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Review

Photocatalysis for Heavy Metal Treatment: A Review

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Abstract: Environmental and human health are threatened by anthropogenic heavy metal discharge into watersheds. Traditional processes have many limitations, such as low efficiency, high cost, and by-products. Photocatalysis, an emerging advanced catalytic oxidation technology, uses light energy as the only source of energy. It is a clean new technology that can be widely used in the treatment of organic pollutants in water. Given the excellent adaptability of photocatalysis in environmental remediation, it can be used for the treatment of heavy metals. In this comprehensive review, the existing reported works in relevant areas are summarized and discussed. Moreover, recommendations for future work are provided.

Keywords: photocatalysis; heavy metal; treatment; removal

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1. Introduction

Heavy metals are defined as metals with relatively high densities (metals where the density is usually greater than 5 g/cm^3), high atomic weights, and high atomic numbers. Heavy metals pose a great threat to the ecosystem, which, in turn, affects human health. The presence of heavy metals, such as mercury, lead, copper, nickel, cadmium, or arsenic, can accumulate in the human body, causing organ failure or cancer and can severely endanger human health. In addition to direct health effects, the heavy metal pollution in in water bodies and the atmosphere can also lead to the poisoning of animals and plants, resulting in reduced crop yields, a shortage of food and water sources, ecological balance, and biodiversity damage. This would further induce large economic losses and disturb geographical and ecological balance because they are difficult to transform or degrade into harmless substances [1,2]. The common uses and health effects of several heavy metal elements are summarized in Table 1. Therefore, the proper disposal of heavy metal pollutants is imperative.

Photocatalysis is a popular technology among these new advanced oxidation technologies and exhibits promise in various areas [3–7]. Figure 1 illustrates a schematic diagram of the basic principle of the photocatalytic process. Generally, photocatalysts have semiconductor structures. When the semiconductor material is irradiated by light, electrons (e^-) located in the valence band may jump to CB and may leave a positively charged hole (h^+) on the VB if the energy of a photon in the incident light is greater than or equal to the bandgap energy between the semiconductor valence band (VB) and the conduction band (CB). This pair of h^+ and e^- can, respectively migrate to the surface of the semiconductor to undergo a series of oxidation and reduction reactions, which are embodied in the conversion of different valence states in the treatment of heavy metals [8–10]. In the photocatalysis process, the most essential limiting factors are the high energy requirements of the incident light caused by the wide bandgap and the easy recombination of photogenerated carriers (e^- and h^+). TiO_2, the most typical photocatalyst, has received the most extensive research. However, its wide bandgap only responds to UV light [11–13]. Hence, more photocatalysts with suitable and efficient bandgaps have been developed and used, such as Bi-based catalysts [14], C_3N_4 [15], and ZnO [16]. At present, there have been many active reports

on photocatalysis in organic wastewater treatment [17], water splitting for hydrogen and oxygen production [18], and nitrogen fixation [19]. Since photocatalysis does not require additional energy input besides light, the active species that are produced have good redox capabilities and do not produce additional pollution [20]. It is highly feasible to use it for redox in water treatment.

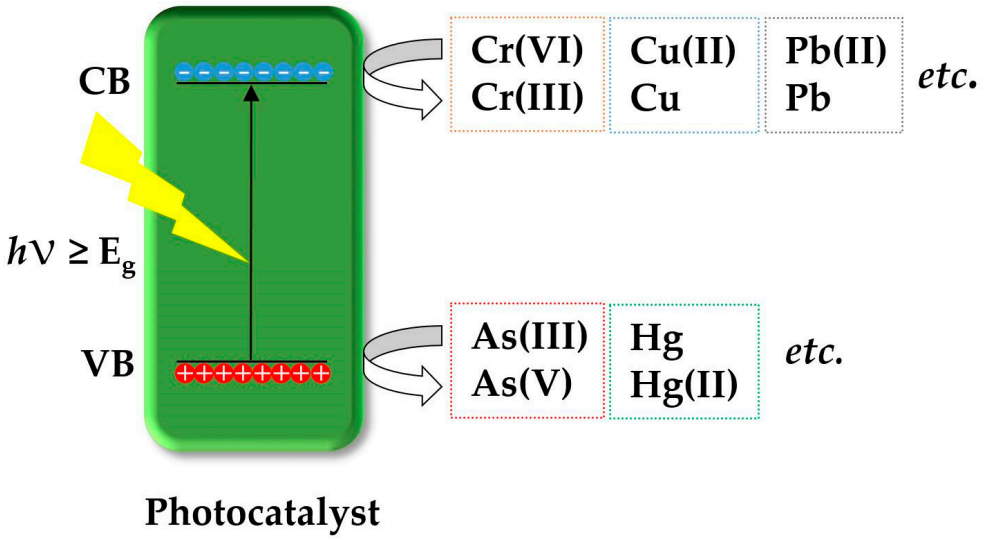

Figure 1. Schematic diagram of photocatalytic treatment of heavy metals.

Table 1. Health effects of exposure to several heavy metal elements (Adapted from [21]).

Heavy Metals	Use/Exposure	Health Effects	Maximum Contamination Level (WHO *) [22]
Chromium (Cr)	Electroplating/Lather tanning/paint industry	Respiratory cancers	50 ppb
Zinc (Zn)	Mining/manufacturing	Metal fume fever/restlessness	/
Cadmium (Cd)	Electroplating/pigment/plastic/polymerization industry	Bone damage/nephrotoxic effects	3 ppb
Mercury (Hg)	Pesticides/chlorine-alkali/paint/petrochemical industry	Dyslexia/neurobehavioral disorders/intellectual retardation/attention deficit hyperactivity disorder	1 ppb
Nickel (Ni)	Electroplating/mining/paint industry	Chronic bronchitis/cancers of the lungs and nasal sinus/decreased lung function	/
Platinum (Pt)	Mining/catalytic converter	Platinosis/allergic reactions/respiratory hypersensitive reaction	/
Arsenic (As)	Mining/wood preservative/biocides	Skin cancers/liver tumours/acute poisoning/gastrointestinal issues	10 ppb

(* WHO—World Health Organization; ppb—parts per billion).

2. Traditional Heavy Metal Treatment

Typical industrial methods employed in wastewater treatment, such as adsorption, chemical precipitation, ion exchange, ozonation, biological methods, and electrochemical methods activated by carbon, can hardly reduce the metal concentration in water to within the regulatory standards effectively [23]. This is because there is a considerable number of heavy metals in water that are complexed with organic chelating agents that come from textile, nuclear, and electroplating sources. With copper as an example, the adsorption efficiency is 49.3% of the original under competitive chelation with EDTA [24]. Figure 2 presents a schematic diagram of the most typical electrochemical water treatment tank. Its complete removal requires the assistance of other technologies, though it can effectively oxidize and reduce heavy metals. Moreover, the requirements of electrochemical treatment on equipment parameters and the huge power consumption also cannot be underestimated.

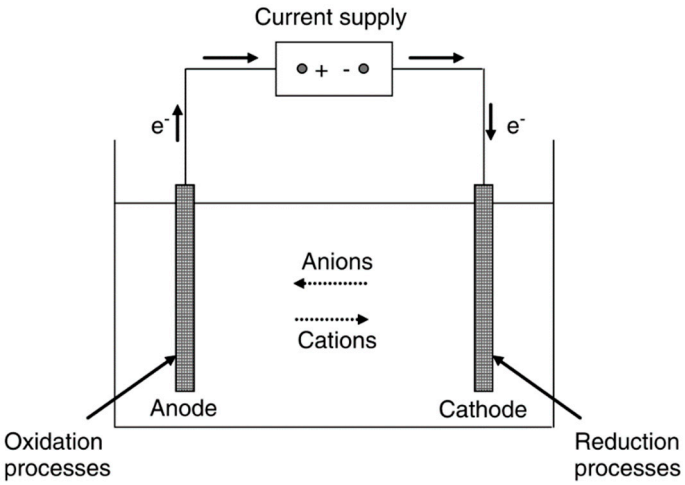

Figure 2. Schematic diagram of electrochemical reactor (Adapted from [25]).

Metals can be precipitated by the addition of coagulants such as alum, lime, alum salts, and other organic polymers. This method is used by almost three-quarters of plating companies. Among them, the most common precipitation methods include sulphide, sodium hydroxide, and carbonate methods. However, the major disadvantage of this process is the large amount of toxic sludge that is produces [26].

Additionally, there are some more processes that can be used to complete heavy metal treatment. Nonetheless, they have their defects, which are summarized in Table 2.

Table 2. Traditional heavy metal processing techniques and their drawbacks.

Techniques	Drawbacks	Ref.
Direct adsorption	Inefficient in the presence of ligand	[24]
Chemical precipitation	Inefficient in the presence of ligand and potential pollution	[26]
Ozonation	Difficulties in separation and potential contamination	[23]
Ultrafiltration	Sludge generation	[27]
Ion-exchange	High cost and partial removal of some ions	[28]
Reverse osmosis	High cost	[29]
Electrowinning	Many equipment restrictions, large investment and continuous power input demand	[30]
Carbon adsorption	High cost and low adsorption rates of water-soluble components	[31]
Phytoremediation	Time-consuming and difficult to regenerate plants	[32]

The good redox ability of photocatalytic technology and the performance and adaptability in the treatment of organic pollutants in water [33] enable it to be used for the recovery of heavy metals. Its main advantage is that it does not require energy input other than light energy, which is different from many traditional processes and is beneficial to its continuous operation [34]. In photocatalytic redox, no polluting intermediates are produced. This is another important advantage. This environmentally friendly feature is consistent with the purpose of water treatment [35]. Finally, photoreactions can be adopted to deposit heavy metals that are easily reduced on the surface of the catalyst in the form of solids to achieve the effect of direct separation from the solution [36]. These characteristics of photocatalysis are not available in many traditional heavy metal processing techniques.

3. Photocatalytic Heavy Metal Treatment

As mentioned above, the unique advantages of photocatalysis equip it with great potential in the treatment of heavy metals [11,14,34,37]. Therefore, it has also attracted the attention of many researchers [38–49]. Some reported examples of the photocatalytic treatment of heavy metals are provided in Table 3. The specific situations of different heavy metals in photocatalytic treatments are detailed as follows.

Table 3. Overview of applications of photocatalytic heavy metal treatment.

Photocatalyst	Heavy Metal	Redox Products	Light Type	Efficiency	Irradiation Time	Ref.
Porous BNNSs/TiO_2	Cr(VI)	Cr(III)	Simulated solar light and visible light	99% and 99%	70 min and 80 min	[50]
TiO_2 hollow sphere	Cr(VI)	Cr(III)	UV light	0.0867 min^{-1}	80 min	[51]
TiO_2	Cr(VI)	Cr(III)	Visible light	100% (formic acid as electron donor)	80 min	[52]
TiO_2 nanotube arrays/Ag-AgBr	Cr(VI)	Cr(III)	Solar light	58.63%	180 min	[53]
CdS/TiO_2	Cr(VI)	Cr(III)	Visible light	2.14×10^{-2} min^{-1}	180 min	[54]
$ZnTiO_3/Zn_2Ti_3O_8$/ZnO	Cr(VI)	Cr(III)	Full spectrum light	47%	150 min	[55]
ZnO–graphene	Cr(VI)	Cr(III)	UV light	98%	240 min	[56]
Ag/ZnO@CF	Cr(VI)	Cr(III)	Full spectrum light	71.82%	210 min	[16]
PW_{12}/CN@Bi_2WO_6	Cr(VI)	Cr(III)	Visible light	98.7%	90 min	[57]
g-C_3N_4/diatomite composites/Ag/AgCl	Cr(VI)	Cr(III)	Visible light	7.4×10^{-2} min^{-1}	45 min	[58]
Nb_2O_5	Cr(VI)	Cr(III)	Full spectrum light	90%	120 min	[59]
ZrO_2	Cr(VI)	Cr(III)/Cr	UV light	About 100%	90 min	[60]
Iron(III) cross-linking alginate hydrogel beads	Cr(VI) and As(III)	Cr(III) and As(V)	Full spectrum light	90% and 100%	150 min	[61]
Cellulose acetate/chitosan/single walled carbon nanotubes/ferrite/titanium dioxide	Cr(VI) and As(V)	Cr(III) and As	UV light	0.0925 and 0.0896 min^{-1}	60 min	[62]
BiOI	As(III)	As(V)	Natural light	1 mg/L to 10 µg/L	3 h	[63]
TiO_2	As(III)	As(V)	UV light	About 100%	30 min	[64]
TiO_2-ZrO_2	Cu(II) and Cr(VI)	Cu and Cr(III)/Cr	UV light	96.29 and 99.17%	630 min	[65]
TiO_2/Alg/FeNPs	Cr(III), Cu(II) and Pb(II)	Cr, Cu and Pb	UV light	98.6%, 98.4% and 99.5%	120 min	[66]
α-Fe_2O_3/g-C_3N_4	Hg(II)	Hg	Visible light	90%	60 min	[67]
BiOI/BiOCl	Hg	HgO/Hg(II)	Visible light	72.4%	50 min	[68]
CeO_2/$BiOIO_3$	Hg	HgO	Visible light	86.53%	30 min	[69]
$BiOIO_3$/MoS_2/C500	Hg	HgO	UV light	78.32%	70 min	[70]
Ag/TiO_2	Cd(II), Ni(II), Zn(II), Mn(II) and Cu(II)	Cd, Ni, Zn, Mn and Cu	UV light	100, 96, 65.13, 58.22 and 56.20%	120 min	[71]
$NiFe_2O_4$-Pd	Pb(II) and Cd(II)	Pb and Cd	Full spectrum light	1.4×10^{-1} and 0.86×10^{-1} min^{-1}	60 min	[72]
Chitosan/Ag	Cu(II), Pb(II) and Cd(II)	Cu, Pb and Cd	Natural sunlight	1.10×10^{-4}, 1.4×10^{-4} and 1.5×10^{-4} mol $dm^{-3}s^{-1}$	240 min	[73]
SnO_2 nanoparticles	Co(II)	Co	UV light	94%	60 min	[74]

3.1. Chromium (Cr)

Chromium is the most studied and most typical metal in heavy metal removal studies. It is a metal with numerous industrial and technological applications in fields such as electroplating, the textile industry, wood preservation, and metallurgy. The production of wastewater containing chromium ions is inevitable with the use of chromium. Cr(VI) ions have been discovered to be more toxic than Cr(III) ions. Compared to Cr(III), which is more thermodynamically stable, long-term exposure to Cr(VI) can damage the nasal septum, cause lung cancer, and result in skin ulcers [75]. Among heavy metal ions, the treatment of Cr(VI) ions is the most studied. Some works have been published on the photocatalytic reduction of Cr(VI) using TiO_2-, ZnO-, CdS-, and ZnS-based catalysts [16,50–62,65].

In 2005, Tuprakay et al. successfully photo-reduced Cr(VI) by using immobilized TiO_2 under a UV light intensity of 171 W/m^2 in 32 h. The Cr(VI) adsorption followed first-order kinetics, while the reduction exhibited zero-order kinetics [76]. Five years later, Idris et al. observed that the initial concentration of the Cr(VI) present before photoreduction plays a crucial role in determining its removal efficiency. At an equilibrium state, the removal efficiency of Cr(VI) at initial concentrations of 25, 50, 75, 100, 125, and 150 mg/L was revealed to be 100%, 100%, 100%, 100%, 70%, and 70% in 100 min, respectively. A further investigation indicates that the percentage adsorption of Cr(VI) decreased with

the increasing initial Cr(VI) concentration. Moreover, this experiment was conducted in sunlight with the use of magnetically separable photocatalyst beads, allowing it to be achieved in less time [77]. The photocatalytic reduction of Cr(VI) is feasible under visible light. Dye-photosensitized TiO_2 samples successfully reduced Cr(VI) under visible light.

Di Iorio et al. reported a high efficiency in Cr(VI) reduction by using alizarin red chelated to TiO_2. This was slightly dependent on the Cr(VI) concentration and was independent of the photon flux and the irradiation wavelength [78]. At a pH of 2, a rapid reduction of Cr(VI) was observed when visible light was irradiated on TiO_2 coated with hydroxyl aluminium tricarboxymonoamide phthalocyanine (AITCPc) in the presence of 4-chlorophenol (4-CP) as a sacrificial donor assisting in preventing the photobleaching of AITCPc [79]. Figure 3a illustrates that the phthalocyanine (Pc) on the surface of TiO_2 will excite electrons and holes when photo-sensitized. This is different from the photocatalysis principle of a single material. Moreover, they will migrate to CB and VB for their respective oxidation and reduction reactions. Figure 3b presents the energy band change after the coupling of TiO_2 and AITCPc. It can also reflect the migration process of excited electrons on AITCPc to the CB of TiO_2. In this way, the coupling effect between different materials can weaken the light utilization efficiency of the entire photocatalytic system, improve the separation efficiency of photogenerated carriers, and enhance the overall reduction ability and efficiency of the entire photocatalytic system to Cr(VI). On the excitation of the dye, an electron was injected into the conduction band to promote Cr(VI) reduction [79,80]. In these photoreduction studies, most of the Cr(VI) ions are reduced to Cr(III) ions, while only a small part is reduced to Cr atoms [60,65].

$$Cr(VI) + e^- \rightarrow Cr(V) \quad (1)$$

$$Cr(V) + e^- \rightarrow Cr(IV) \quad (2)$$

$$Cr(IV) + e^- \rightarrow Cr(III) \quad (3)$$

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7\,H_2O \left(E^0 = +1.33\ V\right) \quad (4)$$

The photocatalytic treatment of Cr(VI) is a complete photoreduction process, which is largely affected by the following three factors:

1. A low pH that favors the net reaction in Equation (3); however, neutral or alkaline conditions favor the precipitation and immobilization of Cr(III) as the oxides or hydroxides, contributing to enhancing separation even further [81–83].
2. The addition of organic compounds can accelerate the reduction of Cr(VI) by acting as hole or ·OH scavengers [84].
3. Cr(VI) reduction is independent of molecular oxygen, especially at a low pH [65].

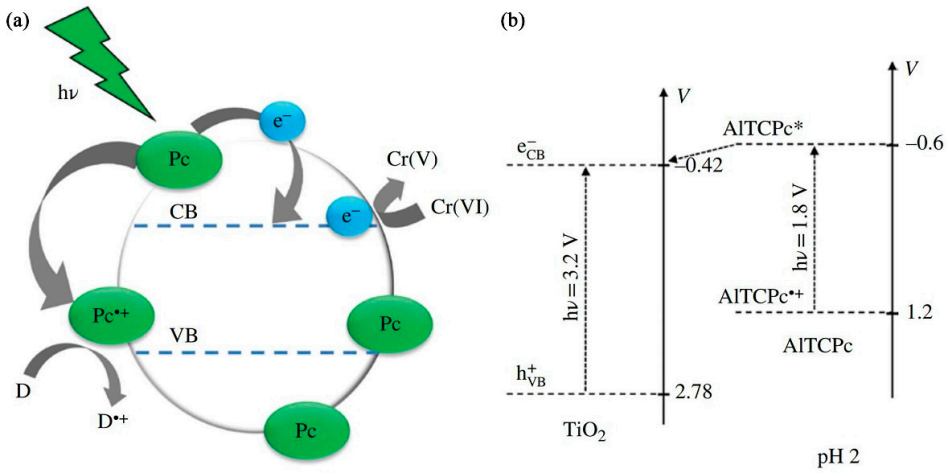

Figure 3. (**a**) Schematic diagram of heterogeneous photocatalytic reduction of Cr(VI) under visible light and (**b**) energy band of TiO_2 modified with AITCPc (Adapted from [79]).

In addition to Cr(VI), there are also studies on the removal of Cr(III) ions. Devagi et al. treated wastewater containing three heavy metal ions: Cr(III), Cu(II), and Pb(II), at the same time. They revealed that the adsorption in their system can significantly contribute to the removal of heavy metal ions instead of photoreduction [66].

3.2. Arsenic (As)

As another common heavy metal element, arsenic is highly toxic. This has been demonstrated through the long-term drinking of arsenic-containing water causing various cancers [64]. In addition to the risk of carcinogenesis and acute poisoning, some investigations suggest that chronic arsenic poisoning can impact mental health and the neurobehavior of children, causing long-term and irreversible social harm [85,86]. In an aqueous solution, arsenic mainly exists in the forms of As(III) and As(V). Compared to As(III), As(V) ions are less toxic and are more easily adsorbed and removed [87]. When pH < 9, it mainly exists in the non-ionic form of H_3AsO_3, which is difficult to remove by simple coagulation precipitation or adsorption because of the neutrality and difficult ionization of H_3AsO_3 [88,89]. Recently, Zhang et al. effectively achieved the removal of Cr(VI)/As(III) by applying iron(III) cross-linking alginate hydrogel beads (Fe-SA) as photocatalyst under simulated sunlight. The Fe-SA system used Fe(II) and CO_2 as intermediates while reducing Cr(VI) and oxidizing As(III) by the photoinduced ligand to metal charge transfer under UV light and adsorbing them (Figure 4). This efficient synergistic system enables the two heavy metals to reach more than 80% in a wide pH range (3–7). In this study, Cr(VI) was reduced to Cr(III) ions, and As(III) was oxidized to As(V) ions. Then, they were adsorbed or settled, allowing them to be removed from the water [61].

Photocatalysis offers a low-cost alternative in treatments to remove arsenic from wastewater. Meichtry et al. impregnated the walls of PET plastic bottles with TiO_2, which is the most typical and most commonly used photocatalyst. As(III) solutions of 1000 µg/L at a pH of 7.8 were placed in the bottles and were irradiated by UV light for 6 h; finally, a removal efficiency of 80–86% was recorded for arsenic; this process could be repeated up to three times without any loss of efficiency [90]. The removal efficiency of 94% was recorded in the photooxidation of As from well water samples (taken from Las Hermanas, Santiago del Estero Province, Argentina). This was performed under solar irradiation with the addition of $FeCl_3$ at the end of the experiment. It was discovered to be within the limits of the World Health Organization (WHO).

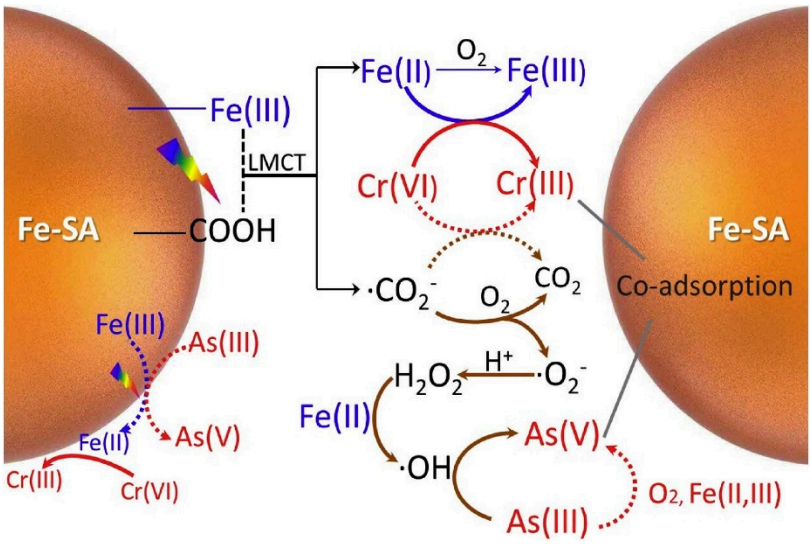

Figure 4. Schematic diagram of photocatalytic simultaneous conversion of Cr(VI) and As(III). (LMCT—ligand to metal charge transfer) (Adapted from [61]).

Simultaneously, there have also been explorations on the reduction and removal of As(V) [62]. Research demonstrates that As(V) can be reduced in the dark by accumulated electrons through the UV irradiation of TiO_2 nanoparticles in alcohol. The accumulation of electrons and their participation in the reduction of As(V) was detected as Ti(III) by UV-vis spectrophotometry [91,92].

3.3. Mercury (Hg)

The ingestion of mercury by organisms can cause permanent enzyme inactivation, leaving a devastating effect on metabolic functions [93]. Unlike other heavy metal forms of pollution, mercury is liquid at room temperature. The flow properties of mercury liquid and steam can significantly boost the permeability and scope of pollution. In cases where ions have similar toxicity to other heavy metals, the elemental form of mercury also has strong toxicity and diffusivity. Thus, Hg(0) and Hg(II) have different photocatalytic treatment methods.

Chen et al. revealed that Ag(I), Pb(II), Hg(II), Cr(VI), and Fe(III) can be reduced by photocatalysis after 65 min of irradiation using TiO_2 as the photocatalyst, with a removal efficiency of 99.7%, 27.2%, 70%, 79.1%, and 100%, respectively [94]. Kadi et al. employed α-Fe_2O_3/g-C_3N_4 to reduce Hg(II) in water under visible light. Within 60 min, 100 mg/L of Hg(II) was completely converted [67]. The photocatalyst adopted in their study exhibited good activity in the photoreduction process and could be used to reduce other heavy metal ions. Regarding mercury ions, simple reduction is not enough for the removal of heavy metal elements. After the mercury ions are reduced to elemental mercury, adsorption may be an indispensable part of this process.

Due to its low water solubility and high volatility, Hg(0) is generally considered more difficult to remove than Hg(II). Several reports have verified that Bi-based photocatalysts show good activity in Hg(0) removal [69,70]. The BiOI/BiOCl microflowers prepared by Sun et al. can effectively photocatalyze oxidation and trap Hg in the gas phase [68]. Different from ordinary heterostructures, the unique multi-level charge transport path of this microflower-like BiOCl/BiOI alternate arrangement structure equips it with better charge transport and photo-generated carrier separation capabilities. The mechanism diagram is illustrated in Figure 5. The experimental results suggest that the Hg removal rate of this microflower BiOCl/BiOI is as high as 72.2%, which is more than four times the efficiency of pure BiOCl and BiOI.

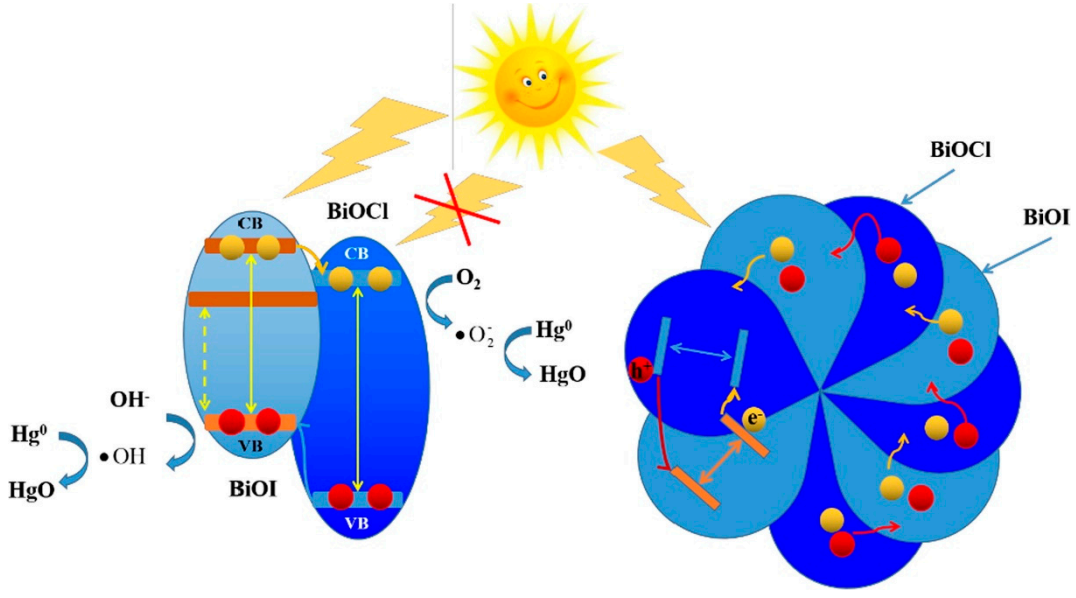

Figure 5. The mechanism of photocatalytic removal of gas-phase Hg(0) under visible light (Adapted from [68]).

To sum up, it is a more feasible and reasonable treatment to oxidize the elemental state of Hg to Hg(II) and to then remove it in the form of HgO.

3.4. Other Heavy Metals

Moreover, there are many kinds of heavy metal elements that are potentially harmful to the environment. These are not as typical as Cr(VI), nor are they as special as Hg. Considering that simple photoreduction combined with adsorption can effectively treat these heavy metals, they are classified into the same category. Cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), manganese (Mn), nickel (Ni), and cobalt (Co) are also common heavy metals. They will threaten environmental safety and human health when existing in the form of ions in the solution.

Wahyuni et al. explained that Cr(VI), Cu(II), and Cd(II) can be reduced photocatalytically, while Pb(II) ions preferably oxidize than reduce because of their negative reduction potential value.

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \qquad \left(E^0 = +0.34\ V\right) \tag{5}$$

$$Cd^{2+} + 2e^- \rightarrow Cd^0 \qquad \left(E^0 = -0.403\ V\right) \tag{6}$$

$$Pb^{2+} \rightarrow Pb^{4+} + 2e^- \qquad \left(E^0 = -0.67\ V\right) \tag{7}$$

In the removal of heavy metals, the influence of pH is a critical factor influencing the sedimentation of ions. According to reports, the optimum pH is 5 in such a system. At this pH, the removal efficiency of 15%, 40%, 45%, and 75% was achieved for Cd(II), Pb(II), Cu(II), and Cr(VI), respectively. At a more alkaline pH (pH 13), Cr(VI) is hardly removed effectively, while the removal rate of Cd(II), Pb(II), and Cu(II) is close to 100%.

4. Discussion and Outlooks

Photocatalytic removal of heavy metals is an essential part of photocatalytic water treatment. At present, the removal of various heavy metal elements using photocatalytic technology has been extensively studied. In this study, the typical works of this research topic are summarized. Although this process has presented advantages, there are still obstacles in its future applications. Possible solutions to existing problems and recommendations for future work are suggested as follows:

1. *Low photocatalytic efficiency:* At present, the efficiency of the photocatalytic reaction remains low. This is reflected not only in the removal of heavy metals but also in other photocatalytic processes. This situation is expected to be improved as more new materials presenting higher catalytic activity and higher stability efficiency or modification methods (such as doping and morphology control) that can improve the photocatalytic activity and stability of existing materials are proposed.
2. *Low light utilization efficiency:* Although natural solar energy resources are extremely abundant, the current light energy that can be utilized by photocatalysis is still very low. From one perspective, this is caused by the poor response of the photocatalyst to visible light. From another perspective, it is related to the current photocatalytic system. The former can be improved through the improvement of materials while the latter may require breakthroughs in reactor design.
3. *Continuous operation method:* It is difficult to remove heavy metals through simple oxidation or reduction. It is a common photocatalytic treatment method to convert difficult-to-treat heavy metal atoms or ions into a form that is easier to adsorb or settle and before removal. Its practical application would lie in the organic combination of the catalytic process and the adsorption/sedimentation process to ensure that the entire process has better overall continuity.
4. *No standard platform*: Although there is a WHO standard for the removal of heavy metals, this standard has not been widely adopted, especially in photocatalysis re-

search. Moreover, the existing research on the use of light sources and other aspects of the divergence is sufficient. To date, no standard platform can use a unified standard to evaluate the photoactivity of different photocatalysts in different laboratories. The establishment of this standard is necessary and urgent.

5. *Technology coupling*: With the current efficiency of photocatalysis, it is significantly difficult to complete the task of water treatment on its own. Generally, the combination of different technologies is effective. It may be a good choice to organically combine the photocatalytic system with the existing water treatment technology.

Current research has demonstrated that photocatalytic technology can play a role in the removal of heavy metals. However, there are still many problems in this process, such as low efficiency, difficult separation, and difficult catalyst regeneration. Therefore, this advanced technology requires further development.

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