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REVIEW ARTICLE

A review on the capability of zinc oxide and iron oxides nanomaterials, as a water decontaminating agent: adsorption and photocatalysis

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Abstract
Water decontamination became a priority-based focused area for environmental scientists and researchers these days. Several contaminants like pesticides (chlorpyrifos, endosulfan, aldrin, lindane, malathion) and heavy metals (As, Pb, Cd, Hg, Cu) are broadly reported in drinking water worldwide. Pesticides and heavy metals build up in drinking water is a danger to all consumers. These pollutants cause a number of deadly diseases like bone deformity, nerve disorder, liver damage and cancer. So, their elimination from drinking water is a must to do thing to save life of the living creatures. Several pollutant removal processes are applied for the eliminations of these contaminants from water, of which adsorption and photocatalysis are latest, effective and focused in this paper. Thus, this review will focused on the recent work done using zinc and iron oxides nanomaterials as adsorbent for the removal of different heavy metals and photocatalysts for the mineralization of various pesticides.

Keywords Drinking water · Pesticides · Heavy metals · Nanomaterials · Adsorption · Photo catalysis · Decontamination

Abbreviations

GC-ECD	Gas chromatography electron capture detector
GC–MS	Gas chromatography mass spectrometry
HLB Cartridge	Hydrophilic-lipophilic balance cartridge
AAS	Atomic absorption spectrometry
BIS	Bureau of Indian Standards
WHO	World Health Organization
DCM	Di chloro methane
DDT	Dichlorodiphenyltrichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDD	Dichlorodiphenyldichloroethane
HCH	Hexachlorocyclohexane
HCB	Hexachlorobenzene
OCPs	Organo chlorine pesticides
OPPs	Organo phosphorous pesticides
ZnO	Zinc oxide nanoparticles
POPs	Persistent organic pollutants
GCN	Graphite carbon nitride

Introduction

The earth is the sink of all kinds of resources that we required for the fulfilment of our daily needs. As the population of the developing countries like India and China increase, it causes a number of threatening effects on our environment and global problems like shortage of hygienic food, potable water, shelter and deterioration of natural recourses. A major outcome of this scarcity is enhancing contaminations in all types of natural resources due to human interventions. As the green revolution comes in form of amendment and applied on general use, the increase in yield is quite impressive but the extensive operation of chemically fabricated fertilizer and pesticides not only deteriorate the natural resources but also accumulate in food chain and causes life threatening disease like cancer, ulcer, etc. (Khetan and Collins 2007; Ramlogan 1997).

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Water is second most required resource after air for the every living organism on the earth. Water resources are exists in two most common forms like ocean and fresh water. As ocean water can’t be used for household, farming and industrial application, only fresh water resources have significant role to fulfil all the above demands. Fresh water resources, because of their high demands, are getting exhausted. Due to this, water streams like river and canal either drying up or become sewage in most of the states of Indian subcontinents. Due to the deterioration of surface water, ground water sources becomes the highly demanded and dependable resource for the society. Ground water resources are mainly contaminated by the polluted water streams like rivers, canals or sewage system through surface water-ground water (SW-GW) interaction or penetration phenomenon (Sophocleous 2002). The sewage wastewater is take part to make water resources unfit for use because most 70% of inappropriate discharged comes from the industrial and municipal sectors in India on daily basis (Gadipelly et al. 2014). Therefore, both type of water resources either become exhausted or polluted by several anthropogenic activities. This paper review the application and usefulness of zinc oxide (ZnO) and iron oxides (IOs) nanomaterials as an adsorbents and photocatalysts for the deportation and degradation of heavy metals, pesticides and some dyes (Fig. 1).

Pollutants in the water system

Water resources are not only over exploited but are also contaminated by anthropogenic activities like domestic waste, industrial discharge and agricultural run offs (Fig. 2).Pollutants like heavy metals and pesticides are reported to be having carcinogenic property and abundantly found in surface water as well as ground water. The drawn out effect of water system with sewage effluents on heavy metal substance in soil, crops and groundwaterhave been reported in the outskirt regions of western Delhi. The 10 years irrigation based on sewage water, shown the noteworthy elevation of zinc, iron, lead and nickel in soil (Rattan et al. 2005).

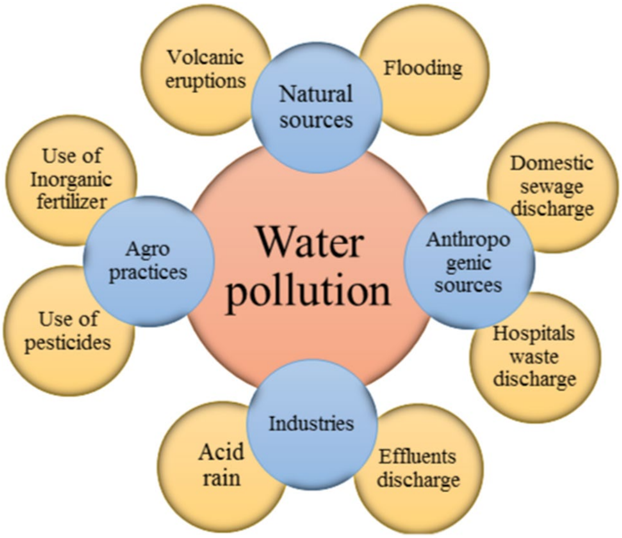
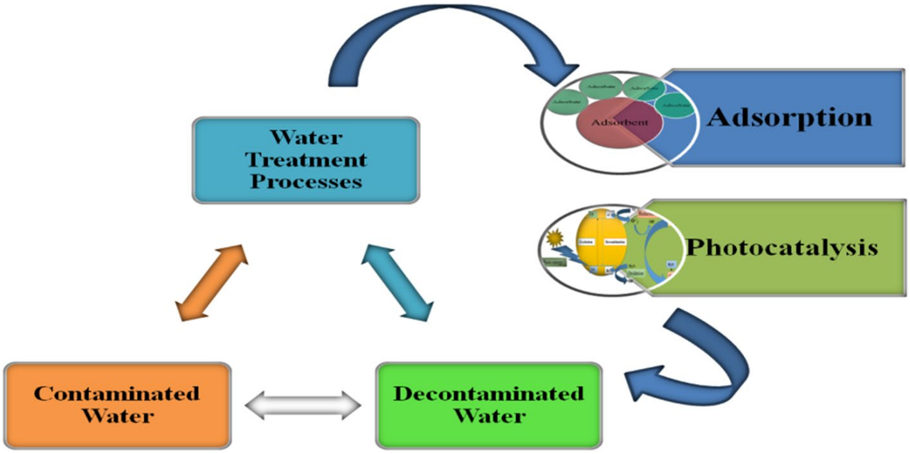


Fig. 2 Different sources of water pollution in India

The side-effects of industrialization in Peenya, the industrial area near Bangalore, on ground water quality was studied by Shankar et al. (2008), and they reported that about 70% of the samples are not suitable for drinking purposes according to the limitations given by BIS (Shankar et al. 2008). Jayadev and Puttaih (2013) analyzed the Vrishabhavathi river and its surroundings water samples and found that river water isn't for drinking by the BIS norms. It is additionally not appropriate to utilize straightforwardly for irrigation also. The concentrations of heavy metals such as lead, chromium, nickel found to be above the permissible limits as given by BIS, and decrease downstream the river (Jayadev and Puttaih 2013). Baride et al. (2012) evaluate the surface and

Fig. 1 Graphical abstract showing the decontamination of water by using adsorption and photocatalysis



ground water from Jalgaon, Maharashtra. More than 60 water samples from nullahs, river and bore wells were collected by pre and post-monsoon sampling. Trace elements like iron, chromium, copper, nickel, zinc, manganese and lead were analyzed using double-beam AAS. The concentration of Mn, Fe and Zn in water samples ranges 0.0001–1.3513 mg/l, 0.0146–1.3237 mg/l and 0.005–0.1993 mg/l, respectively, in post-monsoon season (Baride et al. 2012). Agricultural practices within the Krishni river catchment have negative influence on the river water aspect. Surface water run-off from agricultural land carries agricultural chemicals such as pesticides and fertilizers. Chemical fertilizers have also been demonstrated to contain heavy metals (Gascia et al. 1996). Surface water of River Krishni as well as from the ground water of nearby villages are collected and analyzed for various parameters (physiochemical, heavy metals) and found that water samples from both the sources are heavily contaminated (Bharti et al. 2020a, 2019; Jangwan et al. 2019). Alam and Umer (2013) analyze the level of trace elements such as aluminium, chromium, manganese, iron, nickel, copper, cobalt, zinc, arsenic, cadmium, boron and lead in the ground water samples from the, Baghpat district of west U.P. This analysis shown high amount of aluminium as well as chromium concentration in nearly all samples. Other evaluated heavy metals concentrations are also high as compared to BIS standards (Alam and Umar 2013). The amount of heavy metals like cadmium, copper, cobalt, zinc, nickel, lead, iron and manganese evaluated in many inorganic-based fertilizers such as urea, calcium super phosphate, iron sulfate and copper sulfate as well as in some pesticides. The finding of this analysis shown that superphosphate contain higher amount of Co, Cd, Cu, Zn as an impurity, $CuSO_4$ and $FeSO_4$ have the high level of lead and nickel. All the pesticides are found to be contaminated with Cd and level of trace elements iron, manganese, zinc, lead and nickel found in high quantity in the herbicide (Gascia et al. 1996). River Ganga water tests from the city of Kanpur were extricated by liquid extraction and their quantitative and qualitative analysis done by using GC-ECD method. Amid from the different pesticides analyzed down, higher groupings of γ-HCH (0.259 $\mu g\ L^{-1}$) and malathion (20,618 $\mu g\ L^{-1}$) were identified. Drinking water samples were also analyzed via the same method, and the concentrations of γ-HCH, malathion and dieldrin were found to be 0.900–29.835 $\mu g\ L^{-1}$(Sankararamakrishna et al. 2005). By using solid-phase extraction technique, a total of 67 pesticides like organochlorine, organophosphate, carabamates, pyrethroids, pyrimidines, azoles, triazoles and other class of pesticides were analyzed by GC–MS technique using C_{18} and HLB cartridges (Kouzayha et al. 2012). Drinking water samples in the rural parts of Haryana, India were discovered to be tainted with organochlorine pesticides like HCH isomers, endosulphan, DDT and its metabolites (Kaushik et al. 2012). The samples have been analyzed and reported to be contaminated with different pesticides. The level of atrazine, chlorfenvinphos, α-endosulfan, β-endosulfan, lindane, molinate and simazine were 0.63, 31.6, 0.18, 0.18, 0.24, 0.48 and 0.3 μg L^{-1}found in surface water samples of an agricultural intensive areas of Portuguese. In case of ground water, the maximum concentration of different pesticides are 0.4–56 $\mu g\ L^{-1}$ (Cerejeira et al. 2003). The remnant of DDT and its metabolites, HCH and its isomers, heptachlor and its epoxides and aldrin were analyzed in cereal grains and drinking water samples in Rajasthan, India and wheat samples were reported to be excessively contaminated as the limits given by WHO (Bakore et al. 2004). Samples from 28 domestic wells, after extraction by solid phase extraction methods, were analyzed by GC and reported to be tainted by DDT, endosulfan and lindane. The range for lindane was between 0.68 and 1.38 $\mu g\ L^{-1}$. For DDT, range was 0.15–0.19 $\mu g\ L^{-1}$. For α-endosulfan the range was 1.34–2.41 $\mu g\ L^{-1}$ and for β-endosulfan was 0.21 to 0.87 $\mu g\ L^{-1}$ (Shukla et al. 2006).In addition to this soil and water samples were reported to be taint with different pesticides such aldrin, dieldrin, endrin, HCB, HCH isomers, DDT isomers/ metabolites, endosulfan sulfate, heptachlor and its metabolites, chlordane and methoxychlor in Unnao district of U.P. The range of detected pesticides were in the range from 0.36–104.50 ngg^{-1} and 2.63–3.72 μgL^{-1}in soil and surface water samples, respectively (Singh et al. 2007). Ali et al. (2008) reported the presence of organochlorine pesticides such as α, β and γ BHC's, aldrin, endosulfan, DDE, DDD and methoxychlorin the Hindon river water samples (Ali et al. 2008). Lari et al. (2014) compared the pesticide concentration in surface and ground water of farming intensive areas of Vidarbha, Maharashtra, India. Among the reported pesticides, α, β, γ and δ HCH's, aldrin, dicofol, DDT and its derivatives, α, β endosulphan's and endosulphan-sulfate were organochlorine pesticides, and dichlorovos, ethion, parathion-methyl, phorate, chlorpyrifos and profenofos were organophosphate. In contrast to groundwater, higher concentration of OCPs and OPPs were found in surface water. Among pesticides, water samples were reported to be taint with organophosphates than the organochlorines (Lari et al. 2014). Jayashree and Vasudevan (2007) conducted studies and reported with the level of organochlorinepollution in groundwater of Thiruvallur, Tamil Nadu. The samples were exceptionally tainted with DDT, HCH, endosulfan and their subordinates (Jayashree and Vasudevan 2007). Liquid–liquid extraction technique was used for the extractionof pesticides with the help of DCM as an extracting solvent and reported the presence of aldrin, endrin, dieldrin, endosulfan, heptachlor, α-BHC, β-BHC, δ-BHC, DDT and its derivatives using capillary GCMS (Fatoki and Awofolu 2003). Due to the carcinogenic nature of heavy metals, pesticides and other pollutants, they should be removed from drinking water.

Synthesis methods of metal oxide nanomaterials

The two main approaches which are used for the fabrication of nanomaterials are top-down and bottom-up methods.

The top-down methodology includes fundamentally actual techniques where a mass material is cut into pieces till the ideal size is accomplished. However, by the use of this approach micrometer size can be formed easily but for achieving nanometer size these methods are expensive, where the bottom-up methods involve chemical techniques. These are commanded methods. This restriction prompts the development of particles of wanted size and shape (Arole and Munde 2014; Wolfsteller et al. 2010; Wolf 2006). Various explicit techniques have been created and the widely used ones of those are given in Fig. 3. Top-down approaches include thermal methods, mechanical methods, chemical etching, whereas bottom-up approaches involve sol–gel, vapour deposition, precipitation method, etc. Physical methods involve in top-down approaches are slow processes and non-favourable for large scale fabrication. In contrast to this, chemical or biological methods of bottom-up approaches are fast as compared to top-down approaches (Singh et al. 2010). In any case, in contrast to the compound blend of atoms of an ideal construction, the amalgamation of nanomaterials with uniform size and shape is troublesome. Accordingly, huge scope union of nanomaterials stays a test. In order to control certain morphological characters with certain "chemical" versatility "bottom-up" approach must be followed (Dintinger et al. 2012).

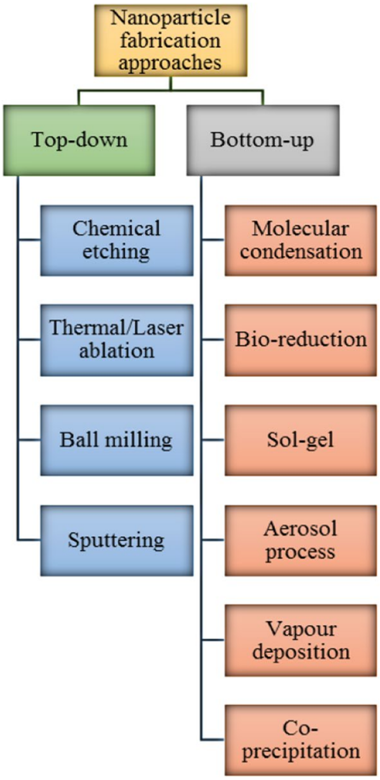


Fig. 3 Various methods used for the fabrication of nanoparticles (Iravani 2011)

Pollutants decontamination processes

Pesticide and heavy metals pollution emerges as the serious environmental concern. Human body require some metals like Fe, Ca, P, Mg K, Na for better functioning. On the other hand some metals like Cd, As, Ni, Pb, Zn have an adverse effect because they can bio accumulate in our body through food chain. Moreover, pesticides and fertilizers are used in farming land to destroy the pests and obtained high yield. In the processing of some fertilizer, heavy metals are employed as an ingredient. These contaminants reported to be found in the samples of water, soil, food etc. These pollutants cause disease like cancer and ulcer. So, removal of these cancer causing elements must be done before their use through water and other resources. Herein we discussed the most efficient, highly used, easily employed drinking water decontamination process i.e., Adsorption and Photocatalysis.

Adsorption process

Adsorption process is the key concern in the field of removal of pollutants from water. The large surface area of a catalyst could enhance the degradation or removal efficiency of pollutants. Adsorption phenomenon is based on the fact that, when the contaminated water comes in the contact with a nanoadsorbent, the pollutants species got adsorbed on the pores, present of the surface of that adsorbent. The surface of nanoadsorbent play an important role in the water decontaminating process. The surface morphology of nanoadsorbent can be studied by using scanning electron microscopy (SEM). The scanning electron microscopy images of some nanomaterials such as ZnO and Fe_2O_3 are shown in Fig. 4, which is helpful for the better understanding of their surface characteristics. Herein the review of different metal oxides nanomaterialsused for the evacuation of different trace elements from aqueous medium by using adsorption phenomenon summarized and their details are given in Table 1.

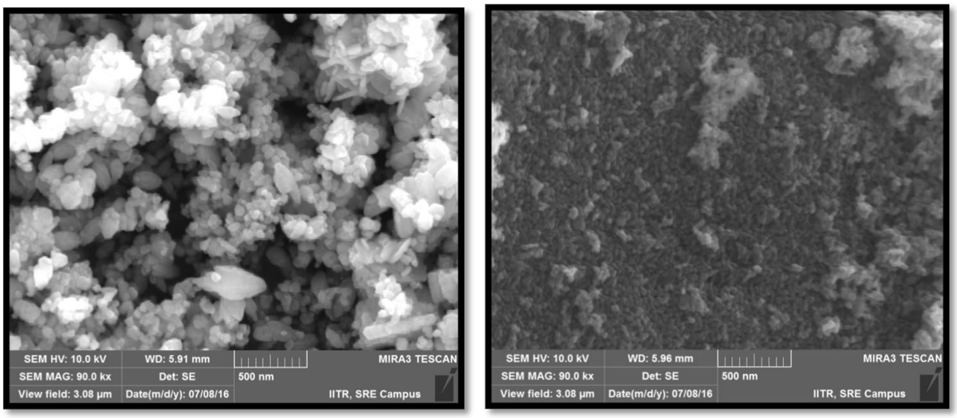


Fig. 4 SEM images of (i) zinc oxide and (ii) iron oxide nanomaterials

Table 1 Removal of heavy metals using metal oxide nanomaterials as an adsorbent

S. No.	Nanomaterials	Removal of heavy metals/trace elements/pollutants	Efficiency of adsorbent	References
1	Zinc oxide	Cd(II), Ni(II)	< 15% Adsorption of Cd, Ni	Le et al. 2019)
		Arsenic	0.85 mg/g adsorption of As	Muensri and Danwittayakul 2017)
		Cd, Cu, Ni, Pb	Cd-50%, Cu-20%, Ni-100%, Pb-70%	Mahdavi et al. 2012)
		Cr(VI)	> 50% adsorption in 220 min	Ahmed and Yousef 2015)
		AB-92 dye	69.55 mg/L adsorption	Salem et al. 2017)
		Cadmium, copper, nickel	Cd-60%, Cu-90%, Ni-50%	Mahdavi et al. 2015)
		Cadmium, lead, cobalt and Congo Red(CR), Methylene Blue (MB) dyes	Cd-156.74 mg/g, Pb-194.93 mg/g, Co-67.93 mg/g, CR-62.19 mg/g, MB-115.47 mg/g adsorption	Somu and Paul 2018)
		Cadmium, chromium, cobalt, nickel	Cd-49.09%, Cr-53.67%, Co-38.70%, Ni-46.11% removal	Khezami et al. 2019)
		Ni(II), Cd(II), Cr(II)	Ni-25%, Cd-55%, Cr-60% approx. removal	Ghiloufi et al. 2016)
		Cadmium, Arsenic, Selenium	Cd-37%, As-95%, Se-64% removal	Bharti 2021)
2	Iron oxides	As (III) from arsenic contaminated water	96% removal	De et al. 2009)
		Arsenic removal	As(III)-99.2%, As(V)-98.4% removal	Mayo et al. 2007)
		Cr (+6)	95–97% removal	Zelmanov and Semiat 2011a)
		Phosphate removal	95–99% removal	Zelmanov and Semiat 2011b)
		As(III) removal	100.3 mg/g adsorption capacity	Dave and Chopda 2014)
		Arsenic, Selenium	As(V)-16.85 mg/g, As(III)-14.26 mg/g, Se(IV)-13.08 mg/g, Se(VI)-6.13 mg/g adsorption	Lee and Kim 2016)
		Pb, Cd, Cu and Zn	Pb-208.17 mg/g, Cd-169.90 mg/g, Cu-111.90 mg/g, Zn-100.24 mg/g adsorption	Zhao et al. 2016)
		Cadmium	72 ppm maximum sorption efficiency	Iqbal et al. 2021)
		Cadmium from waste water and drinking water		Kumar and Chawla 2014)
		Se	Se(IV)-95 mg/g, Se(VI)-15.1 mg/g adsorption capacity	Zelmanov and Semiat 2013)
		Cd, Cu, Ni, Pb	Cd-58%, Cu-100%, Ni-20%, Pb-70%	Mahdavi et al. 2012)
		Aluminium, arsenic, cadmium, cobalt, copper, nickel	Al-50%, As and Cu > 95%, Cd-65%, Co-52%, Ni-50% adsorption	Saad et al. 2012)
		Hg removal from wastewater	85% removal	Velez et al. 2016)
		Lead, chromium, cadmium, copper	Pb-85%, Cr-20%, Cd-70%, Cu-40%	Maiti et al. 2018)
		Cadmium, nickel, copper and lead	100% removal of all at 5 pH	Fato et al. 2019)

ZnO Nanomaterials

The large surface area of nano size zinc oxide materials exhibits effective removal of contaminants like heavy metals. The ZnO nanoparticles are non-toxic and environment friendly in nature also can be easily synthesized. They have vast application in the adsorbent-based elimination of various toxic elements such as cadmium, chromium, manganese and nickel from drinking water. Deportation of Cd can also be done with the use of ion-exchange method. It was based on the hypothesis that at first Cd particles enter in the pores of ZnO and traded basically by hydroxyl bunches which are available on the outside of zinc oxide. These Cd ions undergo through a channel of the crystalline lattice of ZnO before they are exchanged (Le et al. 2019).

ZnO nonmaterial has been widely utilized for the eviction of arsenic, from the water and reported the removal efficiency 0.85 mg As/g (Muensri and Danwittayakul 2017). Removals of Cd, Cu, Ni, Pb heavy metals were reported by using ZnO and other nanoparticles as an adsorbent successfully (Mahdavi et al. 2012). The eradication of different trace elements like chromium, cobalt, nickel, cadmium, copper, arsenic and Selenium was reported by various researchers (Ahmed and Yousef 2015; Salem et al. 2017; Mahdavi et al. 2015; Somu and Paul 2018; Khezami et al. 2019; Ghiloufi et al. 2016; Bharti 2021).

Iron oxides nano-materials

Iron oxides nano-materials have been well studied because of their diverse properties and functionalities. Moreover, iron oxide nanomaterials with low poisonousness, substance latency and biocompatibility show a gigantic potential in mix with biotechnology (Gupta and Gupta 2005). Because of these bio-safe and naturally well-disposed natures, a few strategies are for the most part utilized for the combination of iron oxide nanoparticles like co-precipitation method (Tang et al. 2006). Numerous specialists have been zeroing in their endeavours on creating compound and actual strategies for their union. Recently, a detailed description based of fabrication, characterization, and properties of IOs nanomaterials have been made (Laurent et al. 2008; Teja and Koh 2009). Iron oxide nanoparticles can assume a critical part in the recycling of trace elements. De et al. (2009) fabricate and utilized, iron oxide nanomaterials for the adsorption of As (III) from arsenic contaminated water (De et al. 2009). The impact of nanocrystalline magnetite on arsenic expulsion was studied by Mayo et al. (2007). The fabrication, analysis and use of of Fe^{3+}oxide/ hydroxide based nanoadsorbent for the elimination of Cr (+6) and phosphate were reported by Zelmanov et al. (2011a, b). Application of iron oxide nanomaterials for the eradication of different trace elements like arsenic, copper, chromium, lead, zinc, etc., was studied by Dave et al. (2014). The evacuation of arsenic and selenium from aqueous medium was effectively done by utilizing the iron oxide nanoparticle/ carbon nanotube adsorbent (Lee and Kim 2016). Megneticporous Fe_3O_4-MnO_2nanoparticles wereeffectively blended and applied for the evacuation of specific metals like Pb, Cd, Cu and Zn from the aqueous solution. (Zhao et al. 2016). In addition to the removal phenomenon nanosize magnetic particles become expected adsorbents for the expulsion of cadmium. Iron-based material, for example, hematite structure (α-Fe_2O_3), maghemite structure (γ-Fe_2O_3) and magnetite structure (Fe_3O_4) are eco-friendly, cost effective, easy to synthesize and perform with a high potential toward removal purposes. It has been reported that hematite loaded with biochar efficiently absorbs cadmium ions from aqueous medium (Iqbal et al. 2021). A detailed review based on the evacuation of Cd from waste water and drinking water by using iron and other metal oxides nanoparticle is presented by kumar et al. (2014). Elimination of Se, Cd, Cu, Ni, Pb heavy metals was reported by using Fe_3O_4 and other nanoadsorbent effectively (Mahdavi et al. 2012; Zelmanov and Semiat 2013). The eviction of Cd, Al, As, Co, Cu, Ni, Hg, Zn, Se trace elements by using Fe_2O_3nanomaterials as an adsorbent was reported by various researchers (Saad et al. 2012; Velez et al. 2016; Maiti et al. 2018; Fato et al. 2019).

In addition to zinc oxide and iron oxides nanomaterials, TiO_2 nonmaterials are also widely used adsorbent for the elimination of different heavy metals. The TiO_2 nanoadsorbent have been reported for the removal of arsenic with the removal efficiency 0.99 mg As/g (Muensri and Danwittayakul 2017). Kumar et al. reviewed the effect of titanium-based nanoadsorbent for the elimination of cadmium from waste water and drinking water kumar et al. (2014).

Photocatalysis

Debasement and mineralization of organic pollutants like pesticides have become the critical worry for academic persons globally, on account of their high synthetic dependability, low biodegradability and high persistency in the climate. The total debasement of natural toxins is beyond the realm of imagination by customary methodologies like anaerobic processing, enacted muck absorption, physiochemical treatment, as they just exchange the pollutants starting with one stage then onto the next. However, advanced treatment methods like advance oxidation processes, biological remediation, membrane filtration, ozonation and adsorption have shown to be very promising. Out of these strategies, advance oxidation measure (AOP) utilizing nanoparticle-based semiconductors as a photocatalyst for the corruption of pesticide is considered as generally effective, promising and natural amicable method (Khan et al. 2015). Amidst the various technologies and methods available, the advanced oxidation process of photocatalytic degradation technique using semiconductors has shown to be one of the most promising processes for the drinkingwater as well as wastewater treatment (Raizada et al. 2019; Fujishima and Honda 1972). The initial interest in photocatalysis using semiconductor photocatalysts began in 1972, when water splitting was shown to be possible to form H_2 and O_2 under the conditions of photochemical reactions by using TiO_2 nanomaterial (Andreozzi et al. 1999). The advanced oxidation processes (AOP) are portrayed by a typical reactive property. The capacity of using high reactivity of OH extremists in driving the oxidation measures which are reasonable for accomplishing the total reduction and mineralization of even less responsive pollutants (Quiroz et al. 2011). Highly reactive oxidizing species are involved in the phenomenon of advanced oxidation process, which successfully degrade the organic substance by attacking on them. It was introduced by Glaze et al. for the first time.

$$RH + HO^{\bullet} \rightarrow HR + H_2O \tag{1}$$

These free radicals can be produced by photochemical or non-photochemical procedures.

Types of photocatalysis on the basis of phases of reactant and catalyst

(i) Homogeneous photocatalysis In homogeneous catalysis, both reactant and catalysts are in same phase (Fenton and Fenton-like process). So, everything will be present in a single liquid phase. The catalyst should be separated when the treatment is finished. Various methods are employed for this purpose such as precipitation**,** ion exchange technique and liquid emulsion membrane process. But all these methods add extra cost to catalyst recovery during the treatment process. So, the need of heterogeneous catalysts was realized in order to overcome this problem.

(ii) Heterogeneous photocatalysis In case of catalysis based on heterogeneous situations, the reactant and catalyst present in distinct forms. So, there is no need of catalyst recovery from the system. These types of photocatalysis are based on corruption theory includes the utilization of a strong semiconductor nanocatalyst, which can produce a steady colloidal interruption, under radiation to invigorate a response in the strong/fluid interface. As soon as the nanocatalyst exposure with the contamination solution, which contain reducing as well as oxidizing species in the same aqueous solution, transmission of the charges take place. Nano-materials-based photocatalysis for the remediation of drinking water is the best application of this technology. This method can be utilized for mild's effluents to concentrated toxic multi-elemental complex industrial pollutants (Sonu et al. 2019; Singh et al. 2018; Xia et al. 2021; Sahithya and Das 2015). These semiconductors of nano-size give better results, due to their wide exterior. This interaction depends on the rule that when a semiconductor is presented to a light wellspring of specific frequency, the electrons from valence band are elevated to the conduction band abandoning the positive hole. The created electron–hole sets move to the outside of the semiconductor and corrupt the organic contaminants into nontoxic ones (Sudhaik et al.2020). The band gap energy given by Quiroz et al. (2011) for Fe_2O_3, ZnO and TiO_2 are 2.2 eV, 3.2 eV and 3.2 eV, respectively (Sonu et al. 2019). The required band gap energy as well as actuation wave length of widely used Metal oxides nanocatalyst are given in Table 2.

The photocatalytic efficiency of semiconductors can be enhanced by using hetero-junction semiconductors. These hetero-junction semiconductors are prepared by combining another semiconductor. Photocatalytic activity of $CoFe_2O_4$ will be increase by preparing hetero-junction using other metal oxides (Sudhaik et al. 2020). The Z-Scheme is also an important kind of hetero-junction which can be used to increase the capacity of photocatalytic reactions . In Z-Schemes, redox mediators are commonly used to maintain the high and enhanced redox potentials. The photogenerated electrons are directly transferred to valence band of one semiconductor to conduction band of another semicoinductors (Kumar et al. 2020). Another most employed method used for the enhancement of photocatalyst activity is vacancy creation. These vacancies can be categorized as anion vacancy, cation vacancy and multiple vacancy depending upon the ions loss from the photocatalyst. In addition to these activity enhancement methods, metal-free photocatalysts also exploited due to their extraordinary qualities and cost-friendly nature. One of the mostly used metal-free semiconductors is carbon nitride which is commonly known as GCN (g-C_3N_4). The exceptional physiochemical properties, deserving electronics capabilities and nontoxic nature of GCN, draw the attention of researchers to use as a semiconductors photocatalyst (Sharma et al. 2020; Raizada et al. 2020; Badaway et al.

Table 2 The band gaps and wavelength of activation for some photocatalyst

S. No	Nanomaterials	Band gap energy (eV)	Activation wave length (nm)
1	ZnO	3.2	390
2	Fe_2O_3	2.2	565
3	TiO_2	3.2	387

Table 3 Removal of Different Organic contaminant using metal oxide nanomaterials as a photocatalyst

S. No	Metal oxide	Nanomaterials	Removal of Pollutants	Category of pollutants	References
1	Zinc oxide	ZnONps	Chlorpyrifos	Pesticide (OPP)	Khan et al. 2015)
		C/ZnO/CdSnanocomposites	(4-Chloro phenol)	Pesticide (OCP)	Anandan et al. 2006)
		ZnO NPs	Monocrotophos	Pesticide (OPP)	Anandan et al. 2007)
		La-doped ZnO	Monocrotophos	Pesticide (OPP)	Nguyen et al. 2015)
		ZnO nanoparticles/ZnO nanoparticles Composites	RB198, Acid-32-cyanine 5R, Blue cat 41, Acid 4092, Acid black 1, Rhodamine B, Methylene blue	Dyes	Dehghani and Mahdavi 2018; Golmohammadi et al. 2016; Dehghani and Mahdavi 2015; Golmohammadi 2016; Rokesh et al. 2018; Yu et al. 2013; Salijooqi et al. 2020)
		ZnO /TiO_2 and Fe_3O_4Nps	Chlorpyrifos	Pesticide (OPP)	Zandsalimi et al. 2020)
		Cu-doped ZnOnanorods	Diazinon	Pesticide (OPP)	Zhu et al. 2020)
		ZnO/rGO composite	Dimethoate	Pesticide (OPP)	Navarro et al. 2009)
		ZnO/$Na_2S_2O_8$	Azoxyxtrobin, Kresoxim-methyl, Hexaconazole, Tebuconazole, Triadimenol,Pyrimethanil, Primicarb, Propyzamide	Pesticides (fungicides, insecticides, herbicides)	Monocrotophos pesticide effectively removed by novel visible light driven Cu doped photo-Catalyst. 2019)
		Cu-doped ZnO	Monocrotophos	Pesticide(OPP)	Garrido et al. 2020)
		Fibroin/ZnO	Etoxazole, difenoconazole, myclobutanil andpenconazole	Pesticides (acaricide, fungicides)	Maleki et al. 2019)
		WO_3-doped ZnO NPs	Diazinon	Pesticide (OPP)	Hariharan 2006)
		ZnO NPs	Aliphatic and Aromatic chloro compounds and solvents	Organic contaminants	Bharti 2021)
		ZnO NPs	Monocrotophos	Pesticide (OPP)	Rafaie et al. 2017)
		ZnO nanostructure With Ag NPs	Methylene Blue	Dye	Jing et al. 2013)
2	Iron oxides	Fe_3O_4 NPs	Aldrin, Endrin and Lindane	Pesticide (OCP)	Abdullah et al. 2013)
		γ-Fe_2O_3 NPs	Di and tri chlorophenoxy acetic acid	Pesticide (OCP)	Maji et al. 2012)
		α-Fe_2O_3 NPs	Rhodamine B	Dye	Bharti et al. 2020b)
		Fe_2O_3 NPs	HCH, Aldrin, Dieldrin, Endrin and its metabolite, Endosulfan and its metabolites, DDT and its derivatives, Heptachlor and its metabolites	Pesticide (OCP)	Du et al. 2008)
		Fe (II), Fe (III) oxides and FeOOH	Orange II	Dye	Feng et al. 2000)
		Iron powder	Orange II, C.I. RR-2, C.I. RB-8	Dye	Khedr et al. 2009)
		Fe_2O_3	Congo Red	Dye	Wang 2007)
		Gold/Iron oxide aerogels	Azo dye	Dye	Kadirova et al. 2014)
		Fe_2O_3-activated carbons	Methylene Blue	Dye	Bandala et al. 2002)

2006). In contrast to this metal oxide nanoparticles having exceptional photocatalyst properties are chosen for this review as:

ZnO nanomaterials

ZnO nanomaterials are broadly utilized as an effective photochemical elimination of various contaminants such as organochlorine and organophosphorous pesticides and various dyes, etc (Table 4). The details given below regarding elimination of some pesticides from water:

Pesticides

ZnO nanoparticle has been widely used because of their high excitation energy and non-toxic nature. This review includes the comprehensive investigation of the synthesis of ZnO nanomaterials as well as their application in various fields along with pollutants degradation or removal from the aqueous medium. ZnO nanoparticles have been highly attentive due to their stability, catalytic activity, effective antimicrobial, anticancer activity and UV absorbance quality. The photocatalysis-based elimination of chlorpyrifos was effectively done by using synthesized zinc oxide nanoparticle under UV irradiation (Khan et al. 2015). Badaway et al. (2006) used AOP for the degradation of organophophorus pesticides from water (Lavand and Malghe 2015). The natural light based photo-degradation of organochlorine pesticide (4-Chloro phenol), using ZnO based nanocompositeswas achieved by Lavand and Malghe (2015), Anandan et al. (2006). 100% degradation of organophosphate pesticide monocrotophos was done by using ZnO nanoparticles via photocatalytic degradation process as reported by Anandan et al. (2006), (2007). In addition to this, the elimination of monocrotophos can also be achieved by using doped photocatalyst such as La doped ZnO (Nguyen et al. 2015). Photocatalysis-based eliminations of different pesticides and dyes are given in Table 3 and the comparison of both nanoparticles as a decontaminating agent is given in Table 4: **Dyes** In addition to pesticides degradation, many researchers also reported the photocatalytic degradation of RB198 blue dye, acid-32-cyanine 5R, Blue cat 41 dye, acid 4092 dye, acid black 1 dye, RB and MBdyes successfully, by using ZnO nanomaterials and its composites in different advanced oxidation methods (Dehghani and Mahdavi 2018, 2015; Golmohammadi et al. 2016; Golmohammadi 2016; Rokesh et al. 2018; Yu et al. 2013; Salijooqi et al. 2020).

Table 3 (continued)

S. No	Metal oxide	Nanomaterials	Removal of Pollutants	Category of pollutants	References
3	Titanium dioxide	TiO_2	Aldrin	Pesticide (OCP)	Malato et al. 2002)
		TiO_2	Diuron (Herbicide), Imidacloprid, Formetante, Methomyl (Insecticide)	Pesticides	Malik et al. 2018)
		TiO_2	Dichlorvos, Lindane, Methyl parathion	Pesticide (OCP and OPP)	Synergistic photocatalytic mitigation of imidacloprid pesticide and antibacterial activity using carbon nanotube decorated phosphorus doped graphitic carbon nitride photocatalyst. 2020)
		TiO_2	Monocrotophos, Dichlorvos	Pesticide (OPP)	Lavand and Malghe 2015)

Table 4 Comparison of ZnO and IOs NPs as a decontaminating agent

Pollutants/ NPs	ZnO NPs	IOs NPs
Heavy metals	Cadmium, arsenic, selenium, chromium, cobalt, nickel, copper, lead	Cadmium, arsenic, selenium, chromium, cobalt, nickel, copper, lead, zinc, aluminum, mercury
Pesticides	Chlorpyrifos, 4-Chloro phenol, Monocrotophos, Diazinon, Dimethoate Azoxyxtrobin, Kresoxim-methyl, Hexaconazole, Tebuconazole, Triadimenol, Pyrimethanil, Primicarb, Propyzamide, Etoxazole, difenoconazole, myclobutanil and penconazole	Aldrin, Endrin, Lindane, Di and tri chlorophenoxy acetic acid, HCH, Aldrin, Dieldrin, Endrin and its metabolite, Endosulfan and its metabolites, DDT and its derivatives, Heptachlor and its metabolites
Dyes	Congo red, Methylene Blue, RB198, Acid-32-cyanine 5R, Blue cat 41, Acid 4092, Acid black 1, Rhodamine B	Rhodamine B, Orange II, C.I. RR-2, C.I. RB-8, Congo Red, Azo dye, Methylene Blue

Iron oxide nanomaterials

Pesticides Removal of organochlorine pesticides aldrin, endrin, lindane and di and tri chlorophenoxy acetic acid were achieved by using Fe_3O_4 nanoadsorbent and Fe_2O_3 nanocatalyst respectively (Abdullah et al. 2013; Maji et al. 2012).

Dyes The α-Fe_2O_3 nanoparticles were synthesized, characterized and used as a photocatalyst for the successful elimination of RB dye as reported by Maji et al. (2012), Bharti et al. (2020b).

Others Treatment of textile effluents having high COD, BOD and colour, using Fe^{2+} nanoparticles was achieved by Malik el al. (2018), Zelmanov and Semiat (2008). The other form of iron oxides i.e., Fe_3O_4-based nanomaterials were utilized as a nanocatalyst for the AOPs-based oxidation process by Grigori et al. (2008), Fox and Dulay (1993).

Titanium dioxide nanomaterials

In the year 1972, water is splitting to form H_2 and O_2 under the conditions of photochemical reactions by using TiO_2 nanomaterial, that's where the photocatalysis were, started (Senthilnathan and Philip 2009).

Pesticides The photocatalytic elimination of some pesticides aldrin, diuron, imidacloprid, formetante and methomyl have been reported by using heterogeneous photocatalyst TiO_2 (Malato et al. 2002; Malik et al. 2018). Removal of mixed pesticides including dichlorvos, lindane and methyl parathion have been reported using suspended and immobilezed TiO_2 by photodegradation method (Augugliaro et al. 2006). The 100% removals of monocrotophos and dichlorvos pesticides have been reviewed by using TiO_2-Zeolite nanocomposites (Kitture et al. 2011).

Others Augugliaro et al. (2006) used thetitanium oxide nanocatalyst during the deportation of different kinds of pollutants from both water and gaseous states. The use of TiO_2 nanocatalyst is a milestone in the area of ecological sustainability, because of the ability of TiO_2 towards the elimination of organic and inorganic pollutants (Kitture et al. 2011).

There are various types of nanoparticles reported in the literature i.e., metal nanoparticles, metal oxide nanoparticles, metal sulphide nanoparticles, etc. Out of these metal oxide nanoparticles have been chosen for this review, due to their easy availability, widely used, cost-friendly, environmental compatibility and their ability to withdrawal of organic as well as inorganic contaminants from the water. Recovery of nanoparticles at the end of reactions is another important key factor to choose a photocatalyst and assured its reusability and nontoxicity. The reusability of photocatalyst will be done by using proper separation methods such as centrifugation, filtration, vacuum filtration, plant-based coagulation, chemical-based coagulation etc. (Nurmi et al. 2011; Patchaiyappan et al. 2016).

Conclusions

This paper reviewed the application of zinc oxide and iron oxides nanoparticles for the water decontamination process such as adsorption and photocatalysis. This review stipulate that nanometal oxides adsorbent are favourable decontaminating agents for the withdrawal of heavy metals/trace elements. Their adsorbent efficiency could be enhanced by optimization of working condition like pH, nano-adsorbent quantity, exposure hour, etc. Degradation of pesticides and dyes involve the use of heterogeneous photocatalytic reaction in addition with the use of different semiconducting nanomaterials. Due to their wide band gap zinc oxide and iron oxides are excellent photocatalyst, which can degrade POPs like pesticides easily and effectively. The zinc oxide as well as iron oxides nanomaterials are found to be best adsorbent and photocatalyst, because of their excessive exterior area, easy synthesis, and fine to excellent performance.

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Declarations

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