, microplastics, pesticides, hormones and endocrine disrupting compounds, novel industrial additives, including nanomaterials, etc., are included in this group of harmful substances [127]. TiO<sub>2</sub> and ZnO nanoparticles have also been applied for removal of this type of pollutants from aqueous effluents [128, 129]. For example, a TiO<sub>2</sub>/ZnO nanocomposite with a Ti:Zn molar ratio of 1:0.3 was successfully applied to the photocatalytic degradation of steroid hormones, such as 17 $\alpha$ -ethinylestradiol (EE2) and 17 $\beta$ -estradiol (E2), at low initial concentrations (from 50  $\mu$ g/L to 10 mg/L) [130]. Continuous exposure to these hormones, even at low concentrations, can disrupt the endocrine system [131], inducing serious adverse effects on human health such as infertility and increased incidence of breast, ovarian, and testicular cancer [132]. The obtained TiO<sub>2</sub>/ZnO photocatalyst has showed approximately 25% and 10% mineralization for E2 and EE2, respectively, after 240 min of visible-light irradiation. Moreover, it was verified that the active sites of the nanocomposited can be regenerated by calcination at 600°C for 1 h, enabling its reuse for 3 cycles with minimal reduction in activity [130]. In a similar way, Ag<sub>2</sub>S-ZnO/rGO core-shell structured microspheres were tested for degradation of acetaminophen (APAP), an extensively consumed antipyretic, anti-inflammatory, and analgesic drug. It was verified that APAP removal efficiency depends on the rGO concentration, reaching the maximum photocatalytic performance under visible-light irradiation with a rGO content of 0.2 g/L. The Ag<sub>2</sub>S-ZnO/rGO composites presented enhanced photoca-

lytic performance toward degradation of APAP compared to bare ZnO and ZnO/rGO, which was mainly attributed to the efficient charge transfer at the interfaces of ZnO and Ag<sub>2</sub>S. The prepared composite also showed a great potential for recycling, suggesting the possibility of large-scale applications [133]. Another severe environmental problem is the pollution of water by microplastics ( $\leq$ 5 mm) and nanoplastics (<100 nm) [134]. Due to their small sizes, microplastic particles can be discharged into the environment from treated wastewater effluents. The most common are polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) [135]. Recent research has shown that semiconductor metal oxides can be applied to the photocatalytic removal of microplastics from water samples. For example, low density spherical PP particles suspended in water have decreased their volume by 65% under visible-light irradiation for two weeks in a flow through photocatalytic reactor with ZnO nanorods immobilized onto glass fibers [136]. Therefore, TiO<sub>2</sub> and ZnO-based nanomaterials have a great potential for photodegradation of microplastics, pharmaceutical products, and others emerging pollutants from wastewater effluents.

## Abbreviations

APAP:	Acetaminophen
BPA:	Bisphenol A
CASTEP:	Cambridge serial total energy package
CB:	Conduction band
CQD:	Carbon quantum dot
DFT:	Density functional theory
e <sup>-</sup> :	Electron
E2:	17 $\beta$ -Estradiol
EE2:	17 $\alpha$ -Ethinylestradiol
GGA-PBE:	Generalized gradient approximation - Perdew-Burke and Ernzerhof
h <sup>+</sup> :	Hole
LDA:	Local density approximation
P(VDF-TrFE):	Poly(vinylidene difluoride)-co-trifluoroethylene
PAH:	Polycyclic aromatic hydrocarbons
PAN:	Polyacrylonitrile
PE:	Polyethylene
PET:	Polyethylene terephthalate
Phen:	Phenanthroline
PP:	Polypropylene
PPy:	Polypyrrole
PS:	Polystyrene
PVC:	Polyvinyl chloride
REC:	Rectorite
rGO:	Reduced graphene oxide
RhB:	Rhodamine B
SIESTA:	Spanish initiative for electronic simulations with thousands of atoms
SSC:	Sewage sludge carbon
TiNT:	Titanate
TNM-PFACS:	TiO <sub>2</sub> nanofibers on a porous ceramic support of fly ash

TONR:	Titanium oxide nanorod
UV:	Ultraviolet
VASP:	Vienna ab initio simulation package
VB:	Valence band
V <sub>O</sub> :	Oxygen vacancies
V <sub>Zn</sub> :	Zinc vacancies.

## Data Availability

No underlying data was collected or produced in this study.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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## References

- [1] J. Damodharan, "Nanomaterials in medicine - an overview," *Materials Today: Proceedings*, vol. 37, pp. 383–385, 2021.
- [2] S. Arora, G. Murmu, K. Mukherjee, S. Saha, and D. Maity, "A comprehensive overview of nanotechnology in sustainable agriculture," *Journal of Biotechnology*, vol. 355, pp. 21–41, 2022.
- [3] N. Chausali, J. Saxena, and R. Prasad, "Recent trends in nanotechnology applications of bio-based packaging," *Journal of Agriculture and Food Research*, vol. 7, article 100257, 2022.
- [4] Y. Mo, L. Liao, D. Li et al., "Development prospects of metal-based two-dimensional nanomaterials in lithium-sulfur batteries," *Chinese Chemical Letters*, vol. 34, no. 1, article 107130, 2023.
- [5] A. T. Le, S. Y. Pung, S. Sreekantan, and A. Matsuda, "Mechanisms of removal of heavy metal ions by ZnO particles," *Heliyon*, vol. 5, no. 4, article e01440, 2019.
- [6] R. Mondal and S. De, "Removal of copper(II) from aqueous solution using zinc oxide nanoparticle impregnated mixed matrix hollow fiber membrane," *Environmental Technology and Innovation*, vol. 26, article 102300, 2022.
- [7] N. Soliman and A. Moustafa, "Industrial solid waste for heavy metals adsorption features and challenges; a review," *Journal of Materials Research and Technology*, vol. 9, no. 5, pp. 10235–10253, 2020.
- [8] S. S. Kolluru, S. Agarwal, S. Sireesha, I. Sreedhar, and S. R. Kale, "Heavy metal removal from wastewater using nanomaterials-process and engineering aspects," *Process Safety and Environmental Protection*, vol. 150, pp. 323–355, 2021.
- [9] A. Tripathi and M. R. Ranjan, "Heavy metal removal from wastewater using low cost adsorbents," *Journal of Bioremediation & Biodegradation*, vol. 6, no. 6, p. 315, 2015.
- [10] K. Gupta, P. Joshi, R. Gusain, and O. P. Khatri, "Recent advances in adsorptive removal of heavy metal and metalloids by metal oxide-based nanomaterials," *Coordination Chemistry Reviews*, vol. 445, article 214100, 2021.
- [11] L. Joseph, B. M. Jun, J. R. V. Flora, C. M. Park, and Y. Yoon, "Removal of heavy metals from water sources in the developing world using low-cost materials: a review," *Chemosphere*, vol. 229, pp. 142–159, 2019.
- [12] C. Zamora-Ledezma, D. Negrete-Bolagay, F. Figueroa et al., "Heavy metal water pollution: a fresh look about hazards, novel and conventional remediation methods," *Environmental Technology and Innovation*, vol. 22, article 101504, 2021.
- [13] A. Debnath, P. K. Singh, and Y. C. Sharma, "Metallic contamination of global river sediments and latest developments for their remediation," *Journal of Environmental Management*, vol. 298, article 113378, 2021.
- [14] N. Sharma, K. K. Sodhi, M. Kumar, and D. K. Singh, "Heavy metal pollution: insights into chromium eco-toxicity and recent advancement in its remediation," *Environmental Nanotechnology, Monitoring & Management*, vol. 15, article 100388, 2021.
- [15] N. A. Azeez, S. S. Dash, S. N. Gummadi, and V. S. Deepa, "Nano-remediation of toxic heavy metal contamination: hexavalent chromium [Cr(VI)]," *Chemosphere*, vol. 266, article 129204, 2021.
- [16] A. El-Naggar, N. Ahmed, A. Mosa et al., "Nickel in soil and water: sources, biogeochemistry, and remediation using biochar," *Journal of Hazardous Materials*, vol. 419, article 126421, 2021.
- [17] M. Balali-Mood, K. Naseri, Z. Tahergorabi, M. R. Khazdair, and M. Sadeghi, "Toxic mechanisms of five heavy metals: mercury, lead, chromium, cadmium, and arsenic," *Frontiers in Pharmacology*, vol. 12, article 643972, 2021.
- [18] S. Ata, A. Tabassum, I. Bibi et al., "Lead remediation using smart materials. a review," *Zeitschrift für Physikalische Chemie*, vol. 233, no. 10, pp. 1377–1409, 2019.
- [19] M. Iqbal, N. Iqbal, I. A. Bhatti, N. Ahmad, and M. Zahid, "Response surface methodology application in optimization of cadmium adsorption by shoe waste: a good option of waste mitigation by waste," *Ecological Engineering*, vol. 88, pp. 265–275, 2016.
- [20] R. Shrestha, S. Ban, S. Devkota et al., "Technological trends in heavy metals removal from industrial wastewater: a review," *Journal of Environmental Chemical Engineering*, vol. 9, no. 4, article 105688, 2021.
- [21] P. N. Obasi and B. B. Akudinobi, "Potential health risk and levels of heavy metals in water resources of lead-zinc mining communities of Abakaliki, Southeast Nigeria," *Applied Water Science*, vol. 10, no. 7, pp. 1–23, 2020.
- [22] A. T. Nakhjiri, H. Sanaeepur, A. E. Amooghin, and M. M. Shirazi, "Recovery of precious metals from industrial wastewater towards resource recovery and environmental sustainability: a critical review," *Desalination*, vol. 527, article 115510, 2022.
- [23] C. Algieri, S. Chakraborty, and S. Candamano, "A way to membrane-based environmental remediation for heavy metal removal," *Environments*, vol. 8, no. 6, p. 52, 2021.
- [24] T. Bakalár, M. Búgel, and L. Gajdošová, "Heavy metal removal using reverse osmosis," *Acta Montanistica Slovaca*, vol. 14, no. 3, p. 250, 2009.
- [25] C. Blöcher, J. Dorda, V. Mavrov, H. Chmiel, N. K. Lazaridis, and K. A. Matis, "Hybrid flotation-membrane filtration process for the removal of heavy metal ions from wastewater," *Water Research*, vol. 37, no. 16, pp. 4018–4026, 2003.

- [26] M. A. Renu and K. Singh, "Methodologies for removal of heavy metal ions from wastewater: an overview," *Interdisciplinary Environmental Review*, vol. 18, no. 2, pp. 124–142, 2017.
- [27] X. Tang, H. Zheng, H. Teng et al., "Chemical coagulation process for the removal of heavy metals from water: a review," *Desalination and Water Treatment*, vol. 57, no. 4, pp. 1733–1748, 2016.
- [28] C. Liu, T. Wu, P. C. Hsu et al., "Direct/alternating current electrochemical method for removing and recovering heavy metal from water using graphene oxide electrode," *ACS Nano*, vol. 13, no. 6, pp. 6431–6437, 2019.
- [29] J. Du, B. Zhang, J. Li, and B. Lai, "Decontamination of heavy metal complexes by advanced oxidation processes: a review," *Chinese Chemical Letters*, vol. 31, no. 10, pp. 2575–2582, 2020.
- [30] W. Mortada, A. F. Moustafa, A. M. Ismail, M. M. Hassanien, and A. A. Aboud, "Microwave assisted decoration of titanium oxide nanotubes with  $\text{CuFe}_2\text{O}_4$  quantum dots for solid phase extraction of uranium," *RSC Advances*, vol. 5, no. 77, pp. 62414–62423, 2015.
- [31] D. Zamboulis, E. N. Peleka, N. K. Lazaridis, and K. A. Matis, "Metal ion separation and recovery from environmental sources using various flotation and sorption techniques," *Journal of Chemical Technology & Biotechnology*, vol. 86, no. 3, pp. 335–344, 2011.
- [32] G. Yu, X. Wang, J. Liu et al., "Applications of nanomaterials for heavy metal removal from water and soil: a review," *Sustainability*, vol. 13, no. 2, p. 713, 2021.
- [33] F. T. Senberber, M. Yildirim, N. K. Mermer, and E. M. Derun, "Adsorption of Cr (III) from aqueous solution using borax sludge," *Acta Chimica Slovenica*, vol. 64, no. 3, pp. 654–660, 2017.
- [34] F. Cheronon, N. Mburu, and B. Kakoi, "Adsorption of lead, copper and zinc in a multi-metal aqueous solution by waste rubber tires for the design of single batch adsorber," *Heliyon*, vol. 7, no. 11, article e08254, 2021.
- [35] M. Sharma, D. Choudhury, S. Hazra, and S. Basu, "Effective removal of metal ions from aqueous solution by mesoporous  $\text{MnO}_2$  and  $\text{TiO}_2$  monoliths: kinetic and equilibrium modelling," *Journal of Alloys and Compounds*, vol. 720, pp. 221–229, 2017.
- [36] Ş. Taşar, F. Kaya, and A. Özer, "Biosorption of lead(II) ions from aqueous solution by peanut shells: equilibrium, thermodynamic and kinetic studies," *Journal of Environmental Chemical Engineering*, vol. 2, no. 2, pp. 1018–1026, 2014.
- [37] S. Senthilkumar, P. Kalaamani, and C. Subburaam, "Liquid phase adsorption of crystal violet onto activated carbons derived from male flowers of coconut tree," *Journal of Hazardous Materials*, vol. 136, no. 3, pp. 800–808, 2006.
- [38] N. Soliman, H. S. Mohamed, S. A. Ahmed, F. H. Sayed, A. H. Elghandour, and S. A. Ahmed, "Cd<sup>2+</sup> and Cu<sup>2+</sup> removal by the waste of the marine brown macroalga *Hydroclathrus clathratus*," *Environmental Technology and Innovation*, vol. 15, article 100365, 2019.
- [39] V. V. Dev, K. K. Nair, G. Baburaj, and K. A. Krishnan, "Pushing the boundaries of heavy metal adsorption: a commentary on strategies to improve adsorption efficiency and modulate process mechanisms," *Colloid and Interface Science Communications*, vol. 49, article 100626, 2022.
- [40] T. O. Ajiboye, O. A. Oyewo, and D. C. Onwudiwe, "Simultaneous removal of organics and heavy metals from industrial wastewater: a review," *Chemosphere*, vol. 262, article 128379, 2021.
- [41] T. Naseem and T. Durrani, "The role of some important metal oxide nanoparticles for wastewater and antibacterial applications: a review," *Environmental Chemistry and Ecotoxicology*, vol. 3, pp. 59–75, 2021.
- [42] V. Etacheri, C. di Valentin, J. Schneider, D. Bahnemann, and S. C. Pillai, "Visible-light activation of  $\text{TiO}_2$  photocatalysts: advances in theory and experiments," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 25, pp. 1–29, 2015.
- [43] M. Pelaez, N. T. Nolan, S. C. Pillai et al., "A review on the visible light active titanium dioxide photocatalysts for environmental applications," *Applied Catalysis B: Environmental*, vol. 125, pp. 331–349, 2012.
- [44] X. Kang, S. Liu, Z. Dai, Y. He, X. Song, and Z. Tan, "Titanium dioxide: from engineering to applications," *Catalysts*, vol. 9, no. 2, p. 191, 2019.
- [45] Z. Zhao, H. An, J. Lin et al., "Progress on the photocatalytic reduction removal of chromium contamination," *The Chemical Record*, vol. 19, no. 5, pp. 873–882, 2019.
- [46] V. Dhiman and N. Kondal, "ZnO Nanoadsorbents: a potent material for removal of heavy metal ions from wastewater," *Colloid and Interface Science Communications*, vol. 41, article 100380, 2021.
- [47] M. A. Ahmed, A. T. Elsir, F. Mohammed, H. A. Elbushra, S. Tawer, and N. Eassa, "Photo-reduction of chromium from water by  $\text{TiO}_2$  nanoparticles," *MRS Advances*, vol. 3, no. 42–43, pp. 2667–2674, 2018.
- [48] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, and S. Sugihara, "Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping," *Applied Catalysis B: Environmental*, vol. 42, no. 4, pp. 403–409, 2003.
- [49] L. Liu, R. Li, Y. Liu, and J. Zhang, "Simultaneous degradation of ofloxacin and recovery of Cu(II) by photoelectrocatalysis with highly ordered  $\text{TiO}_2$  nanotubes," *Journal of Hazardous Materials*, vol. 308, pp. 264–275, 2016.
- [50] J. Yang, B. Hou, J. Wang et al., "Nanomaterials for the removal of heavy metals from wastewater," *Nanomaterials*, vol. 9, no. 3, p. 424, 2019.
- [51] M. S. S. Danish, L. L. Estrella, I. M. A. Alemaida et al., "Photocatalytic applications of metal oxides for sustainable environmental remediation," *Metals*, vol. 11, no. 1, p. 80, 2021.
- [52] K. P. Gopinath, N. V. Madhav, A. Krishnan, R. Malolan, and G. Rangarajan, "Present applications of titanium dioxide for the photocatalytic removal of pollutants from water: a review," *Journal of Environmental Management*, vol. 270, article 110906, 2020.
- [53] B. Bakbolat, C. Daulbayev, F. Sultanov et al., "Recent developments of  $\text{TiO}_2$ -based photocatalysis in the hydrogen evolution and photodegradation: a review," *Nanomaterials*, vol. 10, no. 9, p. 1790, 2020.
- [54] P. Li, Q. Cao, D. Zheng et al., "Synthesis of mesoporous  $\text{TiO}_2$ -B nanobelts with highly crystalized walls toward efficient H<sub>2</sub> evolution," *Nanomaterials*, vol. 9, no. 7, p. 919, 2019.
- [55] G. Yang, H. Ding, J. Feng et al., "Highly performance core-shell  $\text{TiO}_2(\text{B})/\text{anatase}$  homojunction nanobelts with active

- cobalt phosphide cocatalyst for hydrogen production,” *Scientific Reports*, vol. 7, no. 1, pp. 1–9, 2017.
- [56] M. Manzoli, F. S. Freyria, N. Blangetti, and B. Bonelli, “Brookite, a sometimes under evaluated TiO<sub>2</sub> polymorph,” *RSC Advances*, vol. 12, no. 6, pp. 3322–3334, 2022.
- [57] B. Abebe, H. A. Murthy, and E. Amare, “Enhancing the photocatalytic efficiency of ZnO: defects, heterojunction, and optimization,” *Environmental Nanotechnology, Monitoring & Management*, vol. 14, article 100336, 2020.
- [58] C. Chen, W. Ma, and J. Zhao, “Semiconductor-mediated photodegradation of pollutants under visible-light irradiation,” *Chemical Society Reviews*, vol. 39, no. 11, pp. 4206–4219, 2010.
- [59] X. Zheng, D. Li, X. Li et al., “Construction of ZnO/TiO<sub>2</sub> photonic crystal heterostructures for enhanced photocatalytic properties,” *Applied Catalysis B: Environmental*, vol. 168–169, pp. 408–415, 2015.
- [60] X. Chen and S. S. Mao, “Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications,” *Chemical Reviews*, vol. 107, no. 7, pp. 2891–2959, 2007.
- [61] F. Chen, W. Yu, Y. Qie, L. Zhao, H. Zhang, and L. H. Guo, “Enhanced photocatalytic removal of hexavalent chromium through localized electrons in polydopamine-modified TiO<sub>2</sub> under visible irradiation,” *Chemical Engineering Journal*, vol. 373, pp. 58–67, 2019.
- [62] M. D. Hernández-Alonso, F. Fresno, S. Suárez, and J. M. Coronado, “Development of alternative photocatalysts to TiO<sub>2</sub>: challenges and opportunities,” *Energy & Environmental Science*, vol. 2, no. 12, pp. 1231–1257, 2009.
- [63] Y. C. Nah, I. Paramasivam, and P. Schmuki, “Doped TiO<sub>2</sub> and TiO<sub>2</sub> nanotubes: synthesis and applications,” *ChemPhysChem*, vol. 11, no. 13, pp. 2698–2713, 2010.
- [64] A. S. Poursani, A. Nilchi, A. Hassani, S. M. Shariat, and J. Nouri, “The synthesis of nano TiO<sub>2</sub> and its use for removal of lead ions from aqueous solution,” *Journal of Water Resource and Protection*, vol. 8, no. 4, pp. 438–448, 2016.
- [65] J. Liao, F. Yang, C. Z. Wang, and S. Lin, “The crystal facet-dependent electrochemical performance of TiO<sub>2</sub> nanocrystals for heavy metal detection: theoretical prediction and experimental proof,” *Sensors and Actuators B: Chemical*, vol. 271, pp. 195–202, 2018.
- [66] V. Patel, Y. Sonvane, and P. Thakor, “Structural and electrical properties of TiO<sub>2</sub> monolayers using first-principle calculations,” *Materials Today: Proceedings*, vol. 47, pp. 563–566, 2021.
- [67] C. Wang, Y. Zhan, Y. Wu et al., “TiO<sub>2</sub>/rectorite-trapped cellulose composite nanofibrous mats for multiple heavy metal adsorption,” *International Journal of Biological Macromolecules*, vol. 183, pp. 245–253, 2021.
- [68] R. Yuan, B. Zhou, D. Hua, and C. Shi, “Effect of metal ion-doping on characteristics and photocatalytic activity of TiO<sub>2</sub> nanotubes for removal of humic acid from water,” *Frontiers of Environmental Science & Engineering*, vol. 9, no. 5, pp. 850–860, 2015.
- [69] J. Zhang, D. Fu, S. Wang, R. Hao, and Y. Xie, “Photocatalytic removal of chromium(VI) and sulfite using transition metal (Cu, Fe, Zn) doped TiO<sub>2</sub> driven by visible light: feasibility, mechanism and kinetics,” *Journal of Industrial and Engineering Chemistry*, vol. 80, pp. 23–32, 2019.
- [70] V. Etacheri, M. K. Seery, S. J. Hinder, and S. C. Pillai, “Oxygen rich titania: a dopant free, high temperature stable, and visible-light active anatase photocatalyst,” *Advanced Functional Materials*, vol. 21, no. 19, pp. 3744–3752, 2011.
- [71] M. Sharma, J. Singh, S. Hazra, and S. Basu, “Adsorption of heavy metal ions by mesoporous ZnO and TiO<sub>2</sub>@ZnO monoliths: adsorption and kinetic studies,” *Microchemical Journal*, vol. 145, pp. 105–112, 2019.
- [72] Y. Wang, X. Liu, L. Guo et al., “Metal organic framework-derived c-doped ZnO/TiO<sub>2</sub> nanocomposite catalysts for enhanced photodegradation of rhodamine B,” *Journal of Colloid and Interface Science*, vol. 599, pp. 566–576, 2021.
- [73] C. B. Anucha, I. Altin, E. Bacaksiz, and V. N. Stathopoulos, “Titanium dioxide (TiO<sub>2</sub>)-based photocatalyst materials activity enhancement for contaminants of emerging concern (CECs) degradation: In the light of modification strategies,” *Advances*, vol. 10, article 100262, 2022.
- [74] A. Maleki, B. Hayati, F. Najafi, F. Gharibi, and S. W. Joo, “Heavy metal adsorption from industrial wastewater by PAMAM/TiO<sub>2</sub> nanohybrid: preparation, characterization and adsorption studies,” *Journal of Molecular Liquids*, vol. 224, pp. 95–104, 2016.
- [75] P. Kumar, S. Kumar, S. Ghosh, and S. K. Pal, “Femtosecond insights into direct electron injection in dye anchored ZnO QDs following charge transfer excitation,” *Physical Chemistry Chemical Physics*, vol. 18, no. 30, pp. 20672–20681, 2016.
- [76] A. T. Le, Z. H. Tan, R. Sivakumar, and S. Y. Pung, “Predicting the photocatalytic performance of metal/metal oxide coupled TiO<sub>2</sub> particles using response surface methodology (RSM),” *Materials Chemistry and Physics*, vol. 269, article 124739, 2021.
- [77] J. Taing, M. H. Cheng, and J. C. Hemminger, “Photodeposition of Ag or Pt onto TiO<sub>2</sub> nanoparticles decorated on step edges of HOPG,” *ACS Nano*, vol. 5, no. 8, pp. 6325–6333, 2011.
- [78] Y. Fang, Y. Zheng, T. Fang et al., “Photocatalysis: an overview of recent developments and technological advancements,” *SCIENCE CHINA Chemistry*, vol. 63, no. 2, pp. 149–181, 2020.
- [79] D.-H. Li, Z. Y. Jiang, Y. M. Lin, and J. M. Zheng, “Theoretical studies of photocatalytic behaviors of isoelectronic Sn/Pb-doped TiO<sub>2</sub>: DFT+U,” *Applied Surface Science*, vol. 555, article 149714, 2021.
- [80] C. Fu, T. Li, J. Qi, J. Pan, S. Chen, and C. Cheng, “Theoretical study on the electronic and optical properties of Ce<sup>3+</sup>-doped TiO<sub>2</sub> photocatalysts,” *Chemical Physics Letters*, vol. 494, no. 1–3, pp. 117–122, 2010.
- [81] X. Yu, J. Xie, H. Dong, Q. Liu, and Y. Li, “Effects of oxygen defects on electronic band structures and dopant migration in Sn-doped TiO<sub>2</sub> by density functional studies,” *Chemical Physics Letters*, vol. 754, article 137732, 2020.
- [82] P. Chen, H. Zheng, H. Jiang et al., “Oxygen-vacancy-rich phenanthroline/TiO<sub>2</sub> nanocomposites: an integrated adsorption, detection and photocatalytic material for complex pollutants remediation,” *Chinese Chemical Letters*, vol. 33, no. 2, pp. 907–911, 2022.
- [83] J. Zhang, M. Yan, G. Sun, and K. Liu, “Simultaneous removal of Cu(II), Cd(II), Cr(VI), and rhodamine B in wastewater using TiO<sub>2</sub> nanofibers membrane loaded on porous fly ash ceramic support,” *Separation and Purification Technology*, vol. 272, article 118888, 2021.
- [84] K. Cheng, Z. Cai, J. Fu et al., “Synergistic adsorption of Cu(II) and photocatalytic degradation of phenanthrene by

- a jaboticaba-like TiO<sub>2</sub>/titanate nanotube composite: an experimental and theoretical study,” *Chemical Engineering Journal*, vol. 358, pp. 1155–1165, 2019.
- [85] L. K. Dhandole, S. G. Kim, H. S. Bae et al., “Simultaneous and synergistic effect of heavy metal adsorption on the enhanced photocatalytic performance of a visible-light-driven RS-TONR/TNT composite,” *Environmental Research*, vol. 180, article 108651, 2020.
- [86] Y. Sun, L. Xu, P. Jin, X. Bai, X. Jin, and X. Shi, “Simultaneous removal of colorless micropollutants and hexavalent chromium by pristine TiO<sub>2</sub> under visible light: an electron transfer mechanism,” *Chemical Engineering Journal*, vol. 405, article 126968, 2021.
- [87] Y. Lu, Y. Cai, S. Zhang et al., “Application of biochar-based materials in environmental remediation: from multi-level structures to specific devices,” *Biochar*, vol. 2, no. 1, pp. 1–31, 2020.
- [88] V. Nayak, K. Soontarapa, R. G. Balakrishna, M. Padaki, V. Y. Zadorozhnyy, and S. D. Kaloshkin, “Influence of TiO<sub>2</sub> charge and BSA-metal ion complexation on retention of Cr (VI) in ultrafiltration process,” *Journal of Alloys and Compounds*, vol. 832, article 153986, 2020.
- [89] S. Q. Wang, W. B. Liu, P. Fu, and W. L. Cheng, “Enhanced photoactivity of N-doped TiO<sub>2</sub> for Cr (VI) removal: influencing factors and mechanism,” *Korean Journal of Chemical Engineering*, vol. 34, no. 5, pp. 1584–1590, 2017.
- [90] C. Di Valentin, G. Pacchioni, and A. Selloni, “Origin of the different photoactivity of N-doped anatase and rutile TiO<sub>2</sub>,” *Physical Review B*, vol. 70, no. 8, article 085116, 2004.
- [91] B. Naik, K. Parida, and C. S. Gopinath, “Facile synthesis of N- and S-incorporated nanocrystalline TiO<sub>2</sub> and direct solar-light-driven photocatalytic activity,” *The Journal of Physical Chemistry C*, vol. 114, no. 45, pp. 19473–19482, 2010.
- [92] W. Shi, W. Yang, Q. Li, S. Gao, P. Shang, and J. K. Shang, “The synthesis of nitrogen/sulfur co-doped TiO<sub>2</sub> nanocrystals with a high specific surface area and a high percentage of {001} facets and their enhanced visible-light photocatalytic performance,” *Nanoscale Research Letters*, vol. 7, no. 1, pp. 1–9, 2012.
- [93] J. Xu, B. Yang, M. Wu, Z. Fu, Y. Lv, and Y. Zhao, “Novel N–F-codoped TiO<sub>2</sub> inverse opal with a hierarchical meso-/macroporous structure: synthesis, characterization, and photocatalysis,” *The Journal of Physical Chemistry C*, vol. 114, no. 36, pp. 15251–15259, 2010.
- [94] N. T. Padmanabhan, N. Thomas, J. Louis et al., “Graphene coupled TiO<sub>2</sub> photocatalysts for environmental applications: a review,” *Chemosphere*, vol. 271, article 129506, 2021.
- [95] F. Vajedi and H. Dehghani, “The characterization of TiO<sub>2</sub>-reduced graphene oxide nanocomposites and their performance in electrochemical determination for removing heavy metals ions of cadmium(II), lead(II) and copper(II),” *Materials Science and Engineering B*, vol. 243, pp. 189–198, 2019.
- [96] Y. Zhao, D. Zhao, C. Chen, and X. Wang, “Enhanced photo-reduction and removal of Cr(VI) on reduced graphene oxide decorated with TiO<sub>2</sub> nanoparticles,” *Journal of Colloid and Interface Science*, vol. 405, pp. 211–217, 2013.
- [97] L. Xu, L. Yang, X. Bai, X. du, Y. Wang, and P. Jin, “Persulfate activation towards organic decomposition and Cr(VI) reduction achieved by a novel CQDs-TiO<sub>2-x</sub>/rGO nanocomposite,” *Chemical Engineering Journal*, vol. 373, pp. 238–250, 2019.
- [98] J. Chen, M. Yu, C. Wang, J. Feng, and W. Yan, “Insight into the synergistic effect on selective adsorption for heavy metal ions by a polypyrrole/TiO<sub>2</sub> composite,” *Langmuir*, vol. 34, no. 34, pp. 10187–10196, 2018.
- [99] J.-Q. Wen, J. M. Zhang, Z. G. Qiu, X. Yang, and Z. Q. Li, “The investigation of Ce doped ZnO crystal: the electronic, optical and magnetic properties,” *Physica B: Condensed Matter*, vol. 534, pp. 44–50, 2018.
- [100] K. Harun, M. K. Yaakob, M. F. Mohamad Taib, B. Sahraoui, Z. A. Ahmad, and A. A. Mohamad, “Efficient diagnostics of the electronic and optical properties of defective ZnO nanoparticles synthesized using the sol–gel method: experimental and theoretical studies,” *Materials Research Express*, vol. 4, no. 8, article 085908, 2017.
- [101] Y. Zhao, L. Li, Y. Zuo et al., “Reduced graphene oxide supported ZnO/CdS heterojunction enhances photocatalytic removal efficiency of hexavalent chromium from aqueous solution,” *Chemosphere*, vol. 286, Part 3, article 131738, 2022.
- [102] I. A. Salem, M. A. Salem, and M. A. El-Ghobashy, “The dual role of ZnO nanoparticles for efficient capture of heavy metals and acid blue 92 from water,” *Journal of Molecular Liquids*, vol. 248, pp. 527–538, 2017.
- [103] R. Bhardwaj, A. Bharti, J. P. Singh, K. H. Chae, N. Goyal, and S. Gautam, “Structural and electronic investigation of ZnO nanostructures synthesized under different environments,” *Heliyon*, vol. 4, no. 4, article e00594, 2018.
- [104] I. N. Reddy, C. V. Reddy, M. Sreedhar, J. Shim, M. Cho, and D. Kim, “Effect of ball milling on optical properties and visible photocatalytic activity of Fe doped ZnO nanoparticles,” *Materials Science and Engineering B*, vol. 240, pp. 33–40, 2019.
- [105] V. Venkatesham, G. M. Madhu, S. V. Satyanarayana, and H. S. Preetham, “Adsorption of lead on gel combustion derived nano ZnO,” *Procedia Engineering*, vol. 51, pp. 308–313, 2013.
- [106] S. B. Khan, M. M. Rahman, H. M. Marwani, A. M. Asiri, and K. A. Alamry, “An assessment of zinc oxide nanosheets as a selective adsorbent for cadmium,” *Nanoscale Research Letters*, vol. 8, no. 1, pp. 1–8, 2013.
- [107] M. R. Shakil, A. M. el-Sawy, H. Tasnim et al., “Single-doped and multidoped transition-metal (Mn, Fe, Co, and Ni) ZnO and their electrocatalytic activities for oxygen reduction reaction,” *Inorganic Chemistry*, vol. 57, no. 16, pp. 9977–9987, 2018.
- [108] A. Taha, E. Da’na, and H. A. Hassanin, “Modified activated carbon loaded with bio-synthesized Ag/ZnO nanocomposite and its application for the removal of Cr (VI) ions from aqueous solution,” *Surfaces and Interfaces*, vol. 23, article 100928, 2021.
- [109] M. Mozammel, N. Najibi Ilkhechi, B. Ghezlbash, and S. Nasiri Khalil Abad, “Antibacterial and heavy ion removal properties of La- and Ti-doped ZnO nanoparticles,” *Materials Research Express*, vol. 6, no. 8, article 085010, 2019.
- [110] I. Ghiloufi, J. el Ghouli, A. E. Modwi, I. AlShunaifi, and L. el Mir, “Removal of lead (II) ion from aqueous solution using Ga-doped ZnO and Ca-doped ZnO nanopowder,” *Zeitschrift für Naturforschung A*, vol. 74, no. 7, pp. 573–580, 2019.
- [111] N. Q. Yang, J. Li, Y. N. Wang, and J. Ma, “Investigation of photocatalytic properties based on Fe and Ce co-doped ZnO via hydrothermal method and first principles,” *Materials Science in Semiconductor Processing*, vol. 131, article 105835, 2021.

- [112] Y. Liu, Q. Y. Hou, H. P. Xu, L. M. Li, and Y. Zhang, "First-principles study of the effect of heavy Ni doping on the electronic structure and absorption spectrum of wurtzite ZnO," *Physica B: Condensed Matter*, vol. 407, no. 13, pp. 2359–2364, 2012.
- [113] A. H. Mashhadzadeh, M. Fathalian, M. G. Ahangari, and M. H. Shahavi, "DFT study of Ni, Cu, Cd and Ag heavy metal atom adsorption onto the surface of the zinc-oxide nanotube and zinc-oxide graphene-like structure," *Materials Chemistry and Physics*, vol. 220, pp. 366–373, 2018.
- [114] F. Doagoo, M. Peyravi, and S. Khalili, "Photo-degradation and discoloration of nitrogen substituted ZnO via multilayer adsorptive membrane for Cr(VI) removal," *Journal of Environmental Chemical Engineering*, vol. 9, no. 2, article 105153, 2021.
- [115] S. Verma, S. A. Younis, K. H. Kim, and F. Dong, "Anisotropic ZnO nanostructures and their nanocomposites as an advanced platform for photocatalytic remediation," *Journal of Hazardous Materials*, vol. 415, article 125651, 2021.
- [116] V. Gurylev and T. P. Perng, "Defect engineering of ZnO: review on oxygen and zinc vacancies," *Journal of the European Ceramic Society*, vol. 41, no. 10, pp. 4977–4996, 2021.
- [117] X. Zhang, C. Shao, Z. Zhang et al., "In situ generation of well-dispersed ZnO quantum dots on electrospun silica nanotubes with high photocatalytic activity," *ACS Applied Materials & Interfaces*, vol. 4, no. 2, pp. 785–790, 2012.
- [118] K. Wetchakun, N. Wetchakun, and S. Sakulsermsuk, "An overview of solar/visible light-driven heterogeneous photocatalysis for water purification: TiO<sub>2</sub>- and ZnO-based photocatalysts used in suspension photoreactors," *Journal of Industrial and Engineering Chemistry*, vol. 71, pp. 19–49, 2019.
- [119] M. Naimi-Joubani, M. Shirzad-Siboni, J. K. Yang, M. Gholami, and M. Farzadkia, "Photocatalytic reduction of hexavalent chromium with illuminated ZnO/TiO<sub>2</sub> composite," *Journal of Industrial and Engineering Chemistry*, vol. 22, pp. 317–323, 2015.
- [120] M. Khosravi, N. Mehrdadi, G. Nabi Bidhendi, and M. Baghdadi, "Synthesis of sewage sludge-based carbon/TiO<sub>2</sub>/ZnO nanocomposite adsorbent for the removal of Ni(II), Cu(II), and chemical oxygen demands from aqueous solutions and industrial wastewater," *Water Environment Research*, vol. 92, no. 4, pp. 588–603, 2020.
- [121] Ş. Parlayıcı, A. Yar, E. Pehlivan, and A. Avcı, "ZnO-TiO<sub>2</sub> doped polyacrylonitrile nano fiber-mat for elimination of Cr (VI) from polluted water," *Journal of Analytical Science and Technology*, vol. 10, no. 1, pp. 1–12, 2019.
- [122] R. Acharya, B. Naik, and K. Parida, "Cr (VI) remediation from aqueous environment through modified-TiO<sub>2</sub>-mediated photocatalytic reduction," *Beilstein Journal of Nanotechnology*, vol. 9, no. 1, pp. 1448–1470, 2018.
- [123] A. A. Yaqoob, T. Parveen, K. Umar, and M. N. Mohamad Ibrahim, "Role of nanomaterials in the treatment of wastewater: a review," *Water*, vol. 12, no. 2, p. 495, 2020.
- [124] W. Liu, S. Tian, X. Zhao, W. Xie, Y. Gong, and D. Zhao, "Application of stabilized nanoparticles for in situ remediation of metal-contaminated soil and groundwater: a critical review," *Current Pollution Reports*, vol. 1, no. 4, pp. 280–291, 2015.
- [125] S. Teixeira, P. M. Martins, S. Lanceros-Méndez, K. Kühn, and G. Cuniberti, "Reusability of photocatalytic TiO<sub>2</sub> and ZnO nanoparticles immobilized in poly(vinylidene difluoride)-co-trifluoroethylene," *Applied Surface Science*, vol. 384, pp. 497–504, 2016.
- [126] N. Z. Arman, S. Salmiati, A. Aris et al., "A review on emerging pollutants in the water environment: existences, health effects and treatment processes," *Water*, vol. 13, no. 22, p. 3258, 2021.
- [127] M. Rigoletto, P. Calza, E. Gaggero, and E. Laurenti, "Hybrid materials for the removal of emerging pollutants in water: classification, synthesis, and properties," *Chemical Engineering Journal Advances*, vol. 10, article 100252, 2022.
- [128] N. Finčur, P. Sfirloagă, P. Putnik et al., "Removal of emerging pollutants from water using environmentally friendly processes: photocatalysts preparation, characterization, intermediates identification and toxicity assessment," *Nanomaterials*, vol. 11, no. 1, p. 215, 2021.
- [129] A. A. Bayode, E. M. Vieira, R. Moodley et al., "Tuning ZnO/GO p-n heterostructure with carbon interlayer supported on clay for visible-light catalysis: removal of steroid estrogens from water," *Chemical Engineering Journal*, vol. 420, article 127668, 2021.
- [130] N. G. Menon, L. George, S. S. V. Tatiparti, and S. Mukherji, "Efficacy and reusability of mixed-phase TiO<sub>2</sub>-ZnO nanocomposites for the removal of estrogenic effects of 17β-Estradiol and 17α-Ethinylestradiol from water," *Journal of Environmental Management*, vol. 288, article 112340, 2021.
- [131] M. G. Kibambe, M. N. B. Momba, A. P. Daso, M. C. van Zijl, and M. A. A. Coetzee, "Efficiency of selected wastewater treatment processes in removing estrogen compounds and reducing estrogenic activity using the T47D-KBLUC reporter gene assay," *Journal of Environmental Management*, vol. 260, article 110135, 2020.
- [132] S. Gupta, S. R. Moulik, P. Pal et al., "Estrogen-regulated expression of *cyp19a1a* and *cyp19a1b* genes in swim-up fry of *Labeo rohita*," *General and Comparative Endocrinology*, vol. 251, pp. 85–93, 2017.
- [133] A. H. Khavar, G. Moussavi, A. R. Mahjoub, R. Luque, D. Rodríguez-Padrón, and M. Sattari, "Enhanced visible light photocatalytic degradation of acetaminophen with Ag<sub>2</sub>[email protected] core-shell microsphere as a novel catalyst: catalyst preparation and characterization and mechanistic catalytic experiments," *Separation and Purification Technology*, vol. 229, article 115803, 2019.
- [134] A. F. López, M. Fabiani, V. L. Lassalle, C. V. Spetter, and M. D. F. Severini, "Critical review of the characteristics, interactions, and toxicity of micro/nanomaterials pollutants in aquatic environments," *Marine Pollution Bulletin*, vol. 174, article 113276, 2022.
- [135] P. Krystynik, K. Strunakova, M. Syc, and P. Kluson, "Notes on common misconceptions in microplastics removal from water," *Applied Sciences*, vol. 11, no. 13, p. 5833, 2021.
- [136] A. Uheida, H. G. Mejía, M. Abdel-Rehim, W. Hamd, and J. Dutta, "Visible light photocatalytic degradation of polypropylene microplastics in a continuous water flow system," *Journal of Hazardous Materials*, vol. 406, article 124299, 2021.