Advances in the Synthesis and Applications of Metal Oxide Nanoparticles: A Comprehensive Review

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ABSTRACT:

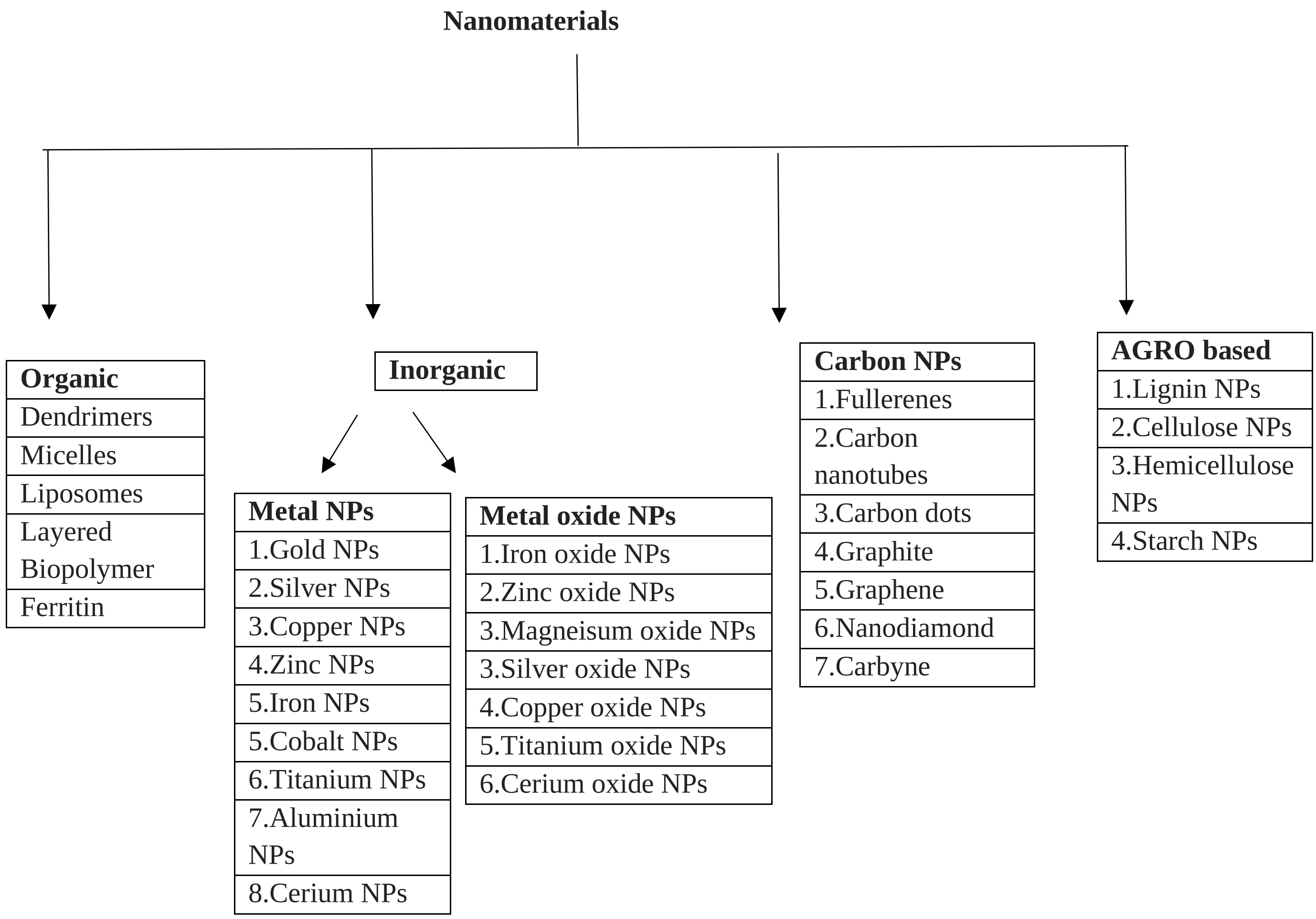
Metal oxide nanoparticles are metal oxide which have the particle size between 1-100nm. Metal oxide nanoparticles include the oxides of various metal such iron oxide, zinc oxide, cupric oxide, magnesium oxide, silver oxide, titanium oxide etc. The synthesis of metal oxide nanoparticles has been widely explored in recent times due to its wide applications. Metal oxide nanoparticles have been greatly exploited due its unique ability to remove various organic and inorganic pollutants from contaminated water. They also show anti-microbial activities against various disease -causing micro-organisms. Apart from this, they also find their applications in drug delivery, biosensing, electronic devices. Synthesis of metal oxide nanoparticles includes physical, chemical and biological method. Water pollution is a serious cause of concern of this century. Various methods have been developed for the purification of wastewater treatment. One of the most important application of metal oxide nanoparticles is their ability to remove various organic and inorganic pollutants from contaminated water. Metal oxide nanoparticles due to its high surface area acts as efficient catalyst and adsorbent. This properties of them make them an efficient source for the photocatalytic degradation and also adsorption of contaminants from contaminated water.

INTRODUCTION:

Nanoparticles are widely explored in the recent times. Several studies have been done to use the nanoparticles to its full potential in recent times. The area of application of nanoparticles are increasing. Nanoparticles have replaced the traditional materials over these years. This is due to their unique physical and chemical properties. They have better stability and selectivity compared to their bulk counterpart as well as high density and high surface area to volume ratio, in addition to high reactivity. These properties confers them the properties of catalyst and adsorbent. Due to the adsorption and catalytic property, they find their application in the waste water treatment. They can remove or degrade various organic and inorganic water pollutants. The pollutants include organic dyes, drugs, pesticides, heavy metals etc. Studies have shown that nanoparticles were able to efficiently remove these pollutants from contaminated water by catalytic degradation and adsorption phenomenon(Chavali & Nikolova, 2019). Metal oxide nanoparticles are metallic oxide having the particle size between 1-100 nm. Some of the most widely used metal oxide nanoparticles for waste treatment are iron oxide NPs, zinc oxide NPs, magnesium oxide NPs, silver oxide NPs, copper oxide NPs etc. The metal oxide nanoparticles are prepared by physical, chemical and biological method. Physical methods of synthesis involves mechanical milling and vapour methods. Chemical synthesis of metal oxide nanoparticles are sol-gel method, co-precipitation method, spray pyrolysis, chemical vapour deposition etc. Biological method is also called as green synthesis and it is carried out by using plants, algae, microbes etc. (Zahra et al., 2022a)

CLASSIFICATION OF NANOMATERIALS

Nanomaterials are classified into different types based on their composition. Mainly they are classified into organic, inorganic, carbon nanoparticles and AGRO based nanoparticles.

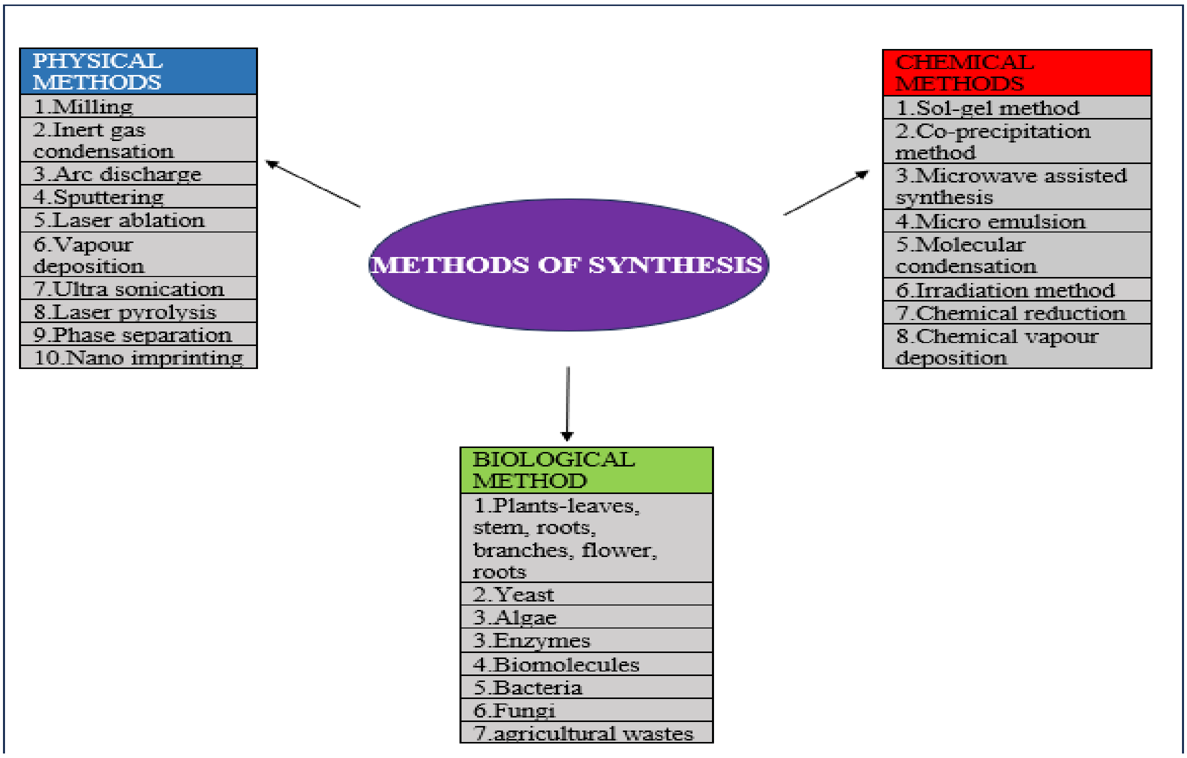


Flow chart 1: classification of nanomaterials

METAL OXIDE NANOPARTICLES

Metal oxide nanoparticles are a distinct class of metal-based nanoparticles that have profound implications in science and technologies owing to their unique properties of high surface to volume ratio, larger surface area, and abundance on earth. Metal oxide nanoparticles are versatile nanoparticles used in various industries(Chavali & Nikolova, 2019). They include magnesium oxide nanoparticles, silver oxide nanoparticles, titanium oxide nanoparticles, iron oxide nanoparticles, zinc oxide nanoparticles, and other metal oxides(Singh et al., 2018). Metal oxide nanoparticles are used as active materials for various kinds of chemical and physical sensors for detecting gases, chemical species, light, temperature, and bio-species etc(Singh et al., 2018). They are also used for the removal of various organic and inorganic pollutants from contaminated water. Metal oxide nanoparticles in recent times are widely used for waste water remediation. They also possess genuine size- and morphology-related tunable features, including physicochemical versatility, particular reactivity and surface chemistry, unique intrinsic functionality, and specific biological effects(Chavali & Nikolova, 2019). They show anti-microbial properties which includes anti-bacterial, anti-fungal etc. Metal oxides with particle size between 1-100nm showed essential applications, which include fluorescence and optical sensors, catalysts, photovoltaic and biomedicine, etc. Besides all these applications, nanomaterials have also been used like gas sensors and anode materials for fuel cells.(Chavali & Nikolova, 2019)

Flow chart 2: classification of metal oxide nanoparticles



METHODS OF SYNTHESIS OF METAL OXIDE NANOPARTICLES:

Metal oxide nanoparticles are synthesised by physical, chemical and biological methods. Physical method of synthesis mainly includes milling, sputtering, laser ablation, ultra sonication etc. chemical method of synthesis are carried out by sol-gel method, co-precipitation method, micro emulsion technique, molecular condensation and others. Biological method of synthesis is a eco-friendly method and is also called as green synthesis. This synthesis is carried out by using plants and microorganisms.

Let us discuss each of the abovementioned synthesis methods in detail

1.BIO-SYNTHESIS

Green synthesis or bio-synthesis have gained greater importance over other methods due to their ability to replace toxic solvents and drastic reaction conditions which are followed by other methods. Green synthesis of nanoparticles has been carried out by different scientist using various plant sources, bacteria, algae, fungi etc(Priya et al., 2021). Different plant sources and different strains of bacteria and fungi have been used for the green synthesis. Plant extracts is widely used to synthesis of metal oxide nanoparticles, and this is due to the presence of essential phytochemicals in plant extracts especially from the leaves. Leaf extract contains various types of phytochemicals such as terpenoids, flavonoids, ketones, aldehydes, amides, and carboxylic acids, which play a major role in formulating and enhancing the bioactivity of the nanoparticles (Danish et al., 2022). Green synthesis is also preferred over other methods due to the numerous availability of bioactive molecules, extraction of biomolecules is well established, faster reaction rates, low-cost and higher efficiency. Natural plant extracts contain numerous beneficial phytochemical molecules that function as strong reducing, stabilizing and capping agents in the fabrication of NPs. (Jadoun et al., 2021)

CONCEPT OF GREEN CHEMISTRY:

The concept of green synthesis focuses on the development of an efficient and reliable method for the preparation and development of chemical compounds and materials by considering the principle of sustainability. This is achieved by various means mainly by

- **Minimizing the use of toxic solvents and reagents.**
- **The reaction should be carried out in such a way that it produces minimal waste products.**
- **Increase the atom economy of the reaction by converting maximum reactant to product. Try to always achieve an atom economy of 95% or above.**
- **Always use solvents which are less harmful or doesn't have toxicity.**
- **Design the entire process in such a way that the toxic products are broken down into non toxic products at the end of the reaction.**
- **They synthesis should be monitored at regular intervals to check whether it generates any pollutants.**
- **Catalytic agents are always preferred over stoichiometric agents;**
- **The reagents used in the synthesis process should be selected in such a way that it reduces the possibility of accidents.**
- **Try to use reagents which are reusable.**

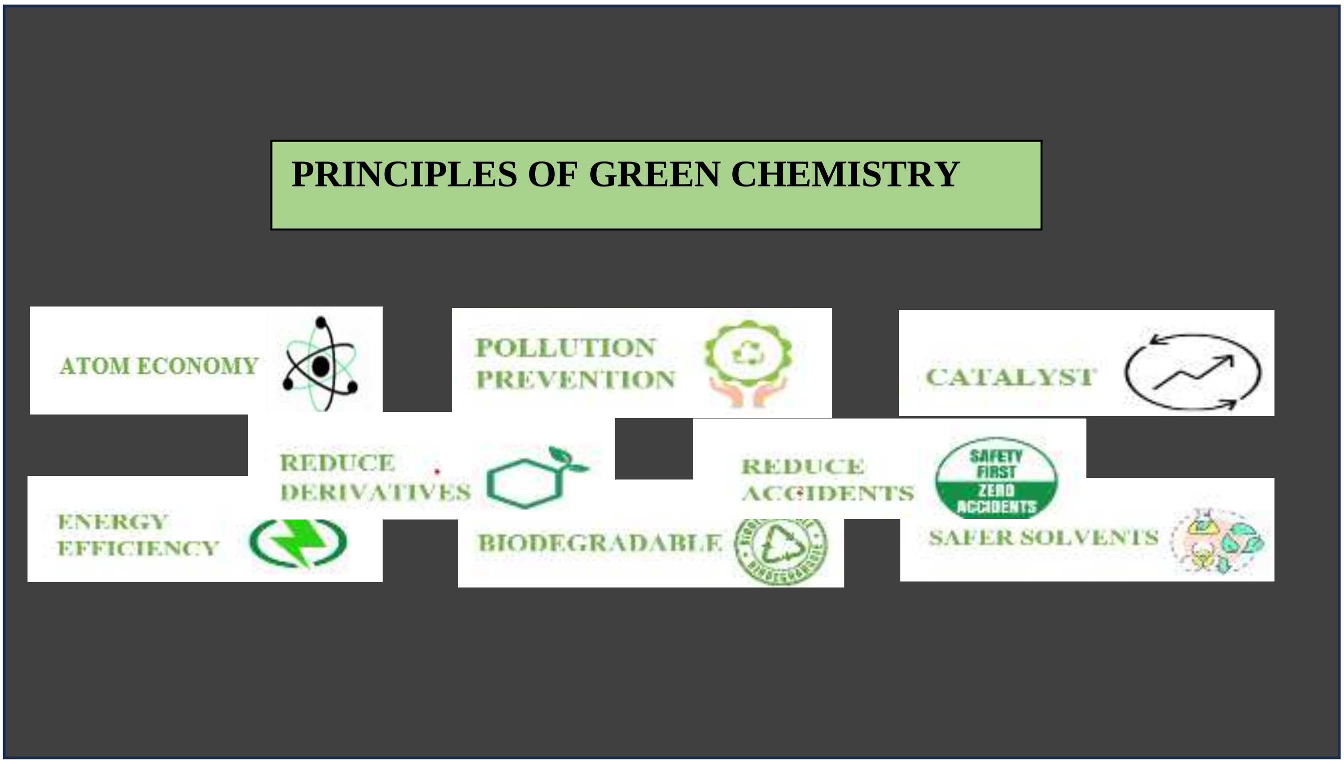


Figure 1: principles of green chemistry

PROCEDURE:

Green synthesis or biosynthesis of metal oxide is carried out by using plant extracts, algae, bacteria, fungi etc. Plant sources are mostly employed due to their easy availability and abundance of phenolic compounds, tannins, flavanoids in their extracts which aids in the formation of particles in the range 1-100nm.

1.Preparation of plant extract from the suitable sources. The biomolecules in the extract perform as a reducing agent by providing electrons to the metal ions, leading to their reduction to the elemental metal. The formed atoms operate as a nucleation centre, followed by a growth period in which adjacent smaller particles combine to create larger NPs. In this regard, plant extracts have the ability to stabilize NPs in the final stage of synthesis, ultimately determining their energetically stable and favourable morphology.(Priya et al., 2021)

2.Preparation of required quantity of precursors. The precursors are mostly the metal salts such as metal chlorides, sulphates, acetates, nitrates etc. The various precursors used for the synthesis of metal oxide nanoparticles is listed in the table below:

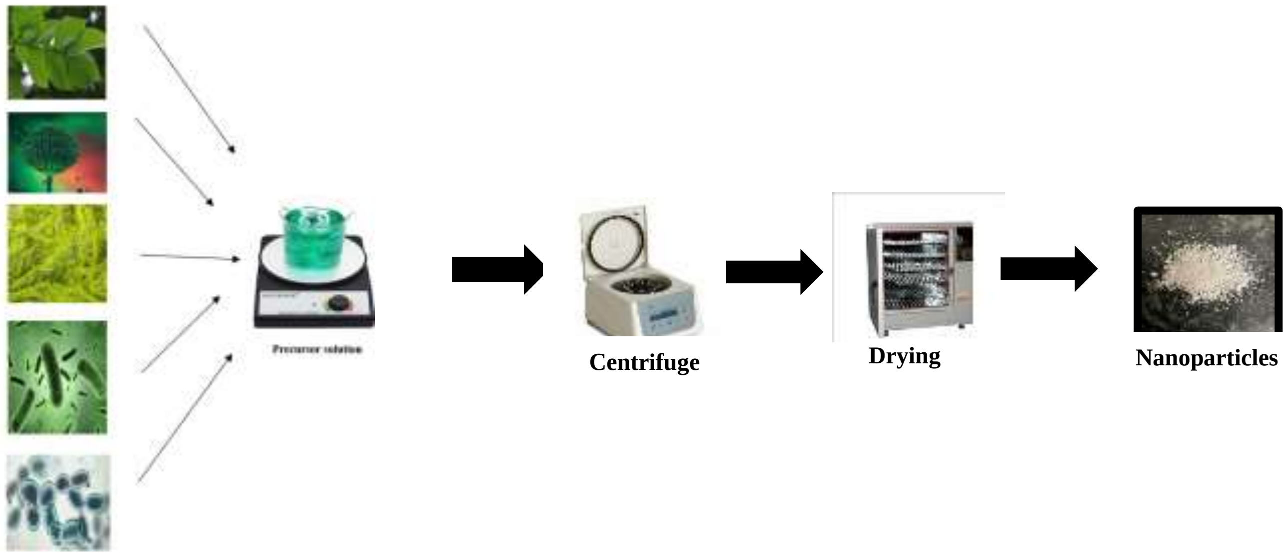
Serial No:	Precursor	Metal oxide nanoparticle
1.	Ferric nitrate(Fe $(NO_3)_3.9H_2O$ Ferric chloride hexahydrate $(FeCl_3.6H_2O)$	Iron oxide nanoparticles
2.	Zinc nitrate(Zn $(NO_3)_2.6H_2O$) Zinc acetate dihydrate [Zn (CH3CO2)2·2H2O]	Zinc oxide nanoparticles
3.	Magnesium nitrate hexahydrate $(Mg(NO_3)_2.6H_2O)$ Magnesium acetate tetra hydrate $[Mg(C_2H_3O_2)_2{\cdot}4H_2O]$	Magnesium oxide nanoparticles
4.	Copper chloride dihydrate $(Cucl_2.2H_2O)$ Copper sulphate($CuSO_4$).	Copper oxide nanoparticles
5.	Titanium tetrachloride ($TiCl_4$)	Titanium oxide nanoparticles

Tabular column 1: Different types of precursors used for the synthesis of metal oxide nanoparticles.

3.The prepared precursor solution and the plant extract is mixed thoroughly and the pH of the solution is adjusted to required value with the help of bases like sodium hydroxide. The pH level which is mostly alkaline is adjusted inroder to get a nanoparticle of better shape, size and stability(Aravind et al., 2021a). Bases like sodium hydroxide and sodium borohydride helps in the reduction of the metal salts and further they will lead to the formation of metal oxide nanoparticles. They also acts as stabilizing agents, thus prevent agglomeration of particles.(Aravind et al., 2021b)

4.The solution is then stirred for a prolonged period of time. Stirring helps in maintaining the homogeniety of the mixture also it enhances the reaction rate. Stirring for prolonnged period prevents agglomeration of the nanoparticles formed and enhances the yield.(Danish et al., 2022)

5.The formed metal oxide nanoparticles are separated by centrifugation at desired rpm usually 5000-1000 rpm and dried.



Reducing agents

Figure 2: schematic representation of synthesis of metal oxide nanoparticles by biological method.

2. CHEMICAL SYNTHESIS

There are several methods for the synthesis of nanomaterials. It includes both top-down and bottom-up approaches. In this article, we r discussing about the mainly employed four methods which are listed below.

- Sol-gel method
- Chemical-vapour deposition
- Colloidal method
- Spray pyrolysis

2.A Sol-gel method:

Sol-gel method is a bottom-up approach of synthesis of metal oxide nanoparticles. Sol-gel method is one of the most commonly employed method of synthesis of metal oxide nanoparticles, widely used for the industrial scale production of metal oxide nanoparticles(Aravind et al., 2021b). This method is capable of producing two or more types of nanoparticles simultaneously, meaning that alloy products are synthesized in one step by mixing two or more metal (or metal oxide) precursors in certain proportions(Aravind et al., 2021a, 2021b). One of the most important characteristics of this method is the low reaction temperature compared to other chemical methods of synthesis. During these reactions, the primary homogeneous molecules (sol) become an infinite, heavy, three-dimensional molecule called a gel. The conversion of tuberculosis to gel is done through a process called "compaction process" and leads to the production of wet gel. For the synthesis of binary or tertiary hybrid systems, a mixture of salts with different chemical compositions is used. Each of the primary salts has a unique reaction rate. The rate of reaction of salts depends on various factors such as pH, concentration, type of solvent, and temperature. The polymer gel formed from the density of the cell is a three-dimensional structure and is formed by joining the cavities. After drying the gel, due to volumetric shrinkage, a solid and rigid structure is obtained. It should be noted that, by controlling the drying conditions of the gel, it is possible to achieve nanosized porosity. The main advantage of this process is the formation of narrow sized particles. The nanoparticles produced by this method showed higher purity of the particles. Metal oxide nanoparticles in most of the cases showed uniform particle distribution. (Zahra et al., 2022b)

SOL-GEL METHOD

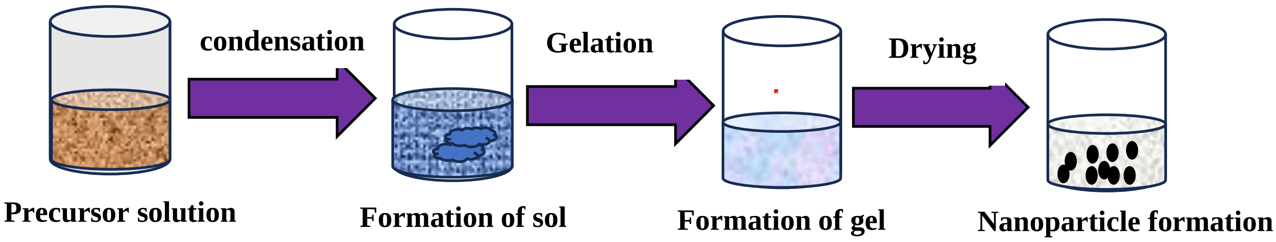


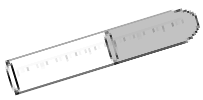
Figure 3: schematic representation sol-gel method for the synthesis of metal oxide nanoparticles.

2.B Co-precipitation method

Co-precipitation is a widely employed method for the synthesis of metal oxide nanoparticles. This method is widely accepted due to its lost cost, simplicity of carrying out the reaction and production of nanoparticles with better size and stability. Metal oxide nanoparticles such as iron oxide nanoparticles, zinc oxide nanoparticles, copper oxide nanoparticles etc are successfully synthesised by this method(Hui & Salimi, 2020). This method is widely accepted due to the easiness of the reaction condition, comparatively low reaction temperature, cheap chemicals are used, the morphology of the particles can be controlled, and purity of the nanoparticles formed is higher. Iron oxide nanoparticles are employed in large scale by this method. The various steps involved in the process are:

- Preparation of metal precursor solution- The precursor solution is the metal salts which is the starting material for the formation of metal oxide or hydroxides. For the synthesis of iron oxide nanoparticles, ferric chloride and ferrous sulphate solutions are used as the precursor solution.(Hui & Salimi, 2020)
- The two solutions are mixed and then base is added and addition of base caused the precipitation of the metal oxide or metal hydroxides. The base is added in-order to achieve the desired pH mostly between pH 8-pH 11.(Kandpal et al., 2014)
- The solution is then stirred for different time period and at different reaction temperature depending on the required properties of the nanoparticles.
- The formed nanoparticles are then separated by centrifugation at an rpm between 4000-8000 rpm.(Kandpal et al., 2014)
- The separated particles are then dried and calcinated.

C0-PRECIPITATION METHOD



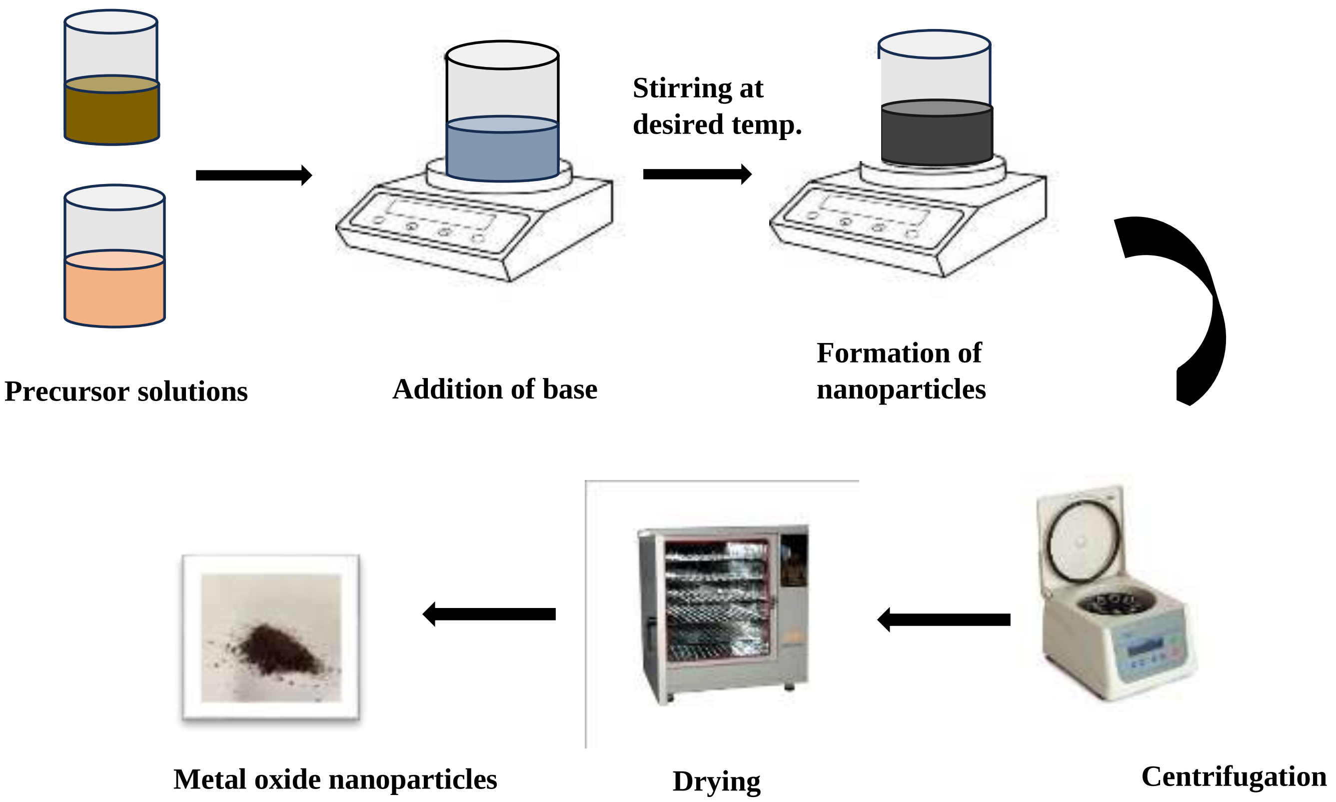


Figure 4: Synthesis of metal oxide nanoparticle by Co-precipitation method.

Comparison between chemical synthesis and green synthesis:

Metal oxide nanoparticles has been prepared by various methods by various researchers. The metal oxide nanoparticles synthesised by chemical method showed better particle size compared to green synthesis. For example, in an synthesis carried out by F. Buarki, H. AbuHassan, F. Al Hannan, F. Z. Hena in the year 2022, showed that the size of iron oxide nanoparticles synthesised using ***Hibiscus rosa sinensis*** flowers showed a particle size of 51nm. In one of the research, carried out by Beh Hui Hui and Midhat Nabil Salimi in the year 2020, iron oxide nanoparticles was synthesised by co-precipitation method and the average particle size was found to be between 9.9-11nm. The size of the particles is affected by various parameters such as pH, stirring rate, reaction time etc. All these parameters must be optimised to get a metal oxide nanoparticle with better particle size and efficiency. Green synthesis of biological synthesis is always preferred over other synthetic methods due to it eco-friendly nature. This method of synthesis does not require any chemical solvent or any toxic reagents. Various researches have concluded that metal oxide nanoparticles synthesised was more stable and shower higher efficiency compared to the metal oxide nanoparticles synthesised by green method.

Comparison between green synthesis And Chemical Synthesis

GREEN SYNTHESIS METHOD	CHEMICAL SYNTHESIS METHOD
1. Green synthesis is the synthesis of nanoparticles from natural sources which includes plants, bacteria, fungi, algae etc.	1.chemical synthesis is the synthesis of nanoparticles using various metal salts and solvents.
2 No organic solvents are used in this synthesis method.	2. Organic solvents are extensively used in the synthesis method.
3.No accumulation of waste products.	3. Accumulation of waste products.

4.Green synthesis is usually a slower process.	4.Faster process compared to green synthesis.
5.The particle size, shape and composition cannot be controlled as efficiently as chemical method	5.Allows for better control of particle size, shape and composition.
6.The nanoparticles cannot be scaled up for industrial production easily.	6.Easier to scale up for industrial production
7.Green synthesis method is cost-effective due to the use of readily available natural products like plant extracts, microorganisms etc.	7.Expensive when compared to green synthesis as it required various chemical reagent for the synthesis of nanoparticles.

Titanium oxide nanoparticles:

Titanium oxide nanoparticles (TiO_2) are one of the most important metal oxide nanoparticles. The titanium oxide nanoparticles are non-toxic, stable, and are resistant to corrosion. Titanium oxide nanoparticles are synthesised successfully by chemical, physical and biological method. The titanium oxide nanoparticles possess various properties such as photocatalytic property, adsorbent, anti-bacterial, anti-fungal and other biological activities. Due to these properties, they are widely used in water remediation.

Green synthesis:

Titanium oxide nanoparticles was successfully synthesised using various plant extracts. The plant sample to be extracted was collected and washed properly. After washing, the plant sample was dried thoroughly and crushed into fine powders. The powder was then boiled for 30 minutes in double distilled water for 30-60 minutes (Aravind et al., 2021a). The contents were filtered and the extract was obtained. For the synthesis of titanium oxide nanoparticles, a precursor solution was prepared. The precursor solution was prepared by using titanium metal salts such as titanium tetrachloride, titanium tetra isopropoxide (TTIP). 50 ml of the precursor solution was prepared and 20ml of the prepared plant extract was added into it dropwise. The solution was then stirred for 3-5h (Jadoun et al., 2021). The colour of the solution changes from pure white to yellowish grey indicates the formation of titanium oxide nanoparticles. The particles were then separated by centrifugation and dried properly.(Aravind et al., 2021a)

Some of the plant samples used are listed below:

Plant	Particle size
Glycosmis cochinchinensis	35-45nm
Jatropha curcas	75nm
Moringa oleifera	12.33nm
Aloe Miller barbadensis	20nm
Psidium guajava	32nm
Piper nigrum	22nm
Coriandrum sativum	34nm
Syzygium aromaticum	32nm
Jasmine flower	32-45nm

Tabular column 2: plant sources used for the synthesis of titanium oxide nanoparticles and their particle size.

Sol-gel method:

Titanium oxide nanoparticles have been synthesised by sol-gel method. The precursor solution used was titanium butoxide. Accurately weighed titanium butoxide was dissolved in ethanol. To the prepared solution, water was added. The ratio of the solution must be TBT: H_2O: EtOH = 1:1.5:20.2. Water is added for hydrolysis(Aravind et al., 2021b). Titanium butoxide and ethanol mixture are stirred using a magnetic stirrer for at least 15 min(Raghavan, 200 C.E.). Distilled water was added dropwise to the above solution, and the precipitate of nanoparticles was observed. The sol obtained is treated with different temperatures of heat at different time intervals. The nanoparticles were then dried.(Alkanad et al., 2022; Raghavan, 200 C.E.)

Hydrothermal method:

0.1N titanium tetrabutoxide solution was dissolved in 20ml of ethanol solution and stirred continuously for 30minutes. To the above solution few drops of distilled water was added to create a dispersive medium(Alkanad et al., 2022). The solution was then subjected to sonication for 20 minutes. After sonication, the solution was transferred into an autoclave for 3h at 150^{0}C. After 3h the solution was then cooled to room temperature and the impurities were removed by washing with deionised water. The nanoparticles were separated by centrifugation. The sample was then dried at 110^{0}C for 5h and then subjected to annelation to obtain nanoparticles of higher purity.(Alkanad et al., 2022)

Iron oxide nanoparticles:

Iron oxide nanoparticles has gained much attention in recent times due to its unique properties such as small size, bio-compatibility, magnetic properties, high surface area to volume ratio etc. Iron oxide nanoparticles have been successfully synthesised by biological method, sol-gel method, hydrothermal method, co-precipitation method, and by thermal decomposition method. Due to its unique properties, they have broad range of application. They are used for waste water remediation to remove organic and inorganic pollutants and wide variety of bio-medical applications.

Green synthesis:

0.1M ferric chloride solution was prepared by dissolving accurately weighed 0.811g ferric chloride anhydrous ($FeCl_3$-M.W=162.21) in 50 ml of double distilled water. The solution was stirred for 5 minutes until all the salt had been dissolved. To the prepared precursor ferric chloride anhydrous solution 50 ml of the freshly prepared *Carica papaya* leaf extract was added slowly(Jadoun et al., 2021). The obtained solution was then stirred for 3 minutes to obtain a homogenous solution. To the above solution prepared 1M sodium hydroxide was added dropwise till the pH becomes 11. The colour of the contents of the beaker changes from light brown solution to black solution. The appearance of black precipitate confirms the formation of iron oxide nanoparticles. After the formation of the precipitate, the solution was stirred for 30 minutes using a magnetic stirrer. After 30 minutes, the contents were transferred into centrifuge tubes and centrifuged at 8000 rpm for 20minutes (Priya et al., 2021). After centrifugation, the supernatant was discarded and the precipitate was collected to a petri plate. The sample was then cleaned with deionized water three times and ethanol to remove any unreacted bio-molecules before drying. The particles were dried in a hot air oven at 55^{0}C for 1 hour. Once completely dried the yield was recorded.(Lee & Chon, 2022)

Some of the plant sources used for the preparation of iron oxides are given below:

SL.NO	PLANT	PARTICLE SIZE(nm)
1	*Sageretia thea*	29
2	*Lageneria siceraria*	30-100
3	*Daphne mezereum*	6-15
4	*Punica granatum*	24-55
5	*Carica papaya*	2.15
6	*Juglans regia*	12.6
7	*Platanus orientalis*	38
8	*Plantago major*	4.6-30
9	*Avecinnia marina*	10-40
10	*Malus pumila*	50-100

Tabular column 3: plant sources used for the synthesis of iron oxide nanoparticles and their particle size.

Co-precipitation method:

0.2M ferrous sulphate heptahydrate solution ($FeSO_4.7H_2O$-MW=278) was prepared by accurately weighing 1.39g of $FeSO_4.7H_2O$ and dissolving it in 25 ml of double distilled water by continuous stirring. 0.1M ferric chloride solution ($FeCl_3$-MW=162.21) was prepared by accurately weighing 0.4055g of $FeCl_3$ and dissolving it in 25 ml of double distilled water with constant stirring. The ratio of ferrous sulphate heptahydrate to that of ferric chloride should be maintained at 2:1 throughout the reaction period. Once both solutions were completely dissolved, the ferrous sulphate solution was added to the ferric chloride solution with constant stirring using a magnetic stirrer and the temperature was maintained at 80^0C(Kandpal et al., 2014). The pH of the solution was adjusted to pH=11 using ammonia solution. The formation of a black precipitate indicates the formation of iron oxide nanoparticles. The solution was then stirred for 60 minutes. The solution was then filtered using Whatman filter paper N0.41 and the filtrate was collected. The sample was washed with de-ionised water and then with ethanol to remove any impurities present. The sample was then dried using a hot air oven for 60 mins at 55^0C.(Hui & Salimi, 2020)

Sol-gel method:

0.15 M of ferric nitrate (Fe (NO)3·9H2O) was dissolved in 50 ml of ethylene glycol (C2H6O2) at 50 °C. The solution was vigorously stirred at this temperature using magnetic stirrer for 90 minutes to make stable sol. The sol was further heated and maintained at 80 °C under continuous stirring until a brown semi-solid (gel) is formed(Thiagarajan et al., 2017). This was followed by aging about 5 days for the condensation and polymerization reactions, and then dried in a hot air oven at 100 °C for 5 hours. This xerogel was annealed under air atmosphere at 800 °C for 150 minutes and the final product was crushed to powder form, which was reddish in colour.(Thiagarajan et al., 2017)

Zinc oxide nanoparticles

Zinc oxide nanoparticles possess unique properties and which make them acceptable for wide variety of application. They have large surface area which is the reason for their high catalytic efficiency. The zinc oxide nanoparticles have been synthesised by using plant extracts, chemical method and physical methods. Zinc oxide nanoparticles are stable, non-toxic, possess anti-microbial activity. They are also used in wide variety of cosmetics and skin care products.

Green synthesis:

0.5 M Zinc acetate trihydrate ($Zn(CH_3COO)_2(H_2O)_3$-MW=219.50) was prepared by accurately weighing and dissolving 5.4875g of zinc acetate trihydrate in 50 ml of double distilled water. The solution was stirred for 5 minutes. To the prepared zinc acetate trihydrate solution 20 ml of the freshly prepared *Carica papaya* leaf extract was added dropwise with constant stirring at 60^0C and the solution was mixed thoroughly(Jayachandran et al., 2021). The solution was adjusted to pH 8 by adding 1M NaOH dropwise with constant stirring. Once the solution attains a pH of 8 a white precipitate of zinc oxide nanoparticles will be formed. The solution was then stirred for 2 hours using a magnetic stirrer(Jayachandran et al., 2021). The contents were then transferred into a centrifuge tube followed by centrifugation at 10000 rpm for 20 minutes (Iqbal et al., 2021). The supernatant liquid was discarded and the precipitate was collected. The sample was washed three times using de-ionised water and then by ethanol to remove all the unreacted biomolecules before drying. The sample was then dried in a hot air oven for 45 minutes at 40^0C. Once completely dried the yield was recorded.(Iqbal et al., 2021)

The various plant sources used for green synthesis of zinc oxide nanoparticles are given below:

Sl.no	plant	Particle size in nm
1	*Agathosma betulina*	15.8
2	*Laurus nobilis leaf*	47.3
3	*Calotropis procera*	24
4	*Ocimum tenuiflorum*	13.8

5	*Salvia officinalis*	11.9
6	*Myristica fragrans*	29
7	*Cayratia pedate*	2.3
8	*Syzygium cumini*	16.4
9	*Solanum nigrum*	29.8
10	*Moringa oleifera*	24

Tabular column 4: plant sources used for the synthesis of zinc oxide nanoparticles and their particle size.

Sol-gel method:

Zinc Oxide nanoparticles were synthesized by using the sol-gel method. To prepare a sol, 2 g of Zinc Acetate Dihydrate and 8 g of Sodium Hydroxide were weighed using a weighing balance(Zahra et al., 2022a). Then, 10 ml and 15 ml of distilled water were measured by a measuring cylinder. After that, 2 g of zinc acetate dihydrate was dissolved in 15 ml of distilled water and 8 g of sodium hydroxide was dissolved in 10 ml of distilled water. The solutions were stirred constantly for about five minutes each(Zahra et al., 2022b). After well mixed, the sodium hydroxide solution was poured into the zinc acetate solution with a constant stirring by a magnetic stirrer for about five minutes. Then, a burette was filled with 100 ml of ethanol and titrated dropwise to the solution containing both sodium hydroxide solution and zinc acetate. After the reaction, a white precipitate was formed(Hasnidawani et al., 2016). The formation of a white precipitate indicates the presence of zinc oxide nanoparticles. The solution was then filtered using a Whatman filter paper. The sample was then washed 3 times with double distilled water and then with ethanol to remove all the impurities present before drying. Once completely cleaned, the samples were dried in a hot air oven for 40 minutes at 45^0C.(Hasnidawani et al., 2016)

Magnesium oxide nanoparticles:

Magnesium oxide nanoparticles show wide variety of applications such as anti-microbial characteristics, efficient catalyst and adsorbent which makes them useful for the removal of contaminants from polluted water. Apart from these properties, they exhibit anti-cancer, anti-oxidant, and anti-diabetic properties. They are also employed as a catalyst for various chemical reactions. Magnesium oxide nanoparticles are synthesised by green method, hydrothermal method, sol-gel method, hydroxide precipitation method etc. Magnesium oxide nanoparticles are odourless, non-toxic and corrosion resistance.

Green synthesis:

The aqueous extract of the dried powder of plant source was heated for 40 minutes at 60^0C-80^0C with continuous stirring and filtered through Whatman's No.1. Then it was subsequently mixed with 0.1 M solution of magnesium nitrate hexahydrate ($Mg(NO_3)_2·6H_2O$) at room temp (25 °C)(Cai et al., 2018a). The pH of the solution was adjusted bet. ween 9-11 using 1N sodium hydroxide solution. The solution was then stirred for 5h at 1000 rpm. The solution was then centrifuged and the particles were separated. Magnesium oxide nanoparticles were washed twice with distilled water and carefully collected, sonicated at 40 °C for 1 h and dried in hot air oven at 90 °C for 2 hours.(Cai et al., 2018b)
The different plant sources used for the synthesis is given below:

Sl.no	plant	Particle size
1	*Abrus precatorius*	23nm
2	*Rosa floribunda*	32nm
3	*Nephelium lappaceum*	60-70nm
4	Aloe vera extract	55nm
5	*Hagenia abyssinica*	23nm
6	*Swertia chirayaita*	45nm
7	*Euphoria tirucalli*	18nm

8	*Moringa oleifera*	15-18nm

Tabular column 5: plant sources used for the synthesis of magnesium oxide nanoparticles and their particle size.

Sol-gel method:

Magnesium oxide nanoparticles were synthesized using magnesium nitrate ($MgNO_2.6H_2O$) as a precursor solution with sodium hydroxide(Gatou et al., 2024). 0.2M magnesium nitrate was dissolved in 100 ml of double distilled water. 0.5M sodium hydroxide solution was added drop wise to the prepared magnesium nitrate solution with constant stirring. White precipitate of magnesium hydroxide appeared in beaker after few minutes(Gatou et al., 2024). The stirring was continued for 30 minutes. The pH of the solutions was 12.5. The precipitate was filtered and washed with deionised water three to four times to remove ionic impurities and then centrifuged for 5 minutes at 5000 rpm/min and dried at room temperature. The dried white powder samples were annealed in air for two hours at 300 and 500ºC.(Gatou et al., 2024)

Characterisation of nanoparticles:

Different techniques have been employed to characterise the prepared nanoparticles. These studies are done in order to determine the size, shape, morphology and other characteristics of the synthesised metal oxide nanoparticles. The analysis methods mainly employed ate mentioned below:

1. UV spectrophotometer analysis.
2. Scanning electron microscope
3. Fourier transform infra-red spectroscopy
4. X-ray diffractometer
5. Transmission electron microscopy

SEM imaging:

Scanning electron microscopy (SEM) is a powerful imaging technique that has revolutionized the way we visualize and analyse materials at the micro and nano scales. With applications spanning across diverse fields such as materials science, biology, and geology, SEM has become an indispensable tool for researchers and industry professionals alike. Scanning Electron Microscopy offers high-resolution images, providing insights into the structure, composition, and properties of various samples. These traits make SEM a useful technique for various applications, including biology, engineering, and forensics. he use of SEM gives the ability to detect nanoparticles and investigate their properties and macro flaws, such as porosity, cracks, secondary phases, and microscopic defects.(Gatou et al., 2024)

Fourier transform infra-red spectroscopy:

Fourier Transform Infrared (FTIR) spectroscopy is a powerful tool for analysing metal oxide nanoparticles. FTIR helps identify the functional groups present on the surface of metal oxide nanoparticles. This is crucial for understanding the chemical composition and surface modifications. It provides information about the molecular structure and bonding environment. For metal oxides, FTIR can reveal the presence of metal-oxygen bonds and other characteristic vibrations. FTIR can be used for quantitative analysis by measuring the intensity of specific absorption bands, which correlates with the concentration of certain functional groups. (Khoso et al., 2021; Mahmoud et al., 2021)

X-ray diffractometer:

X-ray Diffraction (XRD) is a crucial technique for analysing metal oxide nanoparticles, XRD provides detailed information about the crystalline structure of nanoparticles. It helps identify the phase and crystallinity of the metal oxides. XRD helps in identifying different phases present in the sample. This is important for ensuring the purity and desired composition of the nanoparticles. XRD can be used to estimate the crystallite size using the Debye-Scherrer formula. This is particularly useful for nanoparticles, as their small size often leads to peak broadening in the XRD pattern.(Khoso et al., 2021)

Transmission electron microscopy:

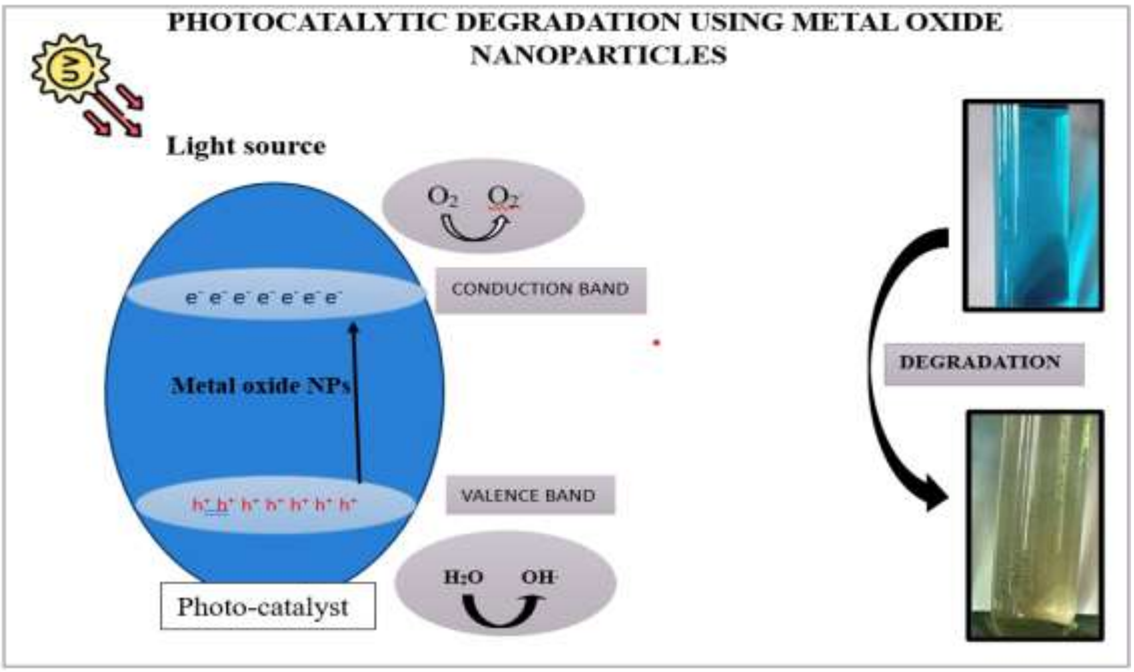
TEM provides high-resolution images that allow for the visualization of nanoparticles at the atomic level. This is crucial for understanding the size, shape, and morphology of metal oxide nanoparticles. TEM can provide detailed crystallographic information through techniques like Selected Area Electron Diffraction (SAED). This helps in identifying the crystal structure and phase of the nanoparticles. EM can be used to determine the size distribution of nanoparticles. This is important for applications where uniform particle size is critical.(Khoso et al., 2021)

Applications of metal oxide nanoparticles:

Metal oxide nanoparticles such as iron oxide nanoparticles, zinc oxide nanoparticles, titanium oxide nanoparticles, magnesium oxide nanoparticles etc are used to remove dyes, drugs, heavy metals and other organic and inorganic impurities from contaminated water. Metal oxide nanoparticles exhibit photocatalytic properties, acts as chemical catalyst and adsorbents. These properties of metal oxide nanoparticles are exploited to make use of them as an efficient material for dealing with the issue of water pollution(Mahmoud et al., 2021). Various researches have been carried out on the applications of metal oxide nanoparticles in waste water remediation. The researches carried out suggested that metal oxide nanoparticles showed degradation of organic and inorganic pollutants as well as adsorption of these contaminants. The metal oxide nanoparticles efficiently degraded various dyes such as methylene blue, methyl orange, rhodamine B, malachite green, cresol blue, indigo etc (Danish et al., 2022). They also removed various heavy metals accumulated in water bodies. Heavy metals such as arsenic, nickel, chromium, manganese., lead etc was removed by metal oxide nanoparticles by adsorption and degradation. Metal oxide nanoparticles showed a wide range of anti-microbial properties against a variety of species of bacteria, fungi etc, Apart from these they also show anti-toxicity effects. They also show biological effects such as anti-oxidant, anti-diabetic and anti-cancer properties. In this review article, let us discuss in detail the removal of heavy metals, drugs and dyes from contaminated water.

1.Removal of dyes and drugs by photocatalytic degradation using metal oxide nanoparticles.

photocatalytic degradation of dye depends upon the light-harvesting efficiency, the efficiency of the photogenerated electron/hole charges and the reaction of photogenerated charges with substrate molecules. Photodegradation of the dye is achieved when UV light interacts with the photocatalyst. Photons having energy equal to or greater than the band gap



of the catalyst, excite the electrons from their valence band (VB) to the conduction band (CB) and produce positive holes (h^+) in the VB. The h^+ of the VB reacts with the water molecules and creates hydroxyl radicals (·OH) while the excited electrons present in the CB react with oxygen molecules and generate superoxide anion radicals ($O_2^{\cdot -}$). These radicals are highly reactive species and effectively degrade dye molecules into simple and small species such as H_2O and CO_2. The metal oxide nanoparticle act as a photocatalyst.

Figure 5: mechanism of photocatalytic degradation of dyes using metal oxide nanoparticles.

2.Removal of heavy metals by adsorption using metal oxide nanoparticles.

Adsorption using nanoparticles is a highly effective method for removing heavy metals from contaminated water. Adsorption with metal oxide nanoparticles is a finest method for heavy metal removal based on the physical interaction between metal ions and sorbents. Adsorbents based on metal oxide nanoparticles is seen as potential for heavy metal removal in view of its low cost, high efficiency, and simplicity of operation for removing trace levels of heavy metal ions.

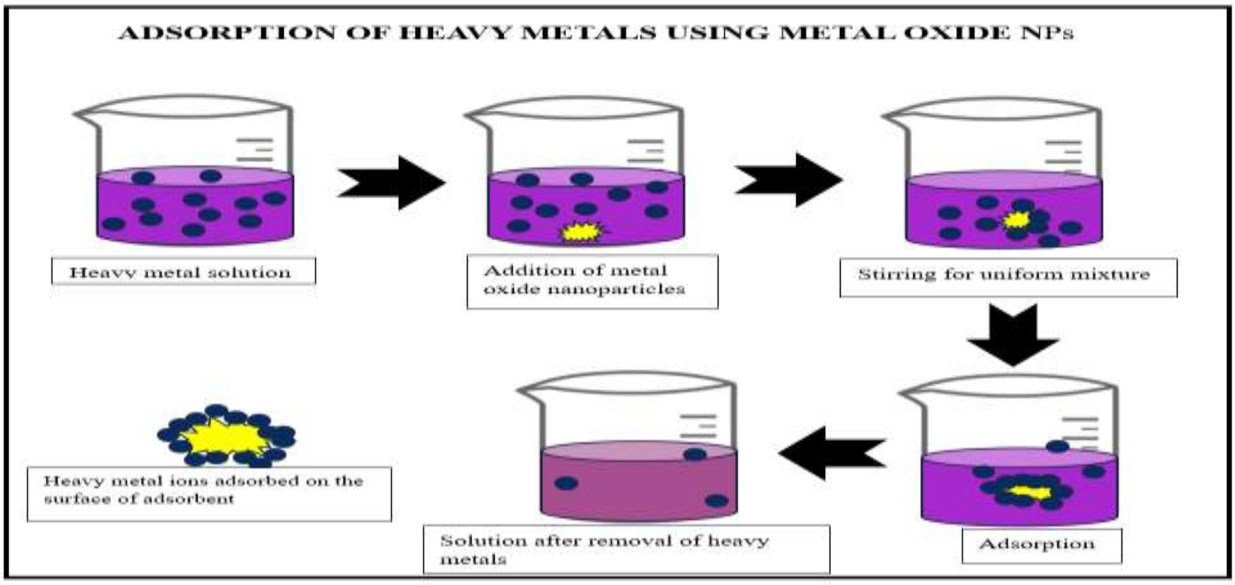


Figure 6: mechanism of removal of heavy metals by metal oxide nanoparticles by adsoprtion

3.Removal of organic pollutants by chemical degradation using metal oxide nanoparticles.

Chemical degradation of organic dye molecules such as methylene blue, malachite green, methyl orange has been carried out by using metal oxide nanoparticles as the chemical catalyst. The addition of hydrogen peroxide to the solution leads to the formation of **OH·.** Thiis will react with the organic dye molecules and lead to its degradation to carbon dioxide. The rate of the reaction or degradation is faster when the reaction is carried out in presence of metal oxide nanoparticles. The metal oxide nanoparticles will behave as catalyst. By this method, various organic dye pollutants can be removed from the contaminated water. This method has been of degradation of organic dyes has been shown below.

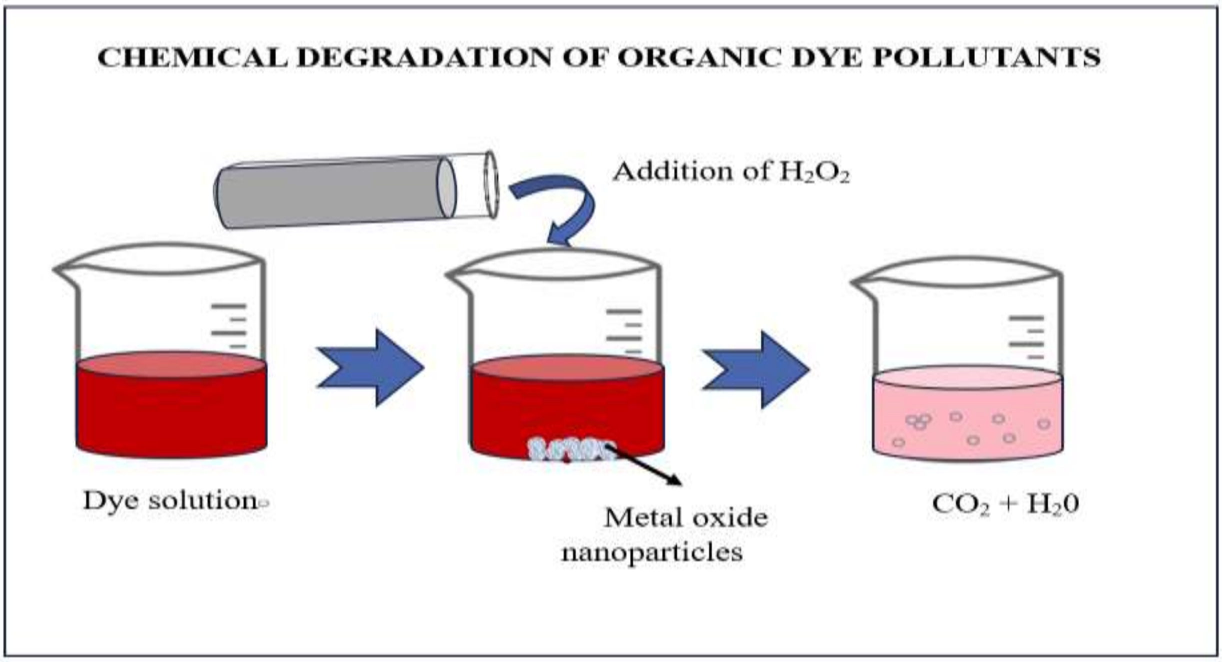


Figure 7: chemical degradation using metal oxide nanoparticles.

Results and discussion:

Sl.no	Pollutant	Metal oxide nanoparticle	Rate of degradation
1	Chromium (VI)	Nickel ferrite nanoparticle (30mg)	89.8% in 90 minutes
2	Lead (II)	Nickel ferrite nanoparticle (40mg) \	77% in 120 minutes
3	Cadmium (II)	Nickel ferrite nanoparticle (30mg	85% in 90 minutes
4.	Nickel (Ni^{2+})	Iron oxide nanoparticles	71% in 60 minutes
5.	Cadmium (Cd^{2+})	Iron oxide nanoparticles	92% in 60 minutes
6.	Phenol	Zinc oxide nanoparticles	56% in 44 minutes
7	Copper (Cu^{2+})	Alumina nanoparticles	81% is 60 minutes
8.	Methylene blue	Titanium oxide nanoparticles@ carbon	80% in 120 minutes
9.	Indigo carmine	Graphene oxide nanoparticles	98% in 30 minutes
10	Neutral red	Graphene oxide nanoparticles	97% in 30 minutes
11	Methylene blue	Silica (SiO_2) nanoparticles	98% in 90 minutes
12	Methyl orange	Silica (SiO_2) nanoparticles	95% in 90 minutes
13	Methylene blue	Magnesium oxide nanoparticles	98% in 110 minutes

14.	Rhodamine blue	Zinc oxide nanoparticles	98% in 120 minutes
15.	Ismate violet 2R	Zinc oxide nanoparticles	65% in 90 minutes
16	Mercury (II)	Iron oxide nanoparticles	87% in 24h
17	Lead (II)	Copper oxide nanoparticles	84% in 60 minutes
18	Nickel (II)	Copper oxide nanoparticles	52.50% in 60 minutes
19	Cadmium (II)	Copper oxide nanoparticles	18% in 60 minutes
20	Methylene blue	Manganese doped zinc oxide nanoparticles	54 % in 60 minutes
21	Malachite green	Titanium oxide and zinc oxide nanoparticles	92% in 60 minutes
22	Malachite green	Lanthanum doped tungsten oxide nanoparticles	100% in 180 minutes
23	Malachite green	Silver-manganese oxide nanoparticles	99% in 60 minutes
24	Rifampicin antibiotic	Copper oxide nanoparticles	98% in 60 minutes
25	Copper	Aluminium oxide nanoparticles	98% in 120 minutes
26	Congo red	Iron oxide nanoparticles	

From the above results, it is clear that metal oxide nanoparticles clearly removed organic and inorganic pollutants from contaminated water. Dyes such as malachite green, methylene blue, methyl orange etc can be removed by metal oxide nanoparticles such as zinc oxide nanoparticles, iron oxide nanoparticles, copper oxide nanoparticles, silicon dioxide nanoparticles, magnesium oxide nanoparticles by photocatalytic degradation and adsorption mechanisms. Toxic heavy metals such as Arsenic, Lead, Chromium, Cadmium etc also can be removed using metal oxide nanoparticles.

Conclusion:

The review article focused mainly on the synthesis and application of metal oxide nanoparticles. The different methods for the synthesis of metal oxide nanoparticles include chemical, physical and biological. In this article, we have discussed about the chemical and biological method. The biological method or green synthesis is preferred over other method due to its sustainable nature. Most of the time chemical method is much efficient in terms of particle size and stability. The article in detail discussed about the synthesis of titanium oxide nanoparticles, iron oxide nanoparticles, zinc oxide nanoparticles and magnesium oxide nanoparticles. Metal oxide nanoparticles is widely used as a potential candidate for eco-friendly and sustainable water treatment. Various researches were conducted to check the efficiency of metal oxide nanoparticles to remove organic and inorganic pollutants from waste water. Contaminants such as dyes, drugs and heavy metals are removed by metal oxide nanoparticles. Various factors effect the degradation and removal such as concentration of the metal oxide nanoparticles, pH of the solution, temperature etc. From the above article, we can conclude that in future metal oxide nanoparticles will be used widely in various waste water treatment systems.

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