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Arsenic and Lead Removal from Water by Nano-photocatalytic Systems (A Review)

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Abstract: Water is an essential component in the world. The presence of heavy metals in water has dramatic effects on health and ecological process in the environment. Heavy metal pollution in water bodies is an existing and developing problem in the world. There are several methods for removing these pollutions in water. A photocatalytic degradation is a useful approach to removal a variety of heavy metals from contaminated water. In this study, we summarized different types of methods for the removal of heavy metals especially arsenic and lead from water. Studies include different nano-photocatalyst and methods such as the use of TiO_2 substrates, TiO_2 nanotubes, and nanocrystals, organic and inorganic nanoparticles based on silica, a variety of nanomaterial-based polymers, magnetic nanoparticles such as zero-valent iron and zinc oxide, or using two or more of these nanomaterials at the same time as an adsorbent or oxidizer of pollutants, all under visible or ultraviolet light. Each method has some limitations and advantages and based on different research that scientists presented, the efficiency of each technique is dependent on some conditions such as pH, adsorption time, solvent type, and UV light, so we still can't introduce the best method. Nowadays researchers are trying to find a method with high efficiency, low cost, least risk for the environment, and without secondary contamination. Hopefully, researchers find many promising methods that can be used with high efficiency in the future by continuing the research.
Keywords: Adsorption, heavy metals, photocatalytic, pollution, water.

1. Introduction

Water is one of the most important sources that uses in industries, agriculture, urban uses etc. Water quality is fundamental for the health of people and sustains ecological processes that support native populations of fish, vegetation, wetlands, and bird lives (Mirzaei et al., 2016; Fataei et al.,). Although implementing rigorous standards on metal emission and recycling them from wastewater and water are effective for controlling these pollutants. (Zhou Q. et al., 2020), increasing the population of the world and supplying sanitary water has become one of the fundamental problems of today's world, and the development of industries and the production of sewage with toxic and complex compounds, has limited the use of conventional processes of wastewater treatment. Heavy metals are metals with relatively high densities that some of them are essential nutrients and some of them are highly poisonous and toxin. Many heavy metals originate yearly from anthropic activities (Smail et al., 2012) and their toxicity has become the focus of many institutions, industries, and environmental groups (Alka S. et al., 2020). The release of heavy metals into the environment due to their toxicity and stability increases the risks to health and the environment. Metals from industrial wastes, agricultural sources, urban runoff, and automobile emissions could also disperse to the surface water via surface runoff or rainwater (Smail et al., 2012).

They could move to soil layers, and eventually reach groundwater (Bichet et al., 2013).

Exposure to heavy metals can cause various diseases such as mental retardation, nerve disorders, memory, and behavioral problems, etc. Some heavy metals were used for industrial purposes and the most important threat of these activities is related to groundwater pollution that is used as a source of drinking water, so the health of people in the world is threatened with the use of these waters (Andjelkovic et al., 2015). For this reason and since these pollutants are badly affecting the aquatic habitats and are flexible to the food chain. (Pandiyan et al., 2020) it is essential to remove them from the environment (Chowdhury et al., 2016). Contamination of drinking water with heavy metals could be poisonous and is carcinogenic to humans (Rengaraj et al., 2007) as they are considered as eminent toxicants which hence to adverse health impacts (Kapoor & Singh, 2021)

There are many techniques that can be used to remove heavy metals from waters like coagulation–flocculation and electrocoagulation, physical and biological adsorption, ion exchange, membrane separation and photocatalytic reduction (Majidnia & Idris, 2015). In this article we discuss about the photocatalytic system.

An efficient and effective method for the removal of heavy metal ions in polluted water is photocatalysis of semi- conductor oxides via oxidative and reductive mechanisms (Nouri Dodaran et al., 2019; Prabhu et al., 2014). Photocatalytic activities are a series of advanced Oxidation technologies to alleviate the problems of water pollution and these activities are effective for treating contaminants in water systems. For this purpose, there are many catalysts for example ZnO, ZnS, perovskites, MoS_2, TiO_2, WO_3, and so on (Byrne et al., 2017).

In order to achieve mentioned objectives, this article aims to review new studied methods based on nanophotocatalysts to remove two toxic and harmful heavy metals (arsenic and lead).

2. Literature reviews

There has been an extensive number of studies about photocatalysis and different catalysts for using that. In this article, we mention some of them.

2.1. Using titania polyvinyl alcohol–alginate beads

Majidnia and Fulazzaky (2016) checked out removal of lead cations (Pb^{2+}) from aqueous solution by Titania polyvinyl alcohol–alginate beads. In this method magnetic nanoparticles were prepared by combining ferrous and ferric chloride in the presence of ammonium hydroxide by alkaline co-precipitation and thus the precipitation of magnetite (Fe_3O_4) appeared to be as black-colored precipitates.

They performed the tests of photoreduction of Pb^{2+} cations by both Titania polyvinyl alcohol-alginate beads (TPVAABs) and maghemite polyvinyl alcohol-alginate beads (MPVAABs) in batch experiments. The results showed that the use of MPVAABs is more effective than TPVAABs after 135 min of reaction time under sunlight irradiation to remove Pb^{2+} cations. They stated use of Titania polyvinyl alcohol–alginate beads are a rapid and reliable method for treating heavy metal-contaminated in the water.

2.2. Using Nanomaterials

Nanomaterials are materials that have the particle size between 1 nm to 100 nm and they are useful tools for removal of heavy metal, because they have unique structure and surface characteristics (Wang et al., 2012).

Lu and Astruc (2018) summarized the application of nanomaterials for the removal of heavy metals in water. We mention them below.

2.2.1. Inorganic nanomaterials

Inorganic nanomaterials are including transition metal oxide, carbon-based nanotube and Si-based nanomaterials.

2.2.1.1. Transition metal oxide

Metal oxides can be used to remove heavy metals from water bodies such as titanium oxide, magnesium oxide, copper oxide, iron, etc. Iron oxide nanomaterials and Fe_3O_4 nanomaterials have used widely to remove heavy metals in water for example polystyrene supported-hydrated hematite (Fe_2O_3) can adsorb arsenic (As^{3+} and As^{5+}) (Cumbal and Sengupta, 2005). Also, nano-Fe_3O_4-silica (SiO_2) can remove heavy metals copper (Cu^{2+}) and Pb^{2+} cations from water.

2.2.1.2. Carbon-based nanotube

Carbon based nanomaterials are one of the most important method to remove heavy metals in the world (Lu and Astruc, 2018). Research studies show that carbon black based nanotube can adsorb Cu^{2+}, Zn^{2+}, palladium (Pd^{2+}) and cadmium (Cd^{2+}) cations (Wang et al., 2009; Chen et al., 2010; Zhou et al., 2010).

2.2.1.3. Silica -based nanomaterials/ Titanate nanotubes

It has been reported that nanoporous silica, silica nanofibers, Si nanotubes, and Si-coated magnetic nanoparticles can remove heavy metals from water ecosystems (Yantasee et al., 2010). In this category, the introduction of molecules bearing sulfhydryl (-SH) groups onto the surface of silica nanofibers can remove mercury (Hg^{2+}) cations from water with high efficiency.

Nie and Teh (2010) used titanate nanotubes as superior adsorbents for removal of Pb^{2+} cations from water. In their study, TiO_2 nanopowder was mixed with sodium hydroxide (NaOH) solution and was moved to autoclave at 140°C for 48 h and then cooled down to room temperature. Then, the precipitate was separated and washed with deionized water a few times until the pH value reached to about 7, followed by twice of alcohol (ethanol) washing. Finally, the sample was dried in air at 80°C for 24. Adsorption experiments were done using the batch equilibration method. For that, titanate nanotubes were added into lead nitrate ($Pb(NO_3)_2$) solution. Then the mixture was shaken in a thermostatic shaker for 48h. Afterward, precipitates were separated by centrifugation and concentration of Pb^{2+} was analyzed by plasma-atomic emission spectrometer. The crystal structure of the products was investigated by X-ray diffraction (XRD) analysis. In their research Adsorption capacity was calculated by following equation:

$$K_d = \frac{(C_0 - C_f)}{C_f} \frac{V}{M}$$

Formula of distribution coefficient (Yantasee et al., 2010)

Where C_0 and C_f are the initial and the final concentration of target species, affinity was quantitated via calculation of distribution coefficient (K_d, mL/g; eq 1), V is the matrix volume, and M is the mass of the sorbent. Energy-dispersive X-ray (EDX) analysis indicated that the chemical composition of the initial nanotubes is $Na_2Ti_4O_9$ and the sodium cations in the titanate nanotubes can be fully replaced by Pb^{2+} cations. At the result, titanate nanotubes allow Pb^{2+} cations enter into nanotubes and the adsorption capacity will increase. Also, the crystal structure of titanate nanotubes can recover after the adsorption cycle, so this technique is an effective method for economic treatment.

2.2.2. Organic nanomaterials

Organic nanomaterials bearing amine ($-NH_2$), hydroxyl (-OH), carboxyl (-COOH), etc. in the surface adsorb heavy metals in water. Metal-organic framework-derived nanomaterials (MOFs), for remediation are highlighted. The application of MOFs for wastewater treatment (adsorption and catalytic degradation) has been emphasized (He et al., 2020).

2.2.2.1 Organic Polymer nanomaterials

It has been reported cellulose nanocrystals, cellulose nanofibers and chitin nanocrystals can remove Silver cations (Ag^+) ions from contaminated water (Liu et al., 2014). Also, nanocellulose fibers with vinyl sulfonic acid help to remove chromium (Cr^{3+}), nickel (Ni^{2+}), Cd^{2+} and Pb^{2+} cations (Kardam et al., 2012).

2.2.2.2. Organic Polymer supported nanomaterials

Amine groups can play significant roles in modified chitosan for the adsorption of heavy metal ions. New recyclable chitosan modified adsorbents (GMCS) for adsorption of Lead cations (Pb^{2+}) is one of these inventions (Ge and Du, 2020)

Synthetic organic polymer-supported nanomaterials (polyaniline (PAN), polystyrene, polyhydroxybutyrate (PHB), poly (tetrafluoroethylene), polyethylene (PE), and nafion) and biopolymer-supported nanomaterials (cellulose, chitosan, and alginate or resin) are important organic materials to remove heavy metals. For example, tetraethylenepentamine-functionalized magnetic cellulose composite removes Hg^{2+}, copper (Cu^{2+}) and Ag^+ cations (Klemm et al., 2011).

2.3. Preparation Titania–silica (TiO_2–SiO_2) photocatalyst by modified sol–gel technique

Harraz et al (2013) investigated on TiO_2–SiO_2 photocatalyst for cyanide (CN^-) degradation and heavy metals removal. A mixture of TiO_2–SiO_2 can be operated as a good catalyst for removal toxic materials. In sol-gel technique the first, the combination of titanium tetrachloride solution ($TiCl_4$) with ammonia solution (NH_4OH) led to production a white precipitate at pH 7. Then precipitate was washed with deionized water to remove the excess Cl^- and NH_4^+ ions. Then a suspension was obtained. Afterward, nitric acid (HNO_3) was added to suspension and that was peptized to form a highly stable titania sol. Then tetraethyl orthosilicate (TEOS) solution was added into the above titania sol. In the next step, modified sol was dried and calcined at 400°C for 3 h to obtain SiO2–TiO2 catalyst. Finally, for heavy metals removal experiments, the wavelength of the used UV lamp is 365 nm and a specific weight of catalyst was suspended into the reactor with 300 ml of nitrate salts mixture (100 ppm of each metal ions: Cr (III), Co (II) and Pb (II)) and eventually removal percentage of heavy metals was calculated by inductive coupled plasma (ICP) analysis. The result shown that the efficiency if this technique is the best for Pb^{2+}. Also, Wang et al., 2017 researched mesoporous TiO_2/SiO_2 nanocomposites under photocatalytic oxidation can convert high-toxic As^{3+} to low-toxic As^{5+}. In their research, P123 and tetraethyl orthosilicate (TEOS) dissolved into ethanol under magnetic stirring for 0.5 h. Under stirring, Tetrabutyl titanate (TBOT) and concentrated hydrochloric acid were added to the above solution. After 0.5h the homogenous solution was transferred into a ceramic vessel and impounded for 18 h at room temperature in air to produce a rigid gel. The gel was covered with a layer of liquid paraffin 2–3 mm thick and heated at 60°C for 18 h for removing ethanol. Then, the liquid paraffin was collected and cleared by filter paper and samples were calcined at 300°C for 4 h and the products were refluxed with ethylene diamine. Afterward, the obtained powders were washed by deionized water and dried at 60°C. Finally, the resulting samples were calcined. The prepared samples are characterized in detail by thermos gravimetric-differential scanning calorimetry, X-ray diffraction, Raman, transmission electron microscopy and nitrogen (N_2) adsorption. The results show effective efficiency for photocatalytic oxidation and adsorption of arsenic.

2.4. WO_3/TiO_2 nanoparticles by modified sol–gel technique/ tungsten trioxide (WO_3)

Mirghani et al (2015) studied photocatalytic reduction of Pb^{2}+ by WO_3/TiO_2 nanoparticles. In their research, tungsten-doped TiO_2 was composed by modified sol–gel. Tungsten was mixed with methanol and hydrochloric acid. Then sulfuric acid was added it and dried in an oven for 12 h at 75°C. Afterward, this compound was calcinated at 450°C for 4 h. finally, scanning electron microscope analysis was done. After UV light (254 nm) Pb^{2+} solution was prepared by dissolving lead nitrate in deionized water at pH 6. Changes in lead concentration was measured using atomic absorption spectrometer. Results show when the percentage of WO_3 in the TiO_2 sample increases, the amount of lead adsorption increases too. Kim et al., (2015) were studied Photocatalytic oxidation mechanism of arsenite on tungsten trioxide under visible light. Under visible light, three oxidant species can be generated: valence-band hole (hvb+), hydrogen peroxide (H_2O_2), and hydroxyl radical (•OH). Results show the oxidation of As^{3+} to As^{5+} was done by hole not by H_2O_2 and •OH.

2.5. Nanocrystalline TiO_2 coatings/ anatase TiO_2 /TiO_2

Little works have been reported on the exact mechanism of adsorption and the effect of insulator silica (SiO_2) on structural change and type of adsorption and its method alone cannot completely omit pollutants, therefore always the problem of secondary pollution remains (Esfandiari et al., 2020).

Yang and Zhang (2010) were used nanocrystallineTiO$_2$ coating under N_2 and quartz crystal microbalance (QCM) method for removing Pb^{2+} from wastewater. QCM is a useful technique for research of the photocatalytic reduction and oxidation of metal ions (Si et al., 2002). The results of QCM measurements shows that the reduction efficiency of Pb^{2+} depends on the organic additives. The reduction of Pb^{2+} is depends on increase of HCOOH concentration. Efficiency of this organic matter for removing Pb is two times higher in comparison with ethanol (C_2H_5OH).

Guan et al., (2012) have reviewed on application of TiO_2 in As removal from water. They stated the adsorption of inorganic and organic arsenic onto TiO_2-based materials are relatively well established, but it needs to continue more researches about combination of TiO_2 with other materials. Base on their study, there are various TiO_2 that researchers used for arsenic removal, for example: Nanocrystalline TiO_2 particles, titanate nanotubes, hydrous TiO_2, granular TiO_2, TiO_2-impregnated chitosan beads and etc.

Li et al., (2014) were used anatase TiO_2 with high surface hydroxyl group density for removing As^{3+} from aqueous solution. Under UV light, anataseTiO$_2$ operates as both a photocatalyst and adsorbent and can adsorb arsenite with high efficiency. In their study, As^{3+} was oxidized by •OH radicals on TiO_2 pillared montmorillonite in the presence of UV light. The results show UV light can increase the number of potential adsorption sites for As^{3+} on TiO_2. Mechanism of As^{3+} adsorption/oxidation on anataseTiO$_2$ with or without UV light is showed in figure 1 (Li et al., 2014).
Also, Li et al., (2012) studied TiO_2 pillared montmorillonite as a photoactive adsorbent for the removal of arsenic under UV irradiation. In their study, after the replacement of inactive sodium ions of montmorillonite with TiO_2, As can remove. The XRD analyses indicated that TiO_2/montmorillonite (MMT) contained Nanocrystalline titanium dioxide that these anatase TiO_2 nanoparticles were responsible for arsenic adsorption and photoactive adsorption. The results show that TiO_2/MMT can effectively remove arsenic from aqueous solutions under a wide range of experimental conditions, including pH, adsorption time and UV light.

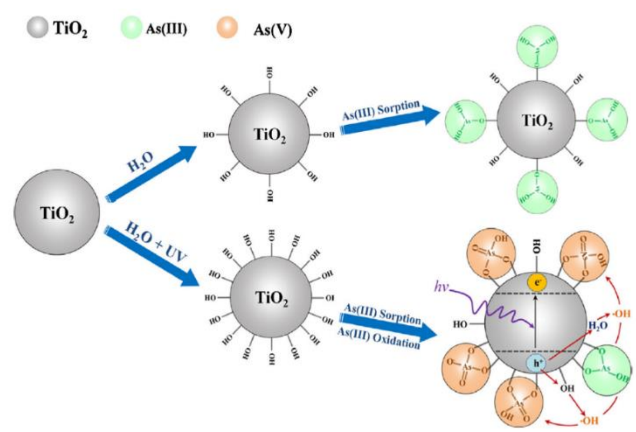

Fig.1-Mechanism of As (III) adsorption/oxidation on anataseTiO$_2$ with or without UV light (Li et al., 2014).

Litter (2017) investigated the role of TiO_2-photocatalytic on removal of Cr, U and As. It is stated that there are three steps in this process: 1- direct reduction by photo generated electrons 2- indirect reduction by intermediates generated by hole or •OH radical oxidation of electron donors (reducing radicals); 3- oxidative removal by holes or •OH radicals. General

TiO_2 photocatalytic mechanism is represented in following:

(1) $TiO_2 + h\nu \rightarrow e_{CB}^- + h_{VB}+$
(2) $e_{CB}^- + h_{VB}+ \rightarrow TiO_2$
(3) $e_{CB}^- + A \rightarrow A^{\bullet -}$
(4) $h_{VB}+ + D_{ads} \rightarrow D_{ads}^{\bullet +}$
(5) $h_{VB}+ + HO_{surf}\text{-}/H_2O_{ads} \rightarrow HO^{\bullet} (+H^+)$
(6) $O_{2ads} + e_{CB}^- (+H^+) \rightarrow O_2^{\bullet -} (HO_2^{\bullet})$
(7) $O_2^{\bullet -} + H_2O \rightarrow HO_2^{\bullet} + OH^-$
(8) $2\ HO_2^{\bullet} \rightarrow O_2 + H_2O_2$
(9) $H_2O_2 + e_{CB}^- (O_2^{\bullet -}) \rightarrow HO^- + HO^{\bullet} (+O_2)$

General TiO_2 photocatalytic mechanism (Litter, 2017)
Where:
e_{CB}^- = reductants
A = electron acceptors
D = donor species
$h_{VB}+$ = oxidants

It has been concluded that this method is a valuable technology for removal of toxic metals and metalloids.
There are many other researches about impact of TiO_2 with different components on heavy metals (Torres and March, 1992; Murruni et al., 2008; Xu et al., 2007; Choi et al., 2010; Ferguson and Hering, 2006; Lee and Choi, 2002; Fostier et al., 2008; Yazdani et al., 2017).

2.6. Simultaneous photocatalytic oxidation and adsorption by TiO_2 and zero-valent iron

López-Mu˜noz et al., (2016) investigated impact of a combined system (TiO_2 + ZVI) under UV-irradiation on arsenic oxidation. The synergism impact of combination of TiO2 and zero-valent iron shows high efficiency for removing As(III) and As(V) in their study and this reaction at pH=3 is more effective in comparison to pH=9.

2.6.1. Zero valent iron activated persulfate process

Hussain et al., (2017) used persulfate (PS) activated with zero valent iron (ZVI) for removal of As^{3+} from aqueous solutions. In their research, ferro cations (Fe^{2+}) was used for activation of persulfate, because this metal is nontoxic, cost effective and environmentally friendly (Vicente et al., 2011). Also, ZVI is low cost, non-toxin, and with easy availability. The results show efficiency of As^{3+} oxidation is 96%.

2.7. Magnetic coper oxide $CuO\text{-}Fe_3O_4$ nanoparticles through photo oxidation and adsorption under light irradiation

Sun et al., (2017) was used $CuO\text{-}Fe_3O_4$ nanoparticles under light irradiation for As^{3+} removal. They demonstrated As^{3+} could be completely oxidized to less toxic As^{5+} by CuO- Fe_3O_4 nanoparticles within 60 min in the photo-oxidation reaction and As^{5+} could be adsorbed onto the surface of nanoparticles. The results show with the excellent photocatalytic performance and high adsorption capability, this method has significant effect on As^{3+} removal. Figure 2 can demonstrate all reactions in this method (Sun et al., 2017).

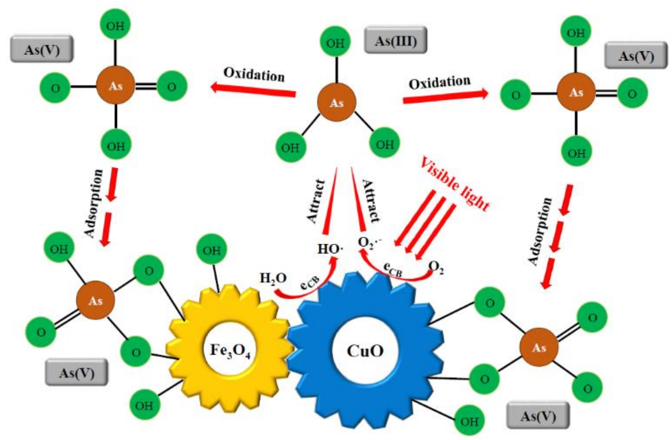

Fig.2 -Photo-oxidation and adsorption mechanism of As^{3+} by $CuO\text{-}Fe_3O_4$, Sun et al., (2018)

Sun et al., (2018) studied the effect of magnetic $CuO\text{-}Fe_3O_4$ nanoparticles under visible light irradiation on degradation of p-arsanilic acid with arsenic. They concluded that magnetic $CuO\text{-}Fe_3O_4$ nanoparticles can convert p-arsanilic acid (p-ASA) to As^{5+} within 36 min completely and released As^{5+} could be adsorbed onto the surface of $CuO\text{-}Fe_3O_4$ nanoparticles with high efficiency above 95%.

2.8. UV/Peroxydisulfate ($S_2O_8^{2-}$)

Yoon et al., 2011 studied on impact of $UV/S_2O_8^{2-}$ on arsenic removal. The results shown $UV/S_2O_8^{2-}$ is an effective oxidation process for arsenic removal.

2.9. Gadolinia-modified ceria photocatalyst

Ayawanna et al., (2015) used gadolinium oxide (Gd_2O_3-modified ceric oxide (CeO_2) particles to remove Pb^{2+} cations from aqueous solutions. They mixed Gd_2O_3 and CeO_2 powder in the 2-proponal for preparing Gd_2O_3-modified CeO_2 photocatalyst particles (Gd_2O_3–CeO_2). Then, the mixture was ground and dried for 4h. Afterward, the mixture calcinated and identified by an X-ray diffractometer. Pb^{2+} cations suspension liquid prepared by mixing Pb^{2+} cations solution and calcined Gd_2O_3–CeO_2. The suspension liquid is placed in an external irradiation-type quartz reactor and agitated for different duration. The results indicated a solid solution $Gd_{0.1}Ce_{0.9}\ O_{1.95}$ phase coexisting with the CeO_2 matrix phase has more ability than two-phase mixture of Gd_2O_3–

CeO_2 to remove Pb^{2+} cations. When the UV irradiates the $Gd_{0.1}Ce_{0.9}O_{1.95}$-CeO_2, electrons in $Gd_{0.1}Ce_{0.9}O_{1.95}$ generated and quickly transferred to the conduction band of CeO_2, and conversely the photo generated holes in CeO_2 quickly transferred to the valence band of $Gd_{0.1}Ce_{0.9}O_{1.95}$ leading to an efficient separation between the photo generated electron–hole pairs in the $Gd_{0.1}Ce_{0.9}O_{1.95}$-CeO_2 photocatalyst.

2.10. Zirconium oxide (ZrO_2) and Zinc Oxide (ZnO) spheres

Cui et al (2013) studied on As (III, V) removal by ZrO_2 spheres. They demonstrated ZrO_2 spheres acts better than ZrO_2 nanoparticles for removal of arsenic. In their study, Zirconium oxychloride octahydrate ($ZrOCl_2.8H_2O$) was used as the raw material, deionized water as the solvent, aqueous ammonia ($NH_3.H_2O$) as the precipitation agent, and Agar powder $(C_{12}H_{18}O_9)n$ as the binding media. They used Fruendlich model for defining adsorption capacity of ZrO_2 spheres (Deliyanni et al., 2007):

$$Q_{qe} = K_F C_{eq}^{\ 1/n}$$

where Q_{eq} is equilibrium sorption capacity ($mgPg^{-1}$) of arsenic adsorbed, C_{eq} is the equilibrium phosphate concentration (mg/L^{-1}) in water samples, and K_F is the Freundlich constants ($mg\ g^{-1}$) $(Lmg^{-1})^{1/n}$. They concluded that these ZrO_2 spheres acted a good adsorption capacity on both As^{3+} and As^{5+} at near neutral pH environment, without the need of pre-oxidation.

Because very limited studies were focused on the use of zinc oxide as an adsorbent for the removal of arsenic from aqueous solutions, a new adsorbent synthesized by gold nanoparticles (AuNPs) and zinc oxide (ZnO)-decorated zirconia (AuNPs/ZnO-ZrO2) through co-precipitation and hydrolysis methods (Jiming Hua 2020) or by precipitation method, ZnO impregnated on agro-waste Biochars which were prepared by carbonization in mild condition, to improve adsorption capacity of arsenic (As^{5+}) and lead (Pb^{2+}) cations. (Cruz G.J.F. et al., 2020)

3. Conclusion

Water is an important element in life of people. Nowadays, water pollution with heavy metals has become a serious problem that is related to rapid urbanization, industrialization and agricultural area development. In most countries of the world, groundwater and surface water are at a serious risk of metal pollution. Severe effects of heavy metals have led to reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. So, the effective removal of heavy metals from water sources is essential to ensure the health and life quality for millions of people that may be threatened by those. Many methods can be used to remove heavy metals, but most of them are expensive and with scant efficiency. Thus, there is great need for the development of simple, low-cost, and highly efficient methods for the removal of heavy metals. Photocatalytic techniques are appropriate methods for removal of heavy metals. In this method, the electron holes created by the incident light can oxidize organic contaminants and the electrons released could be used to reduce metal ions in the water.

There are many photocatalytic techniques for removal of heavy metals from water bodies. Each of them has some advantages and limitations. All scientists are working to find the best solution for removal of these dangerous compounds from water. The meaning of the best method is finding a method with low cost and risk, high efficiency and with the least secondary contamination.

Advantage of inorganic nanomaterials is easy separation, but its limitation is secondary pollution possibility. Advantage of organic nanomaterials is high efficiency and limitation of organic nanomaterials is rather high cost. The benefits of adsorption process by Titania–silica photocatalyst is its simplicity, convenience, and high removal efficiency. Also, this method does not add any toxic pollutant, so health risk of this this process is very low, but performance of this method is not very high.

ZrO_2 spheres are non-toxic, highly stable, and resistant to acid and alkali, have a high arsenic adsorption capacity, and could be easily adapted for various arsenic removal apparatus.

Zero valent iron activated persulfate process is a good method because of its low cost and relatively high stability and solubility, but mechanism of the process remains as a controversial issue since no agreement has been reached over the true identity of the major oxidant species among superoxides, valence band holes, and $^{\bullet}OH$ radicals.

Titanate nanotubes is a good method for economic treatment because of recoverable structure.

In UV/TiO_2 method; As^{3+} is completely oxidized to As5+ by photo-oxidation. This method is a robust and low-cost approach without any damage of adsorbent, but the adsorption capacity of TiO_2 is very low, it causes inefficient removal of As^{5+}.

The advantages of using TiO_2/MMT include its high efficiency for arsenic adsorption, faster adsorption rate, low equilibrium concentration of As^{3+} (0 µg L^{-1}) and As^{5+} (4 µg L^{-1}) with UV irradiation and low cost compared to the Nanocrystalline titanium dioxide.

In magnetic CuO-Fe_3O_4 nanoparticles method, there are high adsorption capacity of both CuO and Fe_3O_4, photoconductive and photochemical properties of CuO, so this method has high efficiency for removal of the heavy metals.

It can be concluded that all methods that are commonly used for heavy metals removal suffer from one or more drawbacks, limitations and scope of application and advantages of each method is depend on some conditions such as pH, adsorption time, solvent type, heavy metal type and UV light, so we can't say that method is better than another.

In summary, more research needs to be done to find the best method with low treatment cost, at least operational complexity and high efficiency.

4. Conflict of interest

The authors declare that they have no conflict of interest.

5. Additional Information and Declarations

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Competing Interests

The author declares there is no competing interests, regarding the publication of this manuscript

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