Metal Oxide Nanoparticles for Water Decontamination

Preeti Jain, Mridula Guin, and N. B. Singh

Abstract Clean water is very important for living being and other activities. However, water is continually being polluted and become harmful. Number of techniques is being used for purification of water and out of that adsorption is found to be the most affordable and fast technique. In recent years, nanotechnology has played an important role in water purification and decontamination. Nanomaterials (NMs) have proved to be a very good adsorbent for the removal of organic and inorganic pollutants and heavy metals from water and also kill microorganisms in the wastewater. Due to electronic structure, electronic, optical, and magnetic properties, metal oxide nanoparticle (NPs) are found to be unique materials for water remediation. Metal oxide-based NMs, such as zinc oxides, iron oxides, manganese oxides, titanium oxides, aluminum oxides, magnesium oxides, cerium oxides, zirconium oxides, etc. have shown their effectiveness for water remediation. Nanosized metal oxides possess many exceptional properties, such as a high removal capacity and selectivity towards heavy metals and organic compounds. Thus, they have great potential as promising adsorbents for heavy metals, dyes and other pollutants. In this chapter synthesis of number of metal oxide NMs and their applications for water decontaminations have been discussed in detail.

Keyword Nanomaterial · Metal oxide · Iron oxide · Zinc oxide · Magnesium oxide · Photodegradation

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1 Introduction

Water is the most important component for various activities on this planet. The distribution of water on the earth is shown in Fig. 1. 97.5% water is in sea and only 2.5% is available in other areas for various activities.

Water is the most important component for various activities on this planet and therefore, clean and pure water is required for development as well as for the survival of living organisms. However, the quality of water is continually deteriorating due to rapid urbanization and industrialization [1–5]. The harmful chemicals going into water bodies are heavy metal ions, inorganic cations, dyes and organic compounds. Pollutants mainly come from different sources (Fig. 2) [6].

Toxic metal ions, from different sources go into water body and make them injurious (Fig. 3) [1].

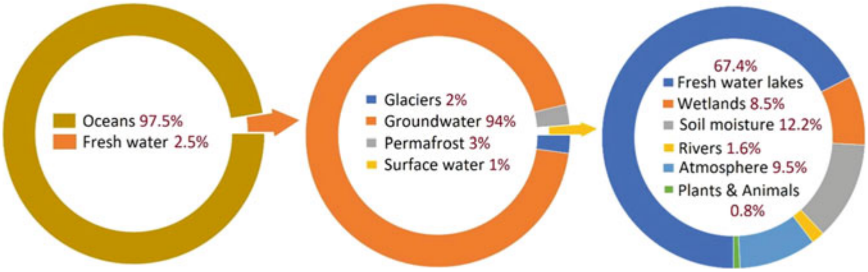


Fig. 1 Distribution of water on earth

Fig. 2 Different sources for pollutants (Reproduced with permission from Elsevier [6])

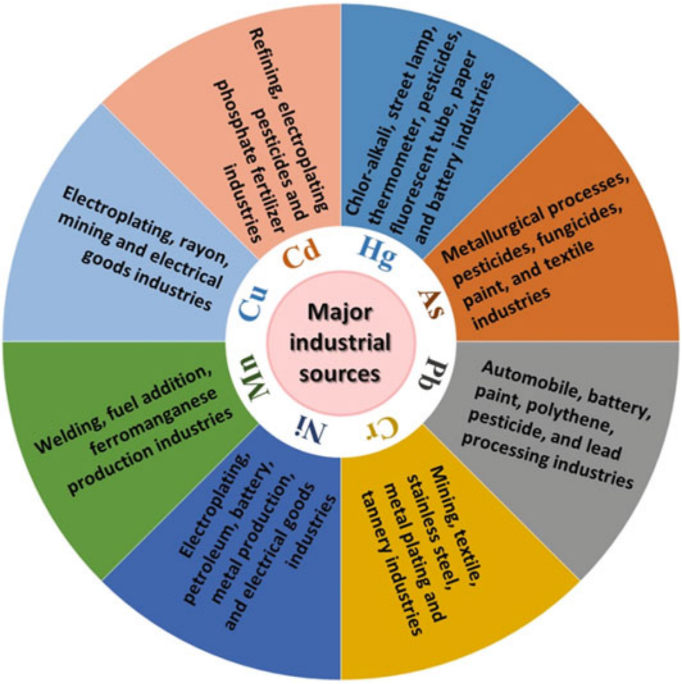


Fig. 3 Major sources for generation of toxic heavy ions (Reproduced with permission from Elsevier [1])

When pollutants are present in water, they are very injurious. Different type of pollutants and their effects are shown in Fig. 4 [7].

These pollutants if increase beyond certain limit becomes harmful to living system and environment. Therefore, these pollutants are to be removed in an environmentally friendly and economical ways [8–10]. There are number of methods used for the removal of pollutants from water and are given in Fig. 5. Out of all, adsorption technique is one of the most convenient techniques for removal of pollutants from water. For this purpose, a suitable adsorbent is needed. Amongst different adsorbents, nanoadsorbents have been reported to be the most effective adsorbents. Some of the adsorbents are given in Fig. 6 [11].

In recent years, it is reported that metal oxide NP and many other NMs are found to be as an effective adsorbent and photocatalyst for the removal of pollutants from water (Fig. 7)[12].

In this chapter removal of pollutants from water using different nano metal oxides as adsorbents a photocatalyst have been discussed.

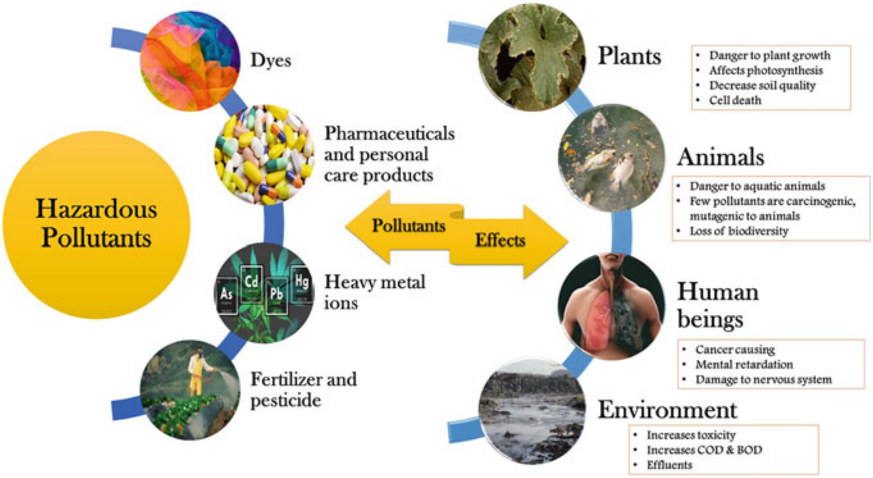


Fig. 4 Pollutants and their impact (Reproduced with permission from Elsevier [7])

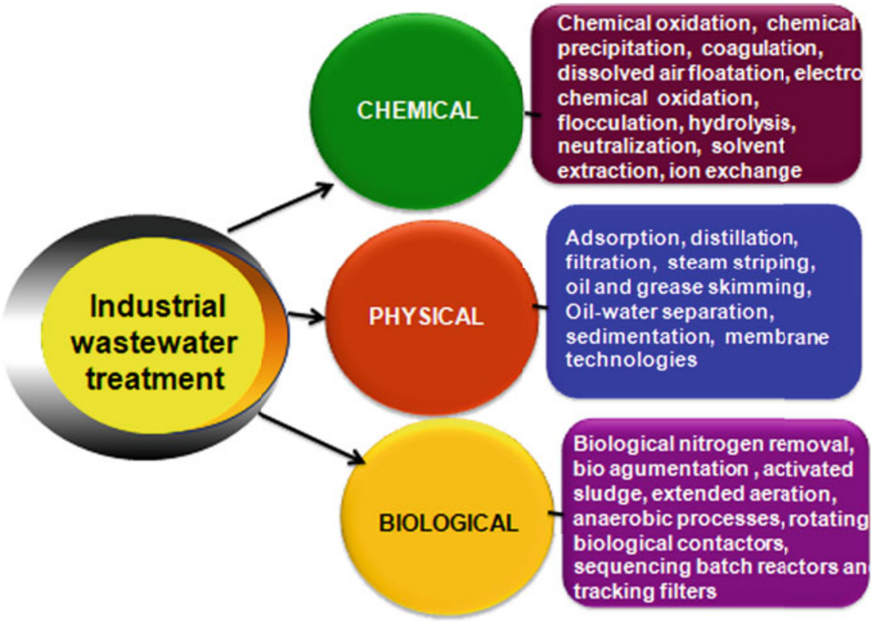


Fig. 5 Water purification methods

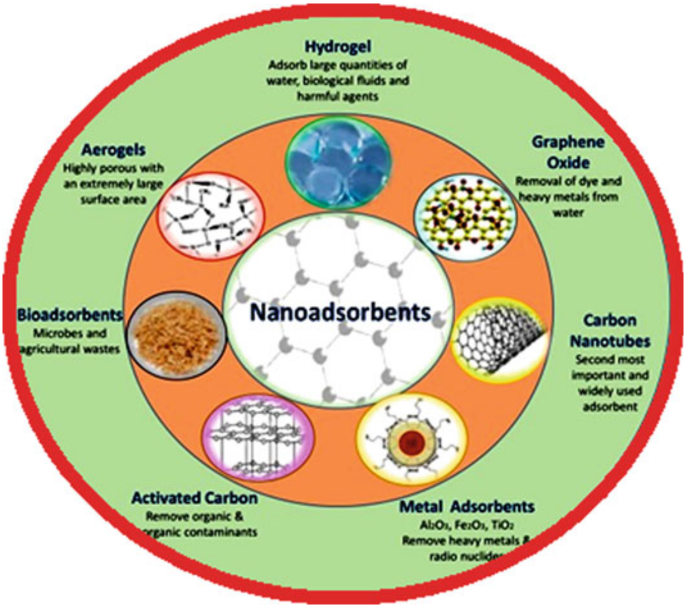


Fig. 6 Nanoadsorbents (Reproduced with permission from Elsevier [11])

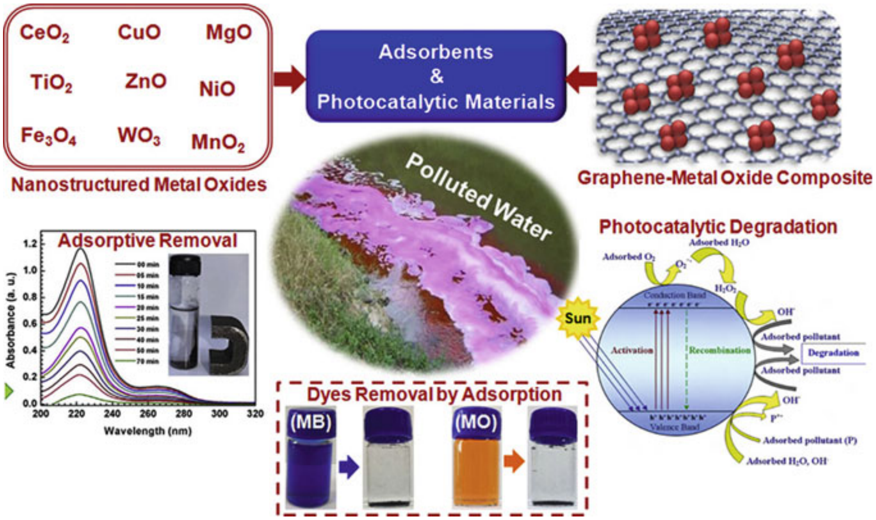
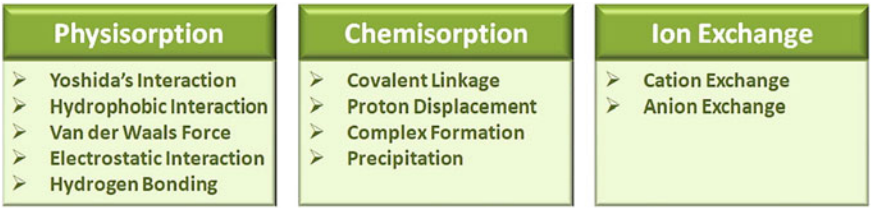


Fig. 7 Adsorption of pollutants by different type of NMs (Reproduced with permission from Elsevier [12])

2 Decontamination by Adsorption

Out of different purification techniques, adsorption is one of the most useful technique, considering the ease of operational aspects, low cost, scalability, high efficacy, and regenerability of adsorbents. Number of adsorbents have been used to remove different pollutants from water [12, 13]. Adsorption is a mass transfer process, which includes accumulating a substance between interfaces of two phases. The adsorption processes are classified into three major categories, i.e., physisorption, chemisorption, and ion exchange (Fig. 8) [3].

The qualitative and quantitative aspects of the adsorption process are evaluated by using different adsorption isotherm models, kinetic models, and thermodynamic parameters. There are number of parameters which affect the process of adsorption (Fig. 9).



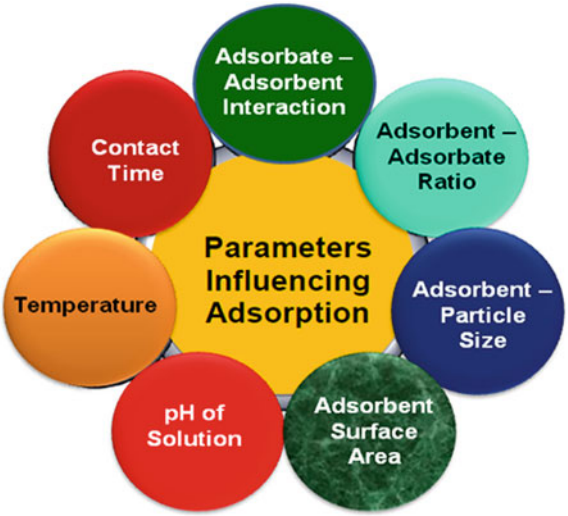
Physisorption
- Yoshida's Interaction
- Hydrophobic Interaction
- Van der Waals Force
- Electrostatic Interaction
- Hydrogen Bonding

Chemisorption
- Covalent Linkage
- Proton Displacement
- Complex Formation
- Precipitation

Ion Exchange
- Cation Exchange
- Anion Exchange

Fig. 8 Different type of adsorption (Reproduced with permission from Elsevier [3])

Fig. 9 Parameters affecting adsorption



3 Photocatalytic Degradation of Pollutants

Prof. Fujishima of Tokyo University, Japan, accidently in 1967, discovered that in presence of TiO_2, water splitted evolving oxygen. This phenomenon was named as photocatalysis. After that various effects of photocalysis was studied with industrial applications. Number of semiconductors with nanodimensions are being used as photocatalysts. Out of all, transition metal oxides are found to be most effective photocatalysts. Many nano metal oxides have been used as photo catalysts for degradation of dyes and organic compounds contaminated with water. Metal oxide NMs are semiconductors with valence band and conduction band separated by band energy of about 3.0 eV and act as photocatalyst (PC). When light of appropriate wavelength and energy hv falls, electron from the valence band jump to conduction band leaving a positive hole ($h_{VB}{}^{+}$) and trapped electron in the conduction band, as given by Eq. (1) [14]

$$PC + hv \rightarrow e^{-}_{\boldsymbol{CB}} + h^{+}_{\boldsymbol{VB}} \tag{1}$$

The electrons liberated through irradiation could be trapped by O_2 absorbed on the surface of the catalyst and give superoxide radicals ($\boldsymbol{O}_2^{-}$):

$$e^{-}_{CB} + O_2 \rightarrow O_2^{-} \tag{2}$$

$O_2{}^{\cdot -}$ obtained reacts with H_2O to form hydroperoxy ($HO_2{}^{\cdot}$) and hydroxyl radicals ($OH^{\cdot}$). These radicals are strong oxidizing agents and decompose the organic molecule, dyes and other type of organic contaminants in water as given by Eq. (3).

$$O_2^{-} + H_2O \rightarrow HO_2 + OH \tag{3}$$

Simultaneously, the photoinduced holes could be trapped by surface hydroxyl groups (or H_2O) on the photocatalyst surface to give hydroxyl radicals ($OH^{\cdot}$):

$$\begin{aligned} h^{+}_{VB} + OH^{-} &\rightarrow OH_{ad} \\ h^{+}_{VB} + H_2O &\rightarrow OH + H^{+} \end{aligned} \tag{4}$$

Finally the organic molecules will be oxidized to yield carbon dioxide and water as follows:

$$OH + \text{organic molecules} + O_2 \rightarrow \text{products } (CO_2 \text{and } H_2O) \tag{5}$$

Meanwhile, recombination of positive hole and electron could take place which could reduce the photocatalytic activity of prepared nanocatalyst:

$$e^{-}_{\boldsymbol{CB}} + h^{+}_{\boldsymbol{VB}} \rightarrow PC \tag{6}$$

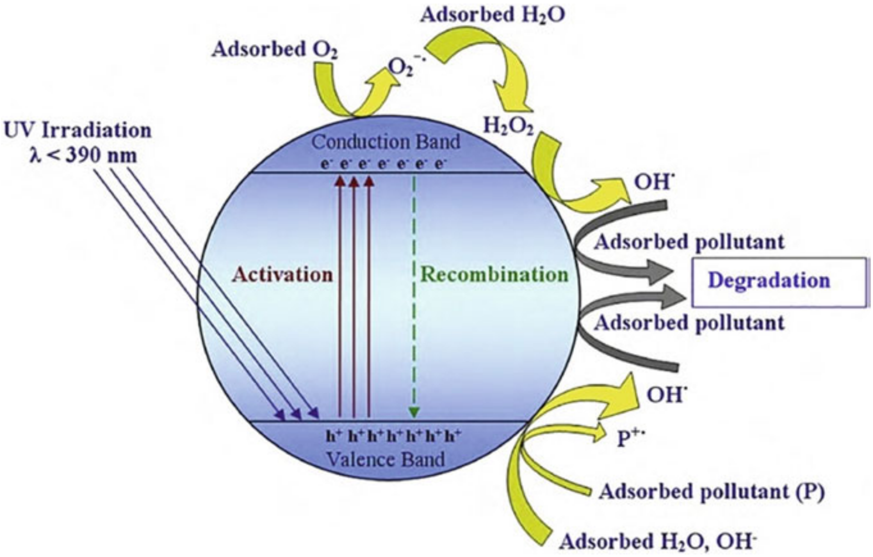


Fig. 10 General mechanism of photodegradation of pollutants by semiconducting metal oxide NM (Reproduced with permission from Elsevier [12])

A wide range of metal oxides such as *tungsten oxides*, copper oxides titanium oxides, zinc oxides, *iron oxides*, magnesium oxide, metal oxides composites, and graphene-metal oxides composites have been studied for photocatalytic degradation and adsorptive removal of organic pollutants viz. *phenolic compounds*, dyes, pesticides, and so on. Figure 10 represents the photocatalytic degradation of organic pollutants, along with the role of the photogenerated hole and electron pairs [12].

Photocatalytic degradation of some organic pollutants in water by titanium dioxides-based NMs and their composites are given in Table 1 [12].

In general photocatalytic degradation is fast and ecofriendly as compared to adsorption technique.

4 Synthesis of Metal Oxide NP

The purpose of synthesizing metal oxide NP is to change the properties of corresponding metal NP. For example oxidizing iron NP are converted into iron oxide NP, which increase the reactivity. In the past ten years, effective synthesis methods to obtain metal/metal oxide NMs with controllable shape, high stability and monodispersion have been extensively studied [15]. In general metal oxide NPs can be synthesized by using Chemical Precipitation, Sol –Gel, Hydrothermal, Chemical Vapour Deposition methods. However, synthesis is divided into three major categories to

Table 1 Titanium dioxide *NM* and their composites as photocatalyst for degradation of *organic pollutants* from *wastewater* (Reproduced with permission from Elsevier [12])

No.	Photocatalyst	Light source	Targeted pollutant	Degradation efficiency (%)
1	Surface-fluorinated TiO_2 assembled on GO	UV	Methylene blue	96
2	TiO_2 NP	UV	Malachite green	99.9
3	Phosphorous acid-modified Degussa P25 TiO_2	Visible	Rhodamine B	~100
4	Glass coated TiO_2 thin films	UV–VIS	Methylene blue	90.3
5	TiO_2/Fe_2O_3 nanocomposite	Visible	Diazinon	95.1
6	Zn^{2+}-doped TiO_2 NP	UV	Malathion	98
7	In and S co-doped TiO_2@rGO	Visible	Atrazine	99.5

understand the difference in methodology, advantages/disadvantages: (i) solution-based methods (ii) gas phase methods and (iii) biological methods (Fig. 11). This classification is based on the type of medium in which the oxidation reaction occurs. The physical and chemical properties of NMs like size, shape, dispersibility, morphology, internal/external defects and crystal structure are generally influenced by the choice of synthesis method which ultimately affects their applications. For example, nano Mg doped ZnO (ZnMgO) fabricated via three different synthesis methods were found different in geometry. Where regular cubic structure was obtained by CVS method, mixture of cubes and tetrapods for metal combustion method and irregular nano rods

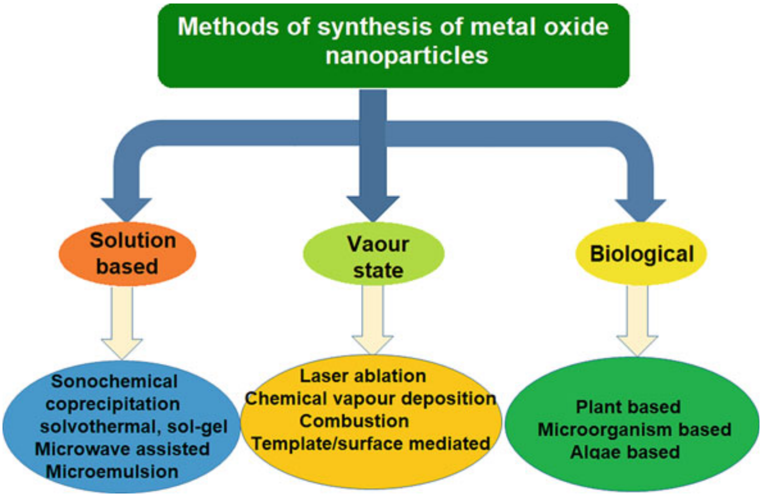


Fig. 11 Synthetic methods of metal oxide NMs

by sol-gel method [16, 17]. To understand the difference in various methods they are briefly discussed in Table 2 [18].

Due to the vast and varying applications of these nanostructures, various synthetic methods have been utilized to synthesize them as discussed in the Table 2. All the described methods provide high quality metal oxide nanocrystals with definite size and shape except the biological method. It is very difficult to control all the required features of NMs like size, shape yield, purity, cost etc. in most of the methods. This problem is more common in the case of multi-metallic oxide NPs. The most effective method with respect to high crystal purity is chemical vapour deposition method [19]. This method is also very useful to give stability to otherwise unstable crystal phase. For example, Zinc oxide NPs in cubic crystal form can only be achieved at very high pressure but chemical vapour synthesis method allows c-ZnO NPs to be dispersed on MgO surface [20].

On the other hand, sonochemical method has been successfully applied to get enhanced photocatalytic performance of TiO_2 NPs [21] and varying magnetic properties of iron oxide NPs [18, 21]. The sol-gel method has been widely used for synthesizing almost all kind of metal oxide NPs. This method is also very useful in doping group 5 oxides, which is often a challenge, for example Co doped Hf-oxide NPs [22]. This method has been utilized by researchers with certain modifications, for example Corr et al. have reported an improved one-step sol-gel aqueous method for the synthesis of iron oxide-silica NPs [23]. To avoid the oxidation of the products at very high temperature, use of ultrasonic conditions is also reported. Some solution-based manufacturing techniques use surfactants [24], which, in addition to affecting particle size, also tend to reduce the degree of aggregation between particles. In addition, solution-based technology combats pollution problems in the resulting metal oxide products. Most of the solution-based methods suffer with the problem of the contamination in the products specially contamination of anions of precursor salt [25]. Biological method is suitable for biomedical applications due to its biocompatibility but face the problem of contamination and composition of NPs also cannot be defined completely [18].

5 Metal Oxide NP Used for Water Purification

Metal oxide NPs are used in different sectors including water remediation as shown in Fig. 12 [26].

Numbers of nano metal oxides discussed below were used for water remediation.

5.1 TiO_2

TiO_2 NPs have become the most widely used NMs for water remediation due to their high photosensitivity, availability, non-toxicity, cost-effectiveness and environmental

Table 2 Summary of most common synthetic methods with their advantages/disadvantages

Category	Method	Specific Reaction conditions	Advantages	Disadvantages	Example
Solution based methods					
Sonochemical method	The solution of metal salt is subjected to a strong ultrasonic vibration flow, which breaks the chemical bond of the compound, resulting in alternating compression and relaxation. which leads to acoustic cavitation. It results in formation, growth, and implosion of bubbles in the liquid	Too high cooling rate will affect the formation and crystallization of the resulting product	Uniform particle size with higher surface area, faster reaction time and improved phase purity of Nps	It requires high energies and pressures in short time	ZnO, MoO_3, CeO_2 V_2O_5, In_2O_3, TiO_2, In_2O_3, $PbWO_4$, $BiPO_4$,$ZnAl_2O_4$, $ZnFe_2O_4$, Eu/Dy-doped
Coprecipitation	Use of a precipitation medium to precipitate out the oxyhydroxide form from a solution of a salt precursor (metal salt) in a solvent (such as water)	pH of medium, nature of alkali andspeed of its addition and the drying modality of synthesized powders affect the size, magnetic properties and degree of agglomeration of the synthesized NMs	Low cost, mild reaction conditions, possibility to perform direct synthesis in water, ease of scale-up, flexibility in modulation of core and surface properties, possibility of using surfactants to improve the surface properties	Low removal efficiency, high energy consumption, and production of toxic sludge	ZnO, $BiVO_4$, MnO_2,MgO,SnO_2, Ni1-xZnxFe_2O_4, $MgFe_2O_4$, Ni–CeZrO_2 and Y_2O_3:Eu^{+3}, Cu-doped ZnO,

(continued)

Table 2 (continued)

Category	Method	Specific Reaction conditions	Advantages	Disadvantages	Example
Solvothermal	By dispersing the solution of starting material in a suitable solvent and exposed it to high temperature and pressure conditions	Composition and concentration of the reactants, ratio of solvent/ reducing agent and various thermodynamic parameters like temperature, pressure and reaction time affect the final particle formation	Nanostructures with different morphologies—such as, nanocubes could be produced and use of surfactants to avoid agglomeration is also possible	Impossibility of observing the reaction process, need for expensive autoclaves	TiO_2, $MnFe_2O_4$, Nb_2O_5, MgO, $CoFe_2O_4$, Fe_3O_4, Ag-Fe_3O_4, Graphene-TiO_2, $CoFe_2O_4$@$BaTiO_3$, Fe_3O_4@NiO and Fe_3O_4@Co_3O_4)
Sol–gel method	Include the hydrolysis of precursor organometallic compound, like alcoxysilane to produce corresponding oxohydroxide, followed by condensation to form a network of the metal hydroxide	Super critical liquids can also be used. it provides the particle size to be tuned by simply varying the gelation time	More bioactive, high quality material, promising in doping of Group 5 oxides, clean to synthesize, excellent control over the texture and surface properties of the materials		ZnO, TiO_2, CuO, MgO, ZrO_2 and Nb_2O_5 Cu-ZnO, Ce-doped ZrO_2 CuO/Cu_2O, oxides of Hf, Ta and Nb, $LiCoO_2$ thin film,

(continued)

Table 2 (continued)

Category	Method	Specific Reaction conditions	Advantages	Disadvantages	Example
Microwave assisted method	It involvesuniform and quick heating of the reaction medium with no temperature gradients using two mechanisms: dipolar polarization and ionic conduction	High heating rates favor rapid nucleation and formation of small and highly monodisperse particles	Very short reaction time without compromising the particle purity or size	Unsuitable to scale up and reaction monitoring is not feasible	CeO_2, Cr_2O_3, ZnO MnO, Fe_3O_4, Mn_2O_3 CaO, CoO, and MgO, $BaTiO_3$,
Microemulsion method	Two immiscible phases (oil and water) interfaced by surfactant molecules form two binary systems. At CMC, reversed micelles are formed. This core act as a nanorecator where variety of chemical reactions take place	Reducing agent/oxidizing agent/precipitating agent is added under vigorous stirring to precipitate the NP	The morphological properties of NMs can be modified by affecting the various self-assembled structures formed in the binary systems	Controlling the deposit parameters is difficult to achieve	ZnO,Fe_2O_3, NiO, TiO_2, CeO_2, CuO, and NPs like $BaAlO_2$, alumina NP doped with iron-oxide

(continued)

Table 2 (continued)

Category	Method	Specific Reaction conditions	Advantages	Disadvantages	Example
Vapour state method					
Laser ablation method	Irradiation of different metal salts submerged in solution by high power laser beam, condense a plasma to produce NP	By increasing the laser fluence and changing the liquid media, the thickness of molten layer can be changed which affect the size of NMs		Chances of nanoparticle agglomeration leads tolack of long-term stabilization	ZnO, Al_2O_3 NiO, ZrO_2, SnO_2, iron-oxide, Au-SnO_2, Cu/Cu_2O
Chemical vapor-based method	Precursor materials in the gaseous state is deposited onto a heated substrate surface at which it reacts or decompose to form NMs	Choice of nature and concentration of the oxidizing agent affect the nucleation process and therefore affects the average size of the NMs	Uniform and contamination-free metal oxide NP and films with flexibility in product composition can be produced	Volatility of the reactants and degree of agglomeration use of toxic, corrosive, flammable, and/or explosive precursor gases	Defect free ZnO nanowires, films, Doped-ZnO, nano cubes and nanospheres of magnetite, SrO, SnO_2, Cu_2O, MgO, CoO and Co_3O_4, CaO.,Eu doped YO, Li-doped MgO
Combustion method	Pure metallic precursor is heated to get it evaporated into a background gas then mixed with second reactant i.e., oxidizing agent	Partial pressure of oxidizing agent can be controlled which determines the nucleation growth and affect the particle size to some extent	Control over phases and morphologies of NMs, successful commercially	Complex process that is rather difficult to control	ZnO, CuO, FeO, Mn_2O_3, CdO, MgO and Co_3O_4 or Ag-MgO composite, Co_3O_4@CuO, La0.82Sr0.18MnO_3

(continued)

Table 2 (continued)

Category	Method	Specific Reaction conditions	Advantages	Disadvantages	Example
Template/surface-mediated synthesis	Fabrication of the desired NMl within the pores or channels of a nonporous template depending on the properties of the template		Can be used to synthesize self-assembly systems with tubular and fibrillary andhighly monodisperse nanostructures with small diameters, enhanced activities, uniform morphology with high surface area		Various morphologies of metal oxide NMl such as rods, tubules and fibrils
Biological method					
Plant based synthesis	By using Plant parts (Enzymatic reaction) and their extract as reducing and capping agents to convert metal salts to metal oxide NPs	It is somewhat possible to control size of particle by controlling the pH, temperature, solvent conditions	Consumes lesser energy, environment-friendly and eliminates the production of toxic wastes, NMs have higher catalytic reactivity, biocompatible, attractive for biomedical applications	Low yield, inability to obtain desired size and/or shape of NP, Slow and time taking	ZnO, CuO, Fe_3O_4, Ag_2O

(continued)

Table 2 (continued)

Category	Method	Specific Reaction conditions	Advantages	Disadvantages	Example
Microorganism based synthesis	By using Microorganisms like bacteria, fungi and molds as reducing and capping agents	By varying parameters like microorganism strain, culture growth medium, size and shape of NPs can be controlled			ZnO, TiO_2, MgO NP by using fungus
Algae based synthesis	Using algae as reducing agent	By varying the species type, the enzymatic reaction may change and affect the properties of NPs			ZnO, CuO, Fe_3O_4, Ag_2O

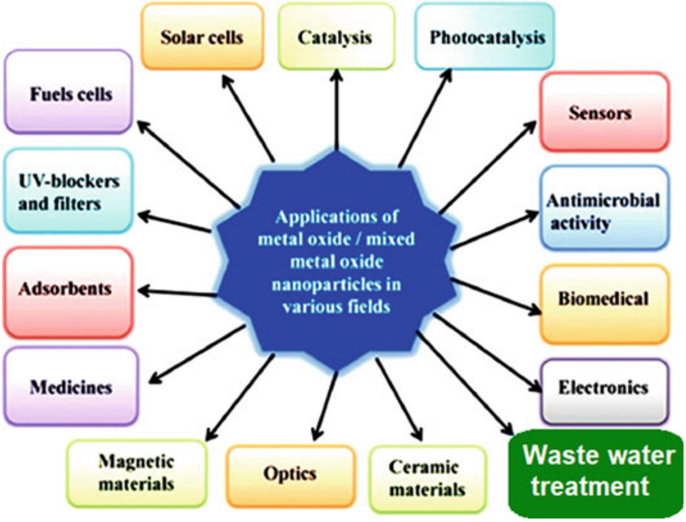


Fig. 12 Applications of nano metal oxides/mixed metal oxides in different areas (Reproduced with permission from Elsevier [26])

friendliness [27]. These NMs have been widely used in the oxidation and reduction conversion of organic and inorganic pollutants in air and water, such as phenolic compounds, metal ethylene diamine tetraacetate complexes, microorganisms in the air and odorous chemicals, halogenated compounds degradation, dye removal, metal and metal removal, etc. [28]. Photodegradation leads to complete oxidation and reduction of organic and inorganic pollutants and converts them into carbon dioxide, water and inorganic acids [29]. Its large band gap energy (3.2 eV) requires ultraviolet excitation to induce charge separation within the particles [30]. TiO_2 and TiO_2 films have been successfully used to degrade atrazine and organochlorine pesticides in water, respectively [27]. Photocatalytic degradation of methyl orange using ZnO/TiO_2 composites has been studied [31]. Non metal elements like N, F, C and S can improve the photocatalytic activity of TiO_2 NMs by narrowing its band gap. This is achieved by the substitution of oxygen by these nonmetals in the TiO_2 lattice [32]. Doping with transition metals like Fe, Co and Cu has also been proved to improve photocatalytic activity of TiO_2 NPs under UV irradiation However, noble metals like silver, have received much attention for this purpose [33].

5.2 *Iron Oxides*

In recent years, the synthesis of iron oxide NMs with modified properties and their applications have gained widespread attention due to their high porosity and surface-to-volume ratio, low cost, strong adsorption capacity, easy magnetic separation response. Iron oxide NMs can act as immobilized carrier to remove contaminants or can also act as photocatalyst/catalyst to degrade the contaminants. Magnetic separation is a unique property of iron oxide NMs which is a challenge due to small size of nanoadsorbents [34]. Therefore, the combination of adsorption process and magnetic separation has been widely used in water treatment and environmental purification. Strong paramagnetic characters of Fe_2O_3 NMs make them effective for the removal of toxic heavy metals like Cd(II), Pb(II) etc. Super magnetic Fe_3O_4 NPs have shown excellent catalytic activity for dye degradation in waste water to convert them in less toxic form. According to reports, the preparation method and surface coating medium play a key role in determining the size distribution, morphology, magnetic and surface chemistry of NMs in the form of NP, nanoellipses nanobelts and nanorings or other nanostructures [35].

Green synthesized iron oxide (Fe_3O_4) NP using an extract of *Excoecaria cochinchinensis* leaves were found much effective for the removal of a contaminant antibiotic (rifampicin) from aqueous media. This was found much more effective as compared to commercially available Fe_3O_4 (Fig. 13) [36].

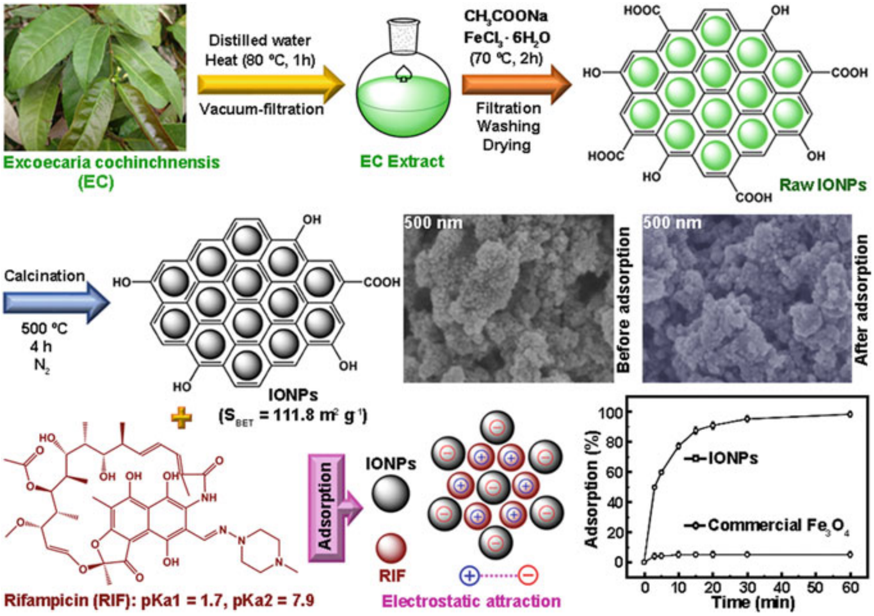


Fig. 13 Green synthesis of Fe_3O_4 and removal of rifampicin (Reproduced with permission from Elsevier [36])

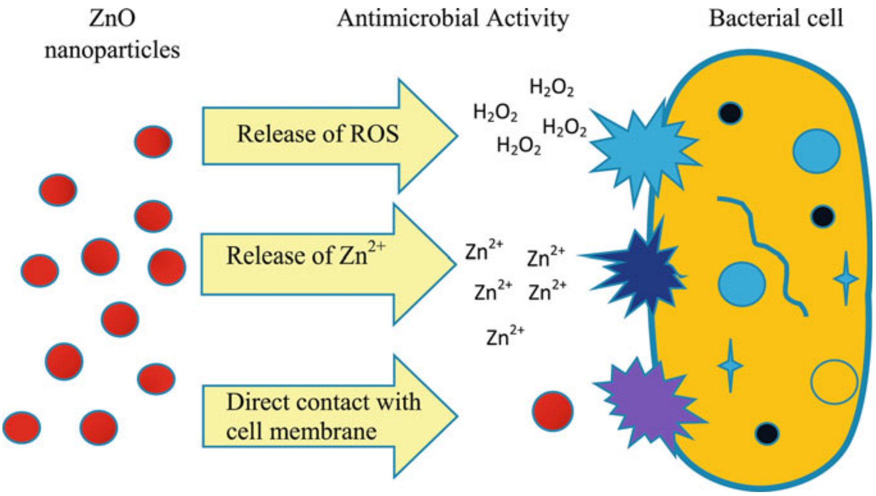


Fig. 14 ZnO disinfection mechanisms (Reproduced with permission from Elsevier [38])

5.3 Zinc Oxide

Zinc oxide is another metal oxide NMs based photo catalyst which shows most promising water treatment due to its high chemical stability and excellent photocatalytic activity. Large number of research groups across the globe have already reported potential applications of ZnO NMs along with their variable morphology and structural characteristics including Nano sheets, nanowires, Nano rods, nanoribbons and complex hybrid structures [37, 38]. ZnO has a wide band gap (3.37 eV), and the excitation binding energy (60 meV) is also large at room temperature which makes it an excellent photo catalyst. In addition, easy availability, low toxicity and antibacterial efficiency of ZnO NMs make them ideal for water treatment. Hollow spheres in these nanostructures are of great interest due to their light trapping efficiency and highly enhanced photocatalytic activity, as well as their high surface area, low density, and good surface permeability [37].

Nano Zno acts as an antibacterial agent and the mechanism of its action is given in Fig. 14 [38].

5.4 Copper Oxide

Due to its inherent compatibility, low-cost manufacturing and excellent electrochemical performance, research on copper oxide NMs has grown significantly in the recent years. It is reported that copper oxide NMs show a little photocatalytic activity which can be significantly enhanced by activating it with H_2O_2 [39]. More than a photo catalyst, CuO NMs are used as a good adsorbent of water pollutants such as congo reed, malachite green, methylene blue, ciprofloxacin, methyl orange dyes and many heavy metals like Pb (II), Hg(II) As (III). The main application of CuO NM in water treatment is its antimicrobial efficiency. Bacterial disinfections, one of the main applications of copper-based NM, which is an essential requirement of potable water. Many biotechnologists have investigated the potential of CuO NMs to disinfect water with respect to microorganisms [9]. Scientific reports suggest few mechanisms behind it (i) Cu is released from copper oxide NPs which damages the bacterial cell membrane and lead to bacterial cell death (ii) interaction with DNA molecule and disorder its helical structure (iii) and by inducing oxidative stress [18].

In many cases metal oxide composites were found more effective in removal of pollutants. Extract of pine needle was used for the synthesis of nano composite of iron and copper oxides (Fe/Cu oxides) and was found an efficient adsorbent for ofloxacin and norfloxacin removal from aqueous media. Mechanism of synthesis and removal of organic pollutant is given in Fig. 15 [36].

5.5 Silver Oxide

Silver oxide exists in many nanostructural forms which includes, NPs, nanohorns, nanorods, and nanopyramids. Silver oxide NM exhibits excellent antibacterial properties which has been already used in many commercial products [40]. A few research groups have reported the photocatalytic activity of these NMs for the degradation of dyes like methylene blue and methyl orange present in water along with their antimicrobial activity [22]. Silver oxide NMs are syntheisezd be various synthetic routes which includes direct precipitation, sol gel, hydrothermal and biological route [41, 42]. These are mostly spherical particles (20–80 nm) with high surface area (10–50 m^2/g) and good magnetic properties.

5.6 Manganese Oxide

Different forms of manganese oxide NP such as MnO, MnO_2, Mn_2O_3, Mn_3O_4 are tested for removel of heavy metals in water decontamination process. They are structurally flexible and display novel physical and chemical properties. The primary benefits of managanese oxide NMs come from their low cost, high activity and non-toxic nature. A large number of heavy metals including Cu(II), Cd(II), Pb(II), As(III), As(V), U(VI) and organic contaminants are successfully removed by MnO_2 and its NPs. The mutual interference of Zn(II), Cd(II) and Pb(II) ions with various nanostructures of MnO_2 e.g. nanoparticle, nanotube and nanobowl are investigated by Zhang et al. [43]. Nanoflakes of MnO_2 are reported for the detection and removal of Cr(III) ion [44]. Differential pulse voltammetric method was used for the detection of Hg(II) ion by MnO_2 nanotubes [45].

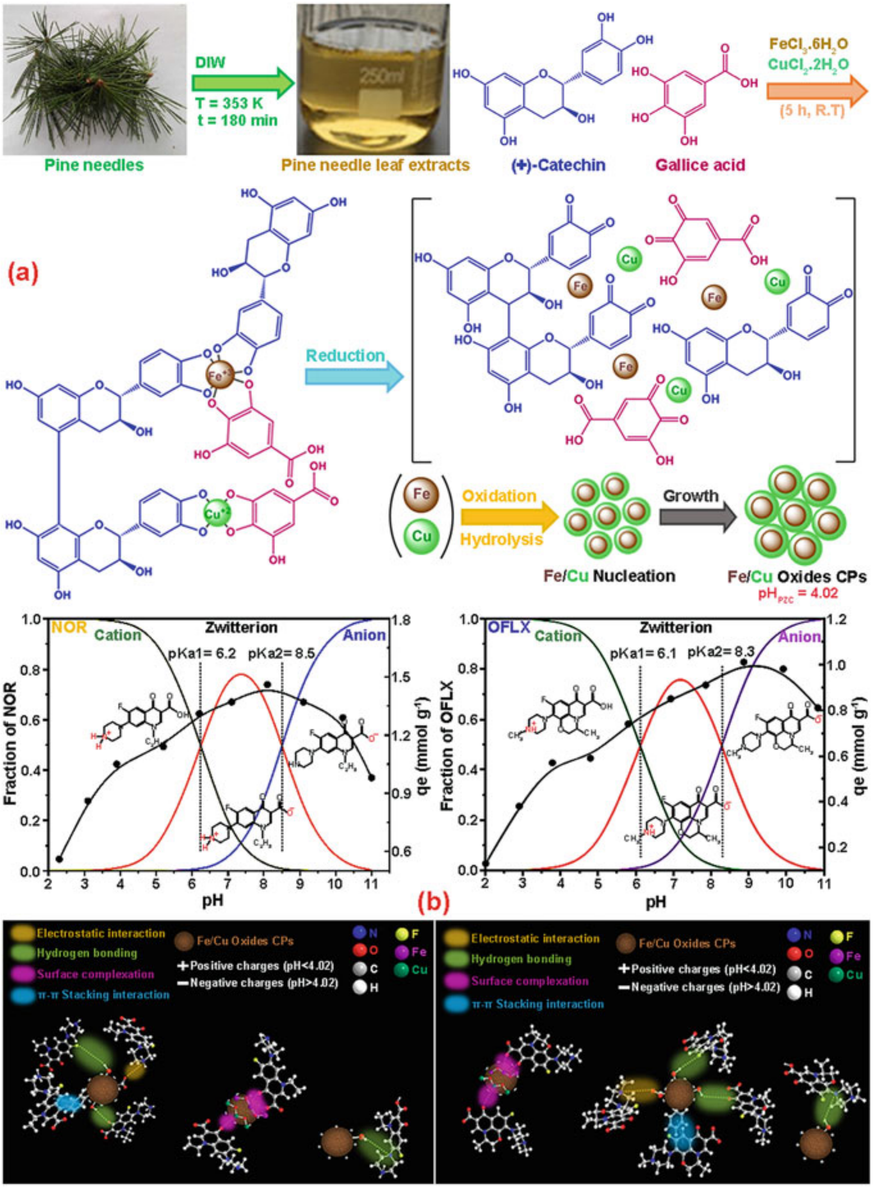


Fig. 15 Synthesis of Fe/Cu oxide (Reproduced with permission from Elsevier [36])

5.7 Cerium Oxide

Cerium oxide (CeO_2), a non-toxic rare earth metal oxide is gaining attention for application as UV-blocking agent, sensing agent and in water remediation. Recently nanoscale CeO_2 is investigated for their applications in removal of heavy metals from water [46]. The properties of nanocrystalline CeO_2 are found to be effective for removal of inorganic heavy metals. Low ionic potential and high basicity leads to dissociation of hydroxy group into hydroxyl ions. The size, porosity, surface area, bulk density etc. are in favor of their selectivity, stability and activity during adsorption process. Recillas et al. reported removal of Cr(VI) metal ions using 12 nm average sized CeO_2 NPs [47]. Their results indicate that low concentration of Cr(VI) (80 mg/L) can be effectively removed by CeO_2 NPs with maximum adsorption capacity of 121.95 mg/g. Arsenic metal in the form of As(III) and As(V) has successfully been removed from water by CeO_2 NPs by Mishra et al. [48]. In their work, the BET surface area of 3–5 nm sized CeO_2 NPs was 257 m^2/g and the adsorption capacity of As(III) and As(V) ions were 71.9 and 36.8 mg/g^{-1} respectively. It is observed that the adsorption capacity of CeO_2 NPs reduced in the presence of some anions such as sulpahte, bicarbonate, dihydrogen phosphate etc. Further, CeO_2 NPs are found to be compatible with other metal oxides for treatment of heavy metals from water [49, 50]. Recently, Meepho et al. have synthesized samaria doped cerium nanopowder (SDC) by doping samaria with different morphologies of cerium nanopowder [51]. The samaria doped cerium nanopowder (SDC) was used for the removal of Cu(II), Zn(II) and Pb(II) ions. The outcome of the investigation indicates that spherically shaped SDC nanopowder was more effective than the plate like SDC nanopowder. The surface modifications of CeO_2 NPs enhance the adsorption of heavy metals in terms of material stability and selectivity. The hydrous CeO_2 NPs with adequate hydoxyl group help in the adsorption of arsenic through inner sphere mechanism. Composite of CeO_2 NPs with graphene oxide has the capability of removal of arsenate and arsenite almost completely (99.99%). A cost-effective adsorbent is developed by supporting CeO_2 NP over carbon nanotube (CNT) for removing AS(V) ions [52]. The only drawback of ceria in water remediation is its high cost which can be taken care by the surface modification or composite formation of ceria.

5.8 Magnesium Oxide

Magnesium oxide NP have high potential in removing pollutants from water. MgO NP are associated with exceptionally high absorption ability, abundantly available, non toxic and inexpensive [53]. These unique properties make it one of the sought-after metal oxides NMs for removing heavy metals from water. MgO NP also displays superb antibacterial activity for both gram-positive bacteria, gram-negative bacteria and spore cells [54]. Reported literature also indicated the effect of size of MgO NP in

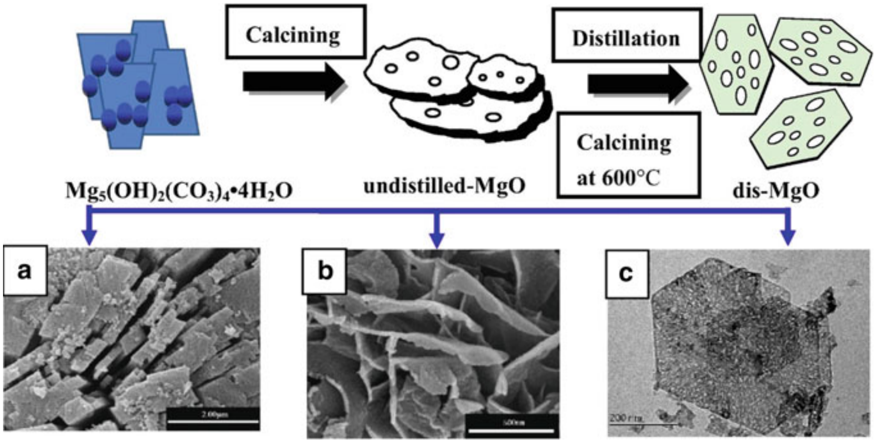


Fig. 16 Schematic illustration for the formation of mesoporous MgO nanosheets. (Reproduced with permission from Elsevier [58])

its bactericidal properties. Cai et al. reported simultaneous removal of heavy metals Cd(II) and Pb(II) and *Escherichia coli* bacteria by MgO NP [53]. Three different nano metal oxide e.g. TiO_2, MgO and Al_2O_3 was investigated for elimination of heavy metals Cd(II), Cu(II), Ni(II) and Pb(II) ions form water [55]. It was observed that the efficiency of MgO NP was better than the other two metal oxide NP. MgO NP follows adsorption and precipitation mechanism for the removal of heavy metals while TiO_2 and Al_2O_3 were via adsorption mechanism only. Interesting work by Madzokere et al. revealed that MgO NP are capable of removing 96% Cu(II) ion compared to the 15% removal ability of commercial MgO [56]. A batch adsorption experiment performed by Xiong et al. indicated excellent adsorption capacity of MgO NP [57]. Langmuir model was used by Jing et al. to establish the remarkably high adsorption of Ni(II) ion over mesoporous MgO nanosheets (Fig. 16) [58]. All these works suggest MgO NP as a very promising material for the removal of heavy metals from water.

5.9 Zirconium Oxide

Among metal oxide NMs, zironia or zirconium oxides also exhibited remarkable potential in removing water pollutants specially the heavy metal ions [59, 60]. They have high thermal and chemical stability, less toxicity and biocompatibility. Zirconia display high resistivity against acids and alkalis. Presence of large number of -OH groups over the surface leads to high surface area which in turn makes zirconia a good adsorbent. Both nanoscale zirconia and hydrous zirconia are excellent for removing heavy metals like Cd(II), Zn(II), Pb(II), arsenate and arsenite ions. Silicate ions adsorb strongly over zirconia surface, thus hampering the adsorption of arsenic ions using zirconia adsorbent. The presence of alkaline earth metals e.g. Ca(II) and Mg(II) ions promote the adsorption of arsenic pollutants by reacting with the silicate ions [61]. It is reported that simultaneous adsorption of arsenate and arsenite is possible over nanocomposite of hydrated zirconia-graphene oxide sheet [62]. The adsorption capacity of this nanocomposite was higher compared to the pristine nano zirconia. In addition to that it is recyclable up to five times. Removal of Cd(II) was investigated by a composite of polystyrene supported nanosized hydrous zirconia [63]. The removal efficiency of this material lies within wide pH range. Further promising result of removal of Pb(II) and Cd(II) ions are observed by nanocomposite based on hydrous zirconium (IV) oxide [64].

Another composite of zirconia with γ-Fe_2O_3 is investigated for the removal of arsenic from leach out water of gold cyanidation industry [65]. The iron oxide core helps in improving the recyclability of the adsorbent by easy separation. To improve the adsorption capacity towards arsenate ions at strong acidic environment, zirconia is encapsulated in D201 (polystyrene anion exchanger [66]. The electrostatic interaction between arsenate ions and D201 and inner sphere complexation explain the mechanism of the adsorption. Presence of sulphate ions restricts the electrostatic interaction and in turn reduces the adsorption capacity.

An interesting report on removal of Cr(VI) by a series of mesoporous transition metal oxides suggests that ZrO_2 as the most attractive adsorbent among other nano metal oxides e.g. TiO_2, HfO_2 and NbO_2 [67]. A hybrid nanocomposite made from ZrO_2/B_2O_3 displayed satisfactory results in removal of Cu(II), Cd(II) and Cu(II) ion [68].

5.9.1 Aluminium Oxide

Aluminium oxide NMs are inexpensive and can be prepared easily. Alumina adsorbents have high efficiency in removing heavy metal ions [69]. Many research works is reported on the application of alumina for the adsorption of several heavy metals. Among several crystalline forms of aluminium oxide, γ-alumina is the most effective for decontamination purpose because of its high surface area [70]. In addition to that γ-alumina has high mechanical strength, excellent thermal stability and high adsorption capacity. Tabesh et al. has reported 97% and 87% removal of Pb(II) and Cd(II) ion respectively by γ-alumina NP [71]. It is observed that adsorption of Zn(II) and Cd(II) ions by alumina become more enhanced in presence of phosphate ions and humic acid while presence of citrate ion reduces the adsorption of Zn(II) ion [72]. Moreover heavy metals ions such as As(III), Hg(II), Ni(II), Cu(II), Cr(VI) are also reported to be removed by alumina NP [73–75].

Applications of some selected nano metal oxides in removal of pathogens, dyes and heavy metals are listed in Tables 3, 4 and 5 respectively.

Table 3 Nanometal oxide in pathogen removal for water purification

Nano metal oxide	Targeted pathogen	Mechanism	References
TiO_2	Escherichia coli and human pathogens	Antibacterial activity	[76]
Ag_2O	Bacillus subtilis, Staphylococcus aureus, Psedomonas aeruginosa, Esherichia coli, Canadida albicans and Aspergillus niger	//	[77]
	Pseudomonas aeruginosa, Staphylococcus aureus, Bacillus subtilis, Escherichia coli	//	[78]
	Streptococcus mutans and Lactobacilli sp.	//	[79]
CuO	Staphylococcus aureus, Escherichia coli, Bacillus licheniformis and Pseudomonas aeruginosa	//	[80]
	Vibrio anguillarum, Proteus mirabilis, Bacillus cereus, Edwardsiella tarda, Staphylococcus aureus, Aeromonas hydrophila, and Aeromonas caviae	//	[81]
	Staphylococcus aureus and Escherichia coli	//	[82]
	Escherichia coli and Salmonella typhimurium	//	[83]
ZnO	Escherichia coli and Enterococcus faecalis	//	[84]
	Escherichia coli and Salmonella typhimurium	//	[85]
	Enterobacter aerogenes and Bacillus subtilis	//	[86]
	Escherichia coli and Bacillus subtilis	//	[87]

6 Challenges

The metal oxide NPs are extensively studied for their application in water purification technology. But the validation and development of nanotechnology for purification of water at mass scale is full of challenges. The toxicity of the nanometal oxides is of primary concern. When nano metal oxides are used for water purification, consumers are exposed to the toxicity of these nano materials. Numerous research works have been performed on toxicity analysis of these materials both in vitro and in vivo [115, 116]. Various factors control the level of toxicity of these engineered NMs. Size of the NMs, dose, administration mode and exposure duration are important factors that controls the toxicity levels. It is reported that large TiO_2 NP with size more than 100 nm are non toxic in nature. Concentration of TiO_2 nanoparticle in the range of 1000–2000 μg/g is found to be toxic [116]. The health issues from TiO_2 NP primarily

Table 4 Nanometal oxide in dye removal for water purification

Nano metal oxide	Targeted dye	Mechanism	References
CuO	Methylene blue	Photocatalytic degradation	[88]
	Basic red 14, Basic violet 16	Adsorption	[89]
	Melachite green oxalate, Methyl orange	Adsorption	[90]
TiO_2	Methylene blue, Rhodamine B	Photocatalytic activity	[91]
	Methyl orange	Photocatalytic activity	[92]
Ag_2O	malachite green	Adsorption	[93]
	Methyl orange	Photocatalytic activity	[94]
	Methylene blue	//	[95]
	AO8	//	[96]
ZnO	Methylene blue	Photocatalytic degradation	[85]
	Azo dye	Adsorption	[97]
	Reactive blue 19, Acid Black 210	Adsorption	[98]

Table 5 Nanometal oxide in heavy metal removal for water purification

Nano metal oxide	Targeted heavy metal	Mechanism	References
TiO_2	Cu, Zn, Pb, Cd, Ni	Adsorption	[99]
	Zn(II),Sr(II)	//	[100]
	Cr(VI), Cr(III)	//	[101]
CuO	As(V)	//	[102]
	Pb(II)	//	[103]
ZnO	Cr(VI)	//	[104]
	Pb(II)	//	[105]
	As(III)	//	[106]
	As(V)	//	[107]
ZrO2	As(III), As(V)	//	[108]
Al2O3	As(V)	//	[109]
MgO	As(III)	//	[110]
MgO	As(V)	//	[111]
$MnFe_2O_4$	As(III), As(V)	//	[112]
Ce-Mn mixed oxide	As(III)	//	[113]
Ce-Fe Mixed oxide	As(V)	//	[114]

come from inhalation not from ingestion with water. Thus toxicity of TiO_2 is not a serious concern. Oral administration of high dose (2.5 mg/g body weight) of ZnO NP is known to be accumulated in different body parts e.g. lung, kidney, liver and spleen. A detailed in vitro toxicity study on ZnO NM is reported by Vandebriel and Jong [117]. The toxicity of silver oxide nanoparticle is found to be more compared to other nano metal oxides. Silver can interact with most of the biomolecules and impart toxicity which in turn leads to cellular apoptosis [115, 118]. Magnetic iron oxide nano particles used for purification of water has insignificant toxic effect and are not serious issue [119]. Thus, technological advancement on nanometal oxide purification system is possible after addressing the toxicity issues convincingly.

Next the economic viability is another challenge that needs to be sorted out. To make the nano metal oxide based water purification technology acceptable it must be affordable. In this regard development of highly effective filtration membrane with multifunctional capabilities is extremely necessary to reduce the cost of the membrane-based purification technology.

In addition to the above issues, the aggregation and dispersion properties of nanometal oxides make the operational conditions critical. Mixing of nano metal oxides in water gets accumulated and forms aggregate. The surface immobilization of the nano metal oxides is used for killing various water borne microbes and pathogens. However, leaching of NMs beyond their acceptable limit is a serious threat for human and other living beings. Report of aggregation of TiO_2 NPs as waste from industry and consumer products in water is well documented [120]. One important strategy to reduce the leaching of nano metal oxide in water is to sediment or coagulates the NPs before supply to the consumers. This method has been successfully applied for TiO_2 and silver oxide NPs [121, 122]. More technological innovations are needed in these directions to make the nano metal oxide-based water purification in large scale.

Thus, to assure the safety of the consumers for the use of nano metal oxides-based purification technology, regulatory board must be formed [123]. In China, the use of NM and its issues are taken care by NSCNN (National Steering Committee for Nanoscience and Nanotechnology) which work closely with National Nanotechnology Standardization Technical Committee [124]. Similarly in Europe REACH63 (Registration, Evaluation, Authorization and Restriction of Chemicals) controls the use of NMs and their impact on health and environment is monitored [125]. Few other developed countries are in process of bringing regulatory law to control the usage of NM based technology products. Till now in India there is no such organization for governing the usage and legal constraints of NMs [126].

7 Conclusions

Water is the most important element on this planet for living things and plants. However, the water is contaminated with different type of toxic materials. The major cause of this pollution is industrial waste going into water bodies. Numbers of techniques have been used for remediation but the adsorption technique is found to be the most effective. Nanomaterials have been considered to be the most important adsorbent. Because of various specific properties, numbers of nano metal oxides and their composites have been found to be a suitable adsorbent for removal of pollutants. Synthesis of nano metal oxides and their applications for water remediation have been discussed. These metal oxides have also been used as photocatalysts. Considering the advantages and disadvantages, further research is needed.

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