Chapter 2

Photocatalytic Heavy Metal Detoxification from Water Systems

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Abstract

Heavy metals are one of the greatest elevating threat to mankind and other living organisms and it is released into the environment due to increasing dumpsites, transports, and industrial sectors. The industrial wastewater containing heavy metal ions easily enters into the food chain through the air, water, and soil; it results in bioaccumulation and biomagnifications of metal ions in human beings. It causes severe chronic health disorders affecting the nervous system, circulatory system, digestive system and other sensitive organs of the human body. Many conventional techniques such as adsorption, coagulation, flocculation, electrochemical treatment, and biological treatment are used for the reduction of heavy metal ions in the aqueous system. The photocatalysis method is one of the emerging effective ways for eliminating the toxic metal ions from the aqueous solution. This chapter elaborates the principle, mechanism and various methods utilized in the photocatalytic reduction of heavy metal ions from the wastewater.

Keywords

Photocatalytic, Heavy Metal, Environment, Mechanism, Wastewater

Contents

Photocatalytic Heavy Metal Detoxification from Water Systems.....	57
1. Introduction.....	58
1.1 Sources of heavy metal pollution	60
1.2 Bio-importance of heavy metals.....	61

1.3	Deleterious Environmental and health effects.....	62
2.	Various heavy metal removal technologies	63
2.1	Advanced oxidation process	63
2.2	Photocatalysis	64
2.3	Principle & mechanism behind photocatalysis.....	66
3.	Photocatalysis for the heavy metal recovery	66
3.1	Chromium (Cr)	68
3.2	Arsenic (As).....	69
3.3	Cadmium (Cd)	70
3.4	Copper (Cu ²⁺).....	71
3.5	Lead (Pb ²⁺).....	71
3.6	Mercury.....	72
	Conclusion & Future perspectives	72
	References	73

1. Introduction

Our universe is basically composed of three fundamental factors such as air, water, and soil in which the entire ecosystem depend upon for survival and growth. The term environment is characterized as the collection of various substantial conditions encompassing the biotic and abiotic factors present in the ecosystem [1]. Water is one of the fundamental requirement for the growth and development of all living beings. Life in the earth cannot be imagined without the presence of water and it always plays a crucial role in the sustenance of the living organisms. The ingress of various hazardous contaminants from the environment into the water bodies damages the quality of the drinking water by making it unfit for drinking and causes water deficiency. The water related problems have become a major concern in many developing countries and it causes various irreversible negative impacts on the environment. Some of the major contaminants released from the industries which affect the wellness of the environment are heavy metals, dyes, pesticides, oils and hydrocarbons, and these contaminants as a great threat to aquatic and terrestrial ecosystem [2]. Heavy metals are an indigenous component of the surface of the earth; furthermore, it is also released during the natural activities such as volcanic eruption and disintegration of rocks. They are a group of metals and metalloids that possess higher solidity multiple times than that of water [3]. The accelerated stride in the

proliferation of industrialization, urbanization, and land utilization sectors are the major reason contributing to the evolution of toxic metal pollution. The heavy metal pollution has become one of the greatest threats globally because of their hazardous consequences on the living beings and ecosystem [4]. Heavy metals generally refer to a group of metals and metalloids which possess atomic weight higher than 4 g/cm^3 which is probably five times or denser than the water. The heavy metals are lethal metallic components of higher atomic weight and density; it is also highly pernicious even in trace concentrations [1]. The heavy metals possess specific gravity more than 5.0 g/cm^3 and their atomic weight lies between the ranges of 63.5 – 200.6. The heavy metals are branched into three major types such as essential, valuable and pernicious metal ions. The noxious and pernicious metal ions are highly capable of causing serious damages to the wellness of the aquatic and terrestrial living organisms. Due to the increased utilization of heavy metal in various industrial and automobile sectors, their discharge into the environment got elevated. In addition, the complex non-degradable nature of the heavy metal retains it in the ecosystem leading to bioaccumulation of toxic metals in the food items [5]. Various anthropogenic activities such as industrial, domestic and commercial sources emit an enormous amount of toxic metal ions into the environment, furthermore, these contaminants endure strongly in the surrounding air, water and soil gradually invades the human body through the food cycle and gets bio-magnified. Some of the heavy metals which are predominantly used in various industrial applications are Copper, Arsenic, Silver, Mercury, Lead, Iron, Cadmium, Platinum, Zinc, Boron, Chromium, Antimony, Selenium and Cobalt [1,6]. In light of their prompt danger to human wellbeing and nature, WHO has declared four toxic metals such as Lead, Arsenic, Cadmium, and mercury in their list of top 10 hazardous chemical substances which are the greatest threat to mankind [3]. The heavy metals can be segregated into two types such as essential and toxic heavy metals. Some of the trace elements such as Zn, Fe, and Cu are required for the enhanced metabolism and growth of the human body; in addition, these essential heavy metals play a vital role in the enzymatic activities taking part in the human body. Certain other heavy metals such Arsenic, Lead, Cadmium, etc., fall under the category of hazardous metal ions which are not required for the function of the human body, in addition, these toxic metals are extremely destructive posing serious threats to the ecosystem [4]. The density and toxicity of a compound are directly proportional to each other, the compounds with higher density possess acute toxicity even at trace concentrations. In the current era, the health complications caused because of these heavy metals are elevated, on the other hand, the utilization of the heavy metals have also been increased in various applications such as agriculture, industries, municipal and household sectors [7]. In order to reduce the catastrophic aftereffect of the heavy metals, Government has enunciated several rules and regulations for the industries and domestic sectors for the proper disposal of heavy metals. Government authorities have made

stringent laws for the treatment of industrial effluent before discharging it into the environment, furthermore has also derived strict permissible limits for the heavy metals to be present in drinking water, industrial effluents and all other drainage systems [2]. The application of phosphate fertilizers in agricultural land emits an enormous concentration of cadmium heavy metal which is one of the most hazardous compounds in damaging the lives [6]. The conventional treatment techniques such as Adsorption, Coagulation, Flocculation, Chemical precipitation, Biological treatment, Ion exchange, Flotation, Advanced oxidation process and Photo catalysis have been used for the treatment of heavy metal [2, 8]. Among, all the techniques the Photocatalysis is seemed to be an efficient technique in the elimination of heavy metal ions, in addition, this technique seemed to possess the capability to overcome all the limitations occurring in conventional methods such as higher cost, lesser performance and secondary waste production. The Photo catalysis technique basically utilizes the solar energy as a main source and it is used in various appliances such as dye degradation, production of hydrogen, reduction of carbon dioxide and generation of heavy metal ions of high valence [9]. This chapter explains the impact of heavy metal ions on the environment and it also demonstrates the effective detoxification of heavy metals present in the aqueous system using the photocatalysis technique.

1.1 Sources of heavy metal pollution

Heavy metal is an integral component of earth's crust and it is naturally present in rocks, sediments, water, soil, microorganism, etc. The heavy metal ores remain in the sediments and rocks in various chemical forms such as sulfides, oxides, or both sulfide and oxide ores [1]. According to the reports stated by UNEP 2004, the persistent nature of the heavy metals leads to the bioaccumulation and biomagnifications of toxic metal ions inside the human body. The natural and anthropogenic sources are the two main reasons contributing to the discharge of toxic metals into the environment and the various sources of heavy metal pollution is depicted in the fig 1. More commonly, heavy metals are present in natural sources such as rocks, soils, and sediments. Furthermore, the human activities such as mining, smelting, and weathering release an enormous amount of toxic heavy metal ion into the atmosphere and the drain released from these processes consist of toxic chemicals, heavy metals and acids [6].

The effluent released from some industries such as textile, leather, electroplating, distilleries, and chemical is composed of elevated levels of toxic metals like Mn, Cu, Pb, Fe, Cr and Ni which can cause dreadful health disorders to mankind. The sources of heavy metals are classified into two types such as point sources and non-point sources. The combustion, agricultural dissipation, soil abrasion, fertilizers usage, and merchandise

repository are some of the non-point sources of the heavy metals. On the other hand, the industries indulging in transport, leather, mining, textiles, chemicals, electroplating, thermal power, smelting, and e-waste are some of the major sources of a point source of heavy metal pollution. The heavy metal particles gushed from its sources gets compiled in the soil surfaces, further, the deposited heavy metals get acquired in the root through soil and consumption of this heavy metal accumulated plant by plants and humans result in bioaccumulation and biomagnifications [4]. The feasibility of the heavy metal is based on the certain physical, chemical and biological parameters such as adsorption, detachment, temperature, solubility, interaction and type of phase in which it is clubbed to [7].

Figure 1: Various sources of heavy metal pollution.

1.2 Bio-importance of heavy metals

Heavy metals occupy an important position in industries for the production of various goods used by humans in their everyday life [1]. The heavy metals act as micronutrients and it also plays a vital role in stabilizing the redox process, regulating the osmotic pressure and enhancement of enzymatic reactions [6]. They occupy an important place in enhancing various physiological and biochemical reactions [7]. The heavy metals such as Lead,

Mercury, and Aluminium are used in the manufacturing process of products such as lamps, utensils and medical equipment [1]. Arsenic at a limited concentration serves as one of the good trace elements with good nutrition. Magnesium plays an important role in the circulatory system as an electrolytic substance and it is highly required by pregnant ladies and feeding mothers. Zinc supports in maintaining the copper concentration in the human body, in addition, it is highly required in increasing the reproductive activity in the males and enhancing the enzymatic activity [1].

1.3 Deleterious Environmental and health effects

European Commission has declared that the chemical substances which are highly noxious, obdurate and acquired in the living cells. Generally, several organic contaminants breakdown into the two major end products such as water and Carbon dioxide but the heavy metals are non-degradable and possess highly enduring properties [6]. Basically, the heavy metals are highly toxic and life-damaging components present in the environment [1]. The heavy metals such as zinc, copper, and iron remain as an indispensable ingredient in enhancing the metabolic activity of the human body [4]. The pernicious nature of heavy metals affects the living beings vigorously when utilized above the required levels, further; it causes dreadful diseases which can affect the intestines, circulatory system, respiratory system and other sensitive organs [1]. The emission of heavy metal into nearby aquatic sources through the industrial effluent results in damaging the maritime creatures by inducing oxygen deficiency and eutrophication in the water resources. In addition, the dissipated heavy metals are reformed into hydrated ions which are exceedingly deadly to the organisms surviving in the water [2]. The uptake of metal ions into the cells spoils the DNA by denaturing the DNA and nuclear proteins, further it induces structural changes and collapse the DNA leading to apoptosis, uncontrolled cell growth and cell cycle modification [7]. The region near the coal mining sites is the predominant sites which are highly affected by the heavy metals. The heavy metals emitted from the mines seeps into the underground and reach the water table resulting in the water pollution [1]. The ionic mode of toxic metals such as Silver, Cadmium, Arsenic and Lead easily interacts with the human body easily and also it is very difficult to separate it from the biomolecules. Further, this heavy metals enter the food chain of a living organism and gets bio magnified [2]. The consumption of heavy metal accumulated green leafy vegetables results in health disorders such as mental retardation, stomach cancer, nutritional deficiency, immunological disorder and depletion of bones [4]. The consumption of lethal heavy metals through food, air and water damages the cell development by production of free radicals which induce oxidative stress to the cells [2]. The heavy metals on adsorption into the cell structure of the living beings affect the internal components such as mitochondria, endoplasmic reticulum,

nucleus, cell membrane, etc. It also damages the enzymatic activity which is indulged in dealing with cell repair, metabolism, and detox activity [7].

2. Various heavy metal removal technologies

In order to eliminate these toxic metals from our ecosystem, several treatment methodologies have been adopted by industries and domestic sectors. Basically, the effluent treatment process is divided into three categories such as physical, chemical and biological treatment. Several conventional technologies such as Adsorption, Precipitation, Electrodialysis, Filtration, Extraction, Ion exchange, Membrane reactors, Electrowinning, Floatation and Advanced oxidation process have been followed in treating the heavy metal contaminated industrial effluents. Several legislations and laws have been enunciated to restrict the emission of heavy metals into the society, but the effluent treatment is not effectively implemented in several industries due to some limitations such as higher utilization of water, huge energy expenditure and persistence of the pollutants [2, 4]. In recent times, the photocatalysis is known to be a developing technique for the sequestration of heavy metal ions. It utilizes a very abundant renewable energy source (i.e.) solar energy and it is used to activate the catalyst for the production of electron-hole pairs which helps in the sequestration of toxic metal ions [10]. The secondary waste emission is a major drawback found in many conventional technologies used in the wastewater treatment sector. Further, to combat this drawback and also to provide an environmentally hygienic technology for the elimination of toxic pollutants the photocatalysis technique is highly preferred among the researchers. Highly non-degradable contaminants such as petroleum and chlorinated hydrocarbons are tedious to degrade in conventional treatment technologies, whereas in the photocatalysis it is efficiently degraded into simpler compounds such as CO₂ and H₂O using the TiO₂/UV catalyst.

2.1 Advanced oxidation process

Advanced oxidation process (AOP) is an emerging eco-friendly technique used in various industrial and research sectors widely. This AOP can be effectively used for the treatment of all kinds of contaminants such as pesticides, insecticides, dyes, heavy metals, aromatic hydrocarbons, chlorinated hydrocarbons, air contaminants and other complicated organic compounds [12]. In order to reduce the hazardous effects of toxic metals, the Advanced Oxidation Process (AOP) was introduced into the effluent treatment to eliminate the heavy metal ions from the environment. In this process, the hydroxyl radicals are originated through which the harmful pollutants are sequestered or reduce into lower reactive compounds [10]. The hydroxyl ions produced formed from the excitation of the electron is the most essential compound required the photocatalysis operation. The hydroxyl ions

(OH⁻) possess a shortened life span, further; they actively participate in effective degradation of organic and chemical compounds into simpler compounds such as CO₂ and H₂O. The photocatalysis is one such advanced oxidation process used widely by majorly utilizing sunlight as the main source for pollutant degradation [12].

2.2 Photocatalysis

The term photocatalysis is derived from the amalgamation of two words such as “Photo” and “catalysis” where photo means light and catalysis meaning chemical reaction. Catalysis is the phenomenon where a compound helps in speeding up the rate of a chemical reaction without getting modified or expended in the reaction. Photocatalysis is a process which utilizes light to actuate a substance which modifies the reaction rate of a chemical reaction without being included itself. Also, the photocatalyst is the substance which can adjust the rate of synthetic response utilizing light illumination. In general, the Chlorophyll pigment present in plants is an ordinary photocatalyst. The distinction between chlorophyll photocatalyst to man-made nano TiO₂ photocatalyst, typically chlorophyll catches daylight to transform water and carbon dioxide into oxygen and glucose, on the other hand, photocatalyst utilizes strong oxidizing chemicals and electron-hole pairs to breakdown the organic compounds into carbon dioxide and water within the sight of photocatalyst, light, and water [11]. Photocatalysis is one of the outstanding technology which works by utilizing solar energy. It is seemed to be an assuring technique in the reduction of heavy metal ions, dye degradation, CO₂ debasement, and energy exchange operations [9].

Figure 2: Types of photocatalysis.

Several semiconductor compounds such as carbon nitride, metal sulfides, metal oxides are used conventionally as active photocatalytic materials [9]. There are various photocatalysts such as GaP, ZnO, ZnS, TiO₂, WO₃, CdS, etc. which are used as photodegraders and reduction of harmful pollutants in the wastewater treatment system. [10]. Over a period of time, many new catalysts such as ligands, organic metal, and inorganic metal frameworks have been formulated for the efficient photocatalysis operation under the UV light radiation [9]. Generally, the photocatalyst is semiconducting materials which generate the electron-hole pairs for breaking down the complicated organic compound into CO₂ and H₂O in the presence of UV or Visible irradiation. Based on the physical state of the compounds, the photocatalysis process is majorly divided into two main types as explained in the figure 2.

By virtue of its semiconductor structure, the TiO₂ is preferred as one of the predominantly used photocatalysts in the wastewater treatment sector. In addition, this TiO₂ catalyst comprises an empty conduction band and electron-filled valence band with a band gap energy of about 2-3.5 eV. The hydroxyl radical synthesized during the photocatalytic reaction is a strong oxidizing agent which is effectively utilized in the remediation of harmful environmental pollutants such as phenols, pesticides, heavy metals, dyes, etc., [13]. The photocatalysis is mainly used for purposes such as air purification, industrial effluent treatment, self-purification, energy conservation and antifouling applications [12]. The application of photocatalysis method is explained in the fig 3.

Figure 3: Various applications of photocatalysis.

2.3 Principle & mechanism behind photocatalysis

The fundamentals of photocatalysis are based on the combination of two major subjects such as photochemistry and catalysis. It requires both the light source and a semiconductor source to originate the chemical operation. Generally, the photons are derived from two light sources such as UV light and visible light sources based upon the type of catalyst utilized in the photocatalysis operation. The semiconductor materials are represented by two bands such as valence band and conduction band. The photon from the light source stimulates the Valence band electron resulting in the transfer of the excited electron from the valence band to the conduction band creating a positive charge in the valence band called hole [10]. The photocatalysis reaction follows a mechanism which involves four steps such as:

- The photons from the light energy are used to provoke the electron-hole pairs
- Segregation of the stimulated charges
- The transition of electrons and holes to the photocatalyst surface to generate heat energy
- The uptake of charges on the photocatalyst surface for redox reactions

Under the influence of the photons emitted from the visible light, the electron present in the valence bands gets stimulated to the conduction band. The stimulation of electron results in the formation of electron-hole pairs which is formed on the surface of the photocatalyst. The formed electron-hole pairs can further work in two capabilities. That is: The formed carrier charges may rejoin and produce energy in the form of heat or they may encounter other electron donor or acceptor and form hydroxyl free radicals for photooxidation reaction [12]. The photocatalysis reaction can end in two ways such as photo-oxidation or photoreduction reaction based on the presence of the electron and hole. The photo oxidation reaction takes place in the presence of electron scavengers, whereas the photo reduction reaction takes place in the presence of the hole scavengers [13].

3. Photocatalysis for the heavy metal recovery

Heavy metal sequestration using photocatalysis process is generally associated with the reduction of heavy metal into simpler form at a lower oxidation state. The main special case is arsenic, which exists in the anionic structure and needs oxidation to be changed over to a high oxidation state. From the beginning, Several AOPs such as TiO_2/UV , O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ are used in the heavy metal sequestration. In recent times, among the various AOPs used generally the Heterogeneous photocatalytic oxidation and reduction technique is preferred at a higher rate [10]. When the photons from the light source are

incident on the semiconductor material present in the photocatalytic reactor, the electron-hole pairs are produced on the conduction band and valence band of the semiconductor. The transfer between the electron-hole pairs from the conduction band to valence band produced oxidizing species which aids in the reduction of heavy metals. Several semiconductors such as ZnO, CdS, ZnS, CeO₂, TiO₂, etc. have been used conventionally for the effective reduction of heavy metals. Out of the various semiconductors used in photocatalyst used in recent times for pollutant removal, the TiO₂ was found to be the most extensively used semiconductor because of some of its properties such as feasibility, durability, non-poisonous nature, and water immiscibility. The photocatalyst is also seemed to be efficient in degrading the endocrine disruptors in the wastewater [14, 15]. The mechanism behind the photocatalysis process is depicted in the figure 4. Some of the characteristics which make the photocatalysis efficient than other techniques are as follows:

- The photocatalysis process does not involve extravagant chemicals for the operation
- This set up works under atmospheric temperature and pressure conditions
- Photocatalysis undergo reduction reaction same as that of the AOPs
- It is an economical method
- It is an enduring, nontoxic and eco-friendly technique

Figure 4: Mechanism behind the photocatalysis process.

Heterogeneous photocatalysts are claimed to be the easy, efficient and economically feasible method for reduction of chromium [16]. Habila et al. have investigated the degradation studies of heavy metal ions composed organic mixture using the core double shell $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ magnetic nanoparticle coated semiconductor photocatalyst. In this work, the TiO_2 catalyst is coated with the magnetic iron oxide nanoparticle which is eco-friendly and easy to synthesize. As the combination of Fe_3O_4 nanoparticles and TiO_2 catalyst lessens the efficacy of the photocatalysis reaction, the SiO_2 is sandwiched between the catalyst and the nanoparticles. The SiO_2 layer enhanced the efficiency of the photocatalyst effectively; also it helped in increasing the mechanical and thermal stability of the semiconductor, thus the core double shell material utilizing photocatalysts degraded the heavy metal ions with high efficiency [17]. Many conventional methods used in the effluent treatment primitively do not completely degrade the harmful contaminants, whereas the photocatalysis effectively removed several organic and inorganic contaminants found in the environment. The ZnO semiconductor material is considered to be other effective photocatalytic material for the elimination of heavy metal ions. In addition, the ZnO is a low cost and higher surface area possessing material for the enhanced degradation of heavy metal ions [18]. The heterogeneous photocatalysis process is applied for various purposes such as dehydrogenation, oxidation, transfer of hydrogen ion, air pollutants elimination, heavy metal deposition, water purification, and sterilization. Furthermore, this method can also be performed for both the liquid phase and gaseous phase [19]. Various heavy metal ions eliminated using the photocatalysis methods are explained below in a detailed manner.

3.1 Chromium (Cr)

Chromium is normally present in various food items such as organic products, vegetables, grains, and meats. Furthermore, It goes into the human body mostly through the nourishment chain. Chromium is one of the vital heavy metal used in various industrial and research sectors as a textile, tannery, electroplating, metallurgy and wood preservatives. Basically, the chromium occurs in two various forms such as Cr(III) and Cr(VI) , whereas the Cr(VI) is found to be the more noxious form of chromium damaging the living organisms and ecosystem. In drinking water, the dimension of chromium is commonly low, however, industrial wastewater can contain the unsafe chromium (IV) ions. Due to its solubility, motility, and toxicity, the chromium heavy metal ions were considered to be one of the biggest danger to the ecosystem globally. According to the World Health Organization (WHO), the permissible limit of Cr(VI) was determined to be 0.05 mg L^{-1} . When comparing with the Cr(VI) ions the Cr(III) was found to be the less toxic and less motile form of chromium. Several photocatalyst semiconductor materials such as TiO_2 , ZnO , WO_3 , ZnS , CdS and SnIn_4S_8 are used in the effective reduction of chromium ions

present in the industrial effluents [10, 20]. Primitively, the Cr(VI) ions are reduced to Cr(III) ions using some of the chemical compounds such as ferrous sulphate, sodium metabisulfite, sodium thiosulfate, sulphur dioxide [18]. The Neodymium doped TiO₂ semiconductor which is fabricated using the sol-gel method is utilized in the reduction reaction of Cr (VI) ions under the incidence of UV light in the work done by Rengaraj et al. The results concluded that the doping of Neodymium on the TiO₂ surface progressively augment the reduction of Cr(VI) ions into the Cr(III) ions [21]. The bismuth carbonate doped with iron oxide (II) is fabricated and utilized effectively for the reduction of most toxic Cr (VI) metal ions to less toxic Cr(II) ions [22]. Hou et al have investigated the elimination of chromium ions from the aqueous solution using photocatalysis and capacitive deionization. In this study the MIL-53 (Fe) semiconductor under the illumination of visible light is used for the reduction of Cr(VI) to Cr(III) ions. The results concluded that the higher concentration of Cr(VI) ions of about 72.2% is eliminated effectively using the photocatalysis technique and it revealed that it is the best effective method for the treatment of chromium contaminated wastewater [9].

3.2 Arsenic (As)

Arsenic is one of the harmful rare earth elements released from manmade sources such as mining, wood preservatives, and biocides, however, it also chiefly originates from some natural sources such as volcano and disintegration of minerals in land and water sources. Arsenic is one of the heavy metal which is highly abundant in the earth's crust, further; it exists in two forms such as trivalent arsenite and pentavalent arsenate. The consumption of Arsenic elements in human beings leads to severe disorders such as arsenicosis, palmoplantar keratosis, cancer, and pigmentation variation. The WHO has established the permissible limits of Arsenic as 10 µg L⁻¹ b. The As(III) is highly toxic form because it easily attaches to the proteins causing cell disruptions[10, 20]. The highly toxic Arsenite As(III) is oxidized to less toxic As(V) form of ion utilizing the photocatalytic oxidation method in the work performed by Dutta et al. In this work, the OH radical which is produced by the benzoic acid is used as the main oxidant for the conversion of As(III) and As(V) ions, the photocatalysis of Arsenic using OH radical is compared with and without TiO₂ semiconductor under the UV light. The results concluded that the Arsenic is effectively reduced into less toxic forms using the OH radicals, further, using this method the permissible limits of Arsenic which is formulated by WHO can be maintained effectively in the industries [23]. Majumder and Chaudhari have examined the potential of solar photocatalytic oxidation of Arsenic from ground water using the Tartarate and Citrate photocatalysts. The results revealed that Arsenic oxidation using this catalyst has effectively reduced the Arsenic concentration from 250-260 µg/L to below 50 µg/L and the As removal efficiency of about 80% is observed in this study [24]. In the work carried

out by Reyna et al the elimination of Arsenic species using the ZnO catalysts under the UV irradiation is investigated. The ZnO catalyst prepared by the sol-gel method is compared with the conventional TiO₂degussa P25 suspension. The results revealed that higher removal efficiency is determined in the ZnO catalyst when compared with TiO₂ catalysts [25].

3.3 Cadmium (Cd)

Cadmium is one of the remarkable toxic heavy metal ion released from the domestic and industrial sectors and it is also considered as a growing threat to human beings and other living organisms. Around, 0.1 mg/kg of cadmium ions are present in the layer of the earth's crust, and nearly 15 mg of Cd/kg is deposited in the earth's environment as rocks and sediments. These metal ions are mostly emitted into the environment through industrial sectors such as textile industries, battery industries, and metallurgical industry. In the United States, for instance, the day-by-day cadmium admission is about 0.4 mg/kg/day, not exactly 50% of the US EPA's oral reference portion. These lower permissible limits are set to decrease the toxic level of cadmium waste generated from plating industry, all the more as of late, to the presentation of general confinements on cadmium utilization in specific nations [7]. Visa and Duta have investigated about the elimination of heavy metals such as Cd²⁺ and Cu²⁺ using the TiO₂ catalyst which is obtained by the hydrothermal processing of TiO₂ Degussa powder and Fly ash powder. The results concluded that this novel substrate effectively degrades the heavy metal ions present in the solution mixture [26]. Le et al have investigated the elimination of cadmium ions using ZnO particles which was fabricated using the solid precipitation technique. The results revealed that only less than 15% of cadmium ions are removed (19). The TiO₂ catalyst is seemed to be an effective photocatalyst for the elimination of cadmium ions and the removal efficiency was about 99.8 was observed in the study conducted by Fatehizadeh et al. The reactor utilized in this study is made of three parts such as ultraviolet source, reaction cell and mixing unit, Further, the removal efficiency of cadmium is affected by parameters such as pH, dose and dispersion of air [27]. The Activated sewage sludge-derived activated carbon coupled with TiO₂nanomaterial is also used as photocatalytic material for cadmium removal in the research work performed by Rashed et al. The results declared that the cadmium metal ions are removed with an efficiency of about 90% and the activated sludge activated carbon TiO₂ enhanced the cadmium removal in the bi-pollutant solution [28]. Davis and Green have examined the photocatalytic oxidation potential of the Cadmium-EDTA complex using the TiO₂ semiconductor. The results of this study declared that the effective removal of Cadmium using TiO₂ was observed on the optimum concentration of about 2×10^{-5} to 10^{-3} M at a pH range of about 3 to 8, Further, the cadmium ions are released as Cd²⁺ after the mineralization process [29].

3.4 Copper (Cu^{2+})

Copper is obtained from the mineral ores of Chalcopyrite, CuFeS_2 . Further, it is also obtained as a major contaminant from the mining, hydrometallurgical, pyrometallurgical industry as effluents and fumes. The copper poisoning causes health disorders such as paralysis, nausea, depression, pneumonia, diarrhea, etc. [1]. Copper is utilized as an important cofactor of various enzymes such as peroxidase, catalase, monoamine oxidase, ferroxidases, etc. which deals with the oxidative stress reactions. In addition, it plays a vital role in the metabolism of carbohydrate, haemoglobin production and collagen crosslinking reactions [7]. Chaudary et al. investigated the elimination of copper metal ions using the TiO_2 or H_2O_2 catalyst. The results declared that the copper ions are recovered efficiently at a pH range of about 1.5 – 4.5, in addition, the removal efficiency can be enhanced by coupling the TiO_2 nanomaterial with the activated carbon concentrated cell system [30]. The higher removal efficiency of about 85% of copper metal ions is observed in the photocatalytic degradation of copper ions using the ZnO nanoparticles semiconductors [19]. In the work carried out by Habila et al., the copper metal ions are effectively recovered using $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ with a higher adsorption capacity of about 125 mg g^{-1} . Further, the higher removal efficiency was observed at pH 5 [17]. In the research work carried out by Kanakaraju et al., the copper metal ion is recovered using the aggregation of the TiO_2/ZnO semiconductor with the calcium alginate beads. The results showed that the copper metal recovery with 50:50 ratio of calcium alginate beads and TiO_2/ZnO photocatalysis showed higher removal efficiency even in three consecutive cycles and it also served as an environmentally friendly method for metal recovery [31]. The chelated copper ion complexes such as copper EDTA and copper cyanide complexes are reduced using the photo anodes which are made up of TiO_2 nanotubes [32].

3.5 Lead (Pb^{2+})

Lead is a bluish grey metal which is found naturally in the layer of the earth's crust. The industrial activities and anthropogenic sources are the main sources of lead pollution. Some of the anthropogenic activities such as combustion of fossil fuels, agriculture, and domestic sources contribute to the emission of lead into the environment. The mining and transportation play a vital role in increasing the level of the lead metal ion. Some of the industries such as battery industry, metal plating industry, paint industry, textile industries, glass industries, chemical industries, and instrument manufacturing industries utilize lead as an important raw material [7]. Sreekanthan et al. investigated the photocatalysis reduction of lead ions using Cu- TiO_2 nanotubes. In this work, the TiO_2 nanotubes are coated with the Cu^{2+} ions through the wet impregnation method. The results concluded that the combination of Cu^{2+} ions with the TiO_2 catalyst effectively increased the photocatalytic

reduction of Pb(II) ions, the higher removal efficiency was observed in an optimum ion concentration of about 20 and 60 ppm at alkaline condition under the incidence of UV light [33]. The Titania based binary oxide materials are utilized in the photocatalytic reduction of the lead ions in the research work performed by Mishra et al. The Titania sample is combined with the zirconia and silica at equal Ratio to enhance the mechanical strength and removal efficiency of the heavy metal ions effectively. Sodium formate is used as the hole scavenger in this method, furthermore, it resulted in heavy metal removal of about 89% in a time period of 60 min [34]. The photocatalytic reduction of Pb(II) using TiO₂ and Pt-TiO₂ powders is investigated by Marunni et al. The investigation results inferred that the metal removal efficacy was observed higher using Pt-TiO₂ when compared using the TiO₂ material [35].

3.6 Mercury

Mercury is one of the notable toxic elements which is rated as the top third element in the ASTRD's Priority list of Hazardous Substances. It causes serious health disorders to humans and living beings. The mercury heavy metal ions is a substantial metal which comes under the transition element series of the periodic table and it occurs in three different forms such as organic, inorganic and elemental form. The toxicity of the mercury ions depends on the chemical form in which it exists. In the optimum room temperature, the natural mercury exists as a fluid which has a high vapor pressure. In addition, Mercury exists as a cation with oxidation conditions of +1 (mercurous) or +2 (mercuric). Mercury is a far-reaching ecological toxicant and contamination which instigates extreme adjustments in the body tissues and causes a wide scope of antagonistic wellbeing impacts. Various chemical forms of mercury which is vigorously affecting the humans and other living beings are mercury vapor (Hg⁰), inorganic mercurous (Hg⁺), mercuric (Hg²⁺), and the natural mercury mixes. The industrial activities such as hardware, battery manufacturing, dentistry, beverage industry, nuclear reactors, and the pharmaceutical industry contribute greatly to the mercury contamination [7].

Conclusion & Future perspectives

The reduction of heavy metals present in wastewater using the photocatalysis technique is broadly explained in this chapter. This technique seems to be outstanding method in reducing the negative impacts exerted by the toxic metal ions on the environment. The photocatalysis method has overcome several limitation and drawbacks that are found in the advanced oxidation process of heavy metal reduction. The AOPs are capable only of converting the toxic heavy metal ions into oxidative species, whereas the photocatalysis can perform oxidation and also reduction reaction to convert the toxic metal ions. In the

photocatalysis process the complexed heavy metal ions into less toxic heavy metal species which do not affect the wellness of the environment. Some of the factors such as pH, initial metal ion concentration, type of the semiconductor, the intensity of light, the mass of photocatalyst have a strong impact on the photocatalysis reduction of toxic metal ions. Photocatalyst advancement would assist us in utilizing the bottomless sun based radiation. Due to its effectiveness in wastewater treatment, much advancement has been made in the photocatalysis such as submersion type and distribution type for heavy metal treatment in industries. This chapter declares that the photocatalysis process is an effective method for treating heavy metal ions in the aqueous solution.

References

- [1] J. O. Duruibe, M. O. C. Ogwuegbu, J. N. Ekwurugwu, Heavy metal pollution and human biotoxic effects, *International Journal of Physical Sciences*, 2 (2007) 112-118.
- [2] C. F. Carolin, P.S. Kuma, A. Saravanan, G. J. Joshiba, Mu. Naushad, Efficient Techniques for the Removal of Toxic Heavy Metals from Aquatic Environment: A Review, *Journal of Environmental Chemical Engineering* 5 (2017) 2782-2799. <https://doi.org/10.1016/j.jece.2017.05.029>
- [3] A. Roychowdary, R. Dutta, D. Sarkar, Heavy Metal Pollution and Remediation, *Green chemistry*, in: B. Torok, T. Dransfield, *Green chemistry*, Elsevier, USA, 2018, pp 359-373. <https://doi.org/10.1016/B978-0-12-809270-5.00015-7>
- [4] P. K. Rai, S. S. Lee, M. Zhang, Y. F. Tsangd, K. H. Kim, Heavy metals in food crops: Health risks, fate, mechanisms, and management, *Environment International*, 125 (2019) 365- 385. <https://doi.org/10.1016/j.envint.2019.01.067>
- [5] S. Rangabhashiyam, P. Balasubramanian, Characteristics, performances, equilibrium and kinetic modeling aspects of heavy metal removal using algae, *Bioresource technology reports*, 5 (2019) 261-279. <https://doi.org/10.1016/j.biteb.2018.07.009>
- [6] A. S. Mohammed, A. Kapri, R. Goel, Heavy Metal Pollution: Source, Impact, and Remedies, In: M. Khan, A. Zaidi, R. Goel, J. Musarrat, *Biomangement of Metal-Contaminated Soils*, *Environmental pollution*, Springer, Dordrecht, 2011, pp 1-28. https://doi.org/10.1007/978-94-007-1914-9_1
- [7] P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla, D. J. Sutton, Heavy Metals Toxicity and the Environment, *HHS Author Manuscripts*, 101 (2012)133–164. https://doi.org/10.1007/978-3-7643-8340-4_6

- [8] L. Fang, L. Li, Z. Qu, H. Xu, J. Xu, N. Yan, A novel method for the sequential removal and separation of multiple heavy metals from wastewater, *Journal of Hazardous Materials*, 342 (2018) 617–624. <https://doi.org/10.1016/j.jhazmat.2017.08.072>
- [9] S. Hou, X. Xu, M. Wang, T. Lu, C. Q. Sun, L. Pan, Synergistic conversion and removal of total Cr from aqueous solution by photocatalysis and capacitive deionization, *Chemical engineering journal*, 337 (2018) 398- 404. <https://doi.org/10.1016/j.cej.2017.12.120>
- [10] P. Chowdhury, A. Elkamel, A. K. Ray, Photocatalytic Processes for the Removal of Toxic Metal Ions, in: S. Sharma, *Heavy Metals In Water : Presence, Removal and Safety*, Royal Society of Chemistry, 2014, pp 25-43. <https://doi.org/10.1039/9781782620174-00025>
- [11] R. Ameta, M. S. Solanki, S. Benjamin, S. C. Ameta, Photocatalysis, *Advanced Oxidation Processes for Waste Water Treatment Emerging Green Chemical Technology*, 2018, pp 135-175. <https://doi.org/10.1016/B978-0-12-810499-6.00006-1>
- [12] <http://www.greenearthnanoscience.com/what-is-photocatalyst.php>
- [13] E. T. Wahyuni, N. H. Aprilita, H. Hatimah, A. M. Wulandari, M. Mudasir, Removal of Toxic Metal Ions in Water by Photocatalytic Method, *American Chemical Science Journal* 5 (2015) 194-201.
- [14] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, *Arabian Journal of Chemistry*, 4 (2011) 361–377. <https://doi.org/10.1016/j.arabjc.2010.07.019>
- [15] V. Belgiorn, L. Rizzo, D. Fatta, C. D. Rocca, G. Lofrano, A. Nikolaou, V. Naddeo, Review on endocrine disrupting-emerging compounds in urban wastewater: occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse, *Desalination*, 215 (2007) 166–176. <https://doi.org/10.1016/j.desal.2006.10.035>
- [16] R. K. Gautam, S. K. Sharma, S. Mahiya, M. C. Chattopadhyaya, Contamination of Heavy metals in aquatic media: Transport, Toxicity and Technologies for remediation, In: S. K. Sharma, *Heavy Metals In Water: Presence, Removal and Safety*, Royal society of chemistry, 2015. <https://doi.org/10.1039/9781782620174-00001>
- [17] M. A. Habila, Z. A. AlOthman, A. M. El-Toni, J. P. Labis, M. Soylak, Synthesis and application of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ for Photocatalytic Decomposition of Organic Matrix Simultaneously with Magnetic Solid Phase Extraction of Heavy Metals prior to ICP-MS analysis, *Talanta*, 154 (2016) 539-547. <https://doi.org/10.1016/j.talanta.2016.03.081>

- [18] F. A. Harraz, O. E. Abdel-Salam, A. A. Mostafa, R. M. Mohamed, M. Hanafy, Rapid synthesis of titania–silica nanoparticles photocatalyst by a modified sol–gel method for cyanide degradation and heavy metals removal, *Journal of Alloys and Compounds*, 551 (2013) 1–7. <https://doi.org/10.1016/j.jallcom.2012.10.004>
- [19] A. T. Le, S. Y. Pung, S. Sreekantan, A. Matsuda, D. P. Huynh, Mechanisms of removal of heavy metal ions by ZnO particles, *Heliyon*, 5 (2019). <https://doi.org/10.1016/j.heliyon.2019.e01440>
- [20] M. I. Litter, Mechanisms of removal of heavy metals and arsenic from water by TiO₂-heterogeneous photocatalysis, *Pure Applied Chemistry*, 87(2015) 557–567. <https://doi.org/10.1515/pac-2014-0710>
- [21] S. Rengaraj, S. Venkataraj, J. W. Yeon, Y. Kim, X. Z. Li, G. K. H. Pang, Preparation, characterization and application of Nd–TiO₂ photocatalyst for the reduction of Cr(VI) under UV light illumination, *Applied Catalysis B: Environmental*, 77 (2007) 157-165. <https://doi.org/10.1016/j.apcatb.2007.07.016>
- [22] M. N. Subramaniam, P. S. Goh, W. J. Lau, A. F. Ismail, The Roles of Nanomaterials in Conventional and Emerging Technologies for Heavy Metal Removal: A State-of-the-Art Review, *Nanomaterials*, 9 (2009). <https://doi.org/10.3390/nano9040625>
- [23] P. K. Dutta, S. K. Pehkonen, V. K. Sharma, A. K. Ray, Photocatalytic Oxidation of Arsenic(III): Evidence of Hydroxyl Radicals, *Environmental Science & Technology*, 39 (2005) 1827-1834. <https://doi.org/10.1021/es0489238>
- [24] A. Majumder, M. Chaudari, Solar photocatalytic oxidation and removal of Arsenic from ground water, *Indian Journal of Engineering & Material sciences*, 12 (2005) 122-128.
- [25] N. R. Reyna, L. H. Reyes, J. L. Guzman-Mar, Y. Cai, K. O. Shea, A. H. Ramirez, Photocatalytical removal of inorganic and organic arsenic species from aqueous solution using zinc oxide semiconductor, *Photochemical Photobiological Sciences*, 12 (2013) 653-659. <https://doi.org/10.1039/C2PP25231G>
- [26] M. Visa and A. Duta, TiO₂/fly ash novel substrate for simultaneous removal of heavymetals and surfactants, *Chemical Engineering Journal*, 223 (2013) 860–868. <https://doi.org/10.1016/j.cej.2013.03.062>
- [27] S. Rahimi, M. Ahmadian, R. Barati, N. Yousefi, S. P. Moussavi, K. Rahimi, S. Reshadat, S. R. Ghasemi, N. R. Gilan, A. Fatehizadeh, Photocatalytic removal of cadmium (II) and lead (II) from simulated wastewater at continuous and batch system,

- Int Journal of Environmental Health Engineering, 3 (2014).
<https://doi.org/10.4103/2277-9183.139756>
- [28] M. N. Rashed, M. A. Eltaher, A. N. A. Abdou, Adsorption and photocatalysis for methyl orange and Cd removal from wastewater using TiO₂/sewage sludge-based activated carbon nanocomposites, Royal society open science, 4(2017).
<https://doi.org/10.1098/rsos.170834>
- [29] A. P. Davis, D. L. Green, Photocatalytic Oxidation of Cadmium-EDTA with Titanium Dioxide, Environmental Science & Technology, 33 (1999) 609-617.
<https://doi.org/10.1021/es9710619>
- [30] A. J. Chaudhary, M. Hassan, S. M. Grimes, Simultaneous recovery of metals and degradation of organic species: Copper and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), Journal of Hazardous Materials, 165 (2009) 825 – 831.
<https://doi.org/10.1016/j.jhazmat.2008.10.066>
- [31] D. Kanakaraju, S. Ravichandar, Y. C. Lim, Combined effects of adsorption and photocatalysis by hybrid TiO₂/ZnO-calcium alginate beads for the removal of copper, Journal of Environmental sciences, 55 (2017) 214-223.
<https://doi.org/10.1016/j.jes.2016.05.043>
- [32] Y. Zhu, W. Fan, T. Zhou, X. Li, Removal of chelated heavy metals from aqueous solution: A review of current methods and mechanisms, Science of the Total Environment, 678 (2019) 253–266. <https://doi.org/10.1016/j.scitotenv.2019.04.416>
- [33] S. Sreekantan, C. W. Lai, S. M. Zaki, The Influence of Lead Concentration on Photocatalytic Reduction of Pb(II) Ions Assisted by Cu-TiO₂ Nanotubes, International Journal of Photoenergy, 2014. <https://doi.org/10.1155/2014/839106>
- [34] T. Mishra, J. Hait, N. Aman, R. K. Jana, S. Chakravarty, Effect of UV and visible light on photocatalytic reduction of lead and cadmium over titania based binary oxide materials, Journal of Colloid and Interface Science, 316 (2007) 80-84.
<https://doi.org/10.1016/j.jcis.2007.08.037>
- [35] L. Murrini, G. Leyya, M. I. Litter, Photocatalytic removal of Pb(II) over TiO₂ and Pt-TiO₂ powders, Catalysis Today, 129 (2007) 127-135.
<https://doi.org/10.1016/j.cattod.2007.06.058>