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Treatment Of Waste Water By Using Nano Particles

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Abstract: Water plays a crucial role every life. There are a multitude of problems that can occurred without water. The availability of safe and clean water is decreasing day by day and it is expected that this problem of clean water will increase in upcoming decades. So, to address this problem various water purification techniques have been adopted. But in the current era, the requirement for growing economy is to supply of high-quality drinking water to society with cheaper technology.

For this, nanotechnology and nano particles such as metal oxides, carbon nano tubes and many more has led to various efficient ways for treatment of waste water in more precise or accurate ways on both small and large scale nano particles give better result in treatment of waste water because of its excellent adsorption properties, enhanced photo catalysis, high reactivity and high surface area. That can be used efficiently for removing toxic metal ions, organic and inorganic solutes from waste water.

I. *INTRODUCTION*

Water is an essential natural resource on the earth. It is very important for the survival of all living organisms. We cannot live without water. About 71% water is there on the earth surface, Out of 71%, 97% water is present in oceans. Only 3% water is fresh but out of 3%, 2.5% water is present in groundwater or in glaciers etc. It means 0.5% water is available for drinking, which is getting deteriorating continuously due to contamination. The spread of a wide range of contaminants in surface water and groundwater has become a critical issue worldwide due to rapid growth of industrialization, domestic and agricultural activities which bring about the life time threatening diseases. Many contaminants present in waste water such as heavy metals, inorganic compounds, organic pollutants, dyes & many other compounds·

[1]These are very harmful for us. Among all of these chemicals, dyes and heavy metals are considered as the main pollutants in waste water. Dyes are highly carcinogenic and toxic when these dyes are thrown into water without proper treatment causing serious risks to human & aquatic life. Heavy metals are very hazardous & poisonous even at low concentration. They could be disposed into water through the mining, metallurgy & household waste water etc. Heavy metals such as lead, mercury, arsenic, zinc, copper, nickel and chromium causes a severe risks to human health because they can be biologically collected in the food chain

.[2] Heavy metals are very harmful to human health & environment. Excessive intake of heavy metal can lead to serious issue such as damages to kidneys, lungs, mental and central nervous function. Purification water is not only essential for humans but also for different purposes. To remove there, pollutants various conventional waste water treatment methods such as chemical, physical and biological processes can used, but there we can be limited because of high cost process and in some cases, their processes, are poorly efficient (new compounds can from during treatment in waste water).

[3]So, for treatment of waste water we need an alterations approach and that approach can be Nanotechnology because technically and economically nanotechnology. provides on alternative way to waste water treatment in a better way as compared to conventional waste water treatment.

This technology conducted on particles or materials on the nanometer scale which is about 1 to 100 nanometers so that, at atomic level new structures and materials can built.

The properties of materials at nano levels is completely different when we compared. it with macro level material. Due to these different properties, Nanotechnology, is quite significant for waste water treatment.

I.1. Wastewater

Water that contains unwanted substances which affect water quality and unsuitable for use. Fresh water use in industries, agricultural field & household, purposes also and after the use it become waste water. Sources of waste water are as follows:

Figure1: Different Sources of wastewater.

Constituents of waste water are organic substances, suspended solids, dissolved organic salts, pathogenic. & non-pathogenic microorganisms and toxic heavy metals.

Conventionally, treatment of waste water method has many limitations which are listed in **Table 1**.

Table1: Limitations of conventional waste water treatment.

Method	Limitations
Chemical Precipitation	For precipitation, excess of reagent is required and it is not a selective method
Biological treatment	Intermediate from by micro-organisms can destroy microbial cell sand time consuming & expensive
Liquid-Liquid extraction	High equipments needed
Thermaloxidation	High cost method
Membrane	Small and medium sized membrane require high investment cost
Ultrafiltration	This method fails to remove soluble inorganic Salts & high energy require
Microfiltration	Fail to remove metals like fluorides, nitrates and colored dyes also.
Electrochemistry	High cost required for equipment setup & need high energy

I.2. Nanomaterials

Nanotechnology implement on those materials or particles which have at least one dimension in range of 1- 100 nm such materials or particles called nanomaterials or nanoparticles.

Nanomaterials have different characteristic such as unique biological, physical and chemical properties as compared to macro level particles. Nanoparticles shape and sizes are main parameter for their different behaviour. Nanoparticles are categorized into different groups depending on their size, shape, chemical and physical properties each which are carbon- based nanoparticles, lipid based nanoparticles, semiconductor nanoparticles and metal nanoparticles.

I.2.1. Synthesis of Nanomaterials

Two main approaches can applied for synthesizing nanomaterials which areas follows:-

(i) **"Bottom Up" approach** -In this approach, materials form from the bottom (atom to atom connection) or individual atoms or molecules combined and form larger and complex nanostructure.

(ii) **"Top Down" approach**- In this approach, nanomaterials form by breaking down bulk material into nano sized particles.

There approaches play an important role in determining main properties of nanomaterials such as stability, adsorption ability or degree of catalysis.

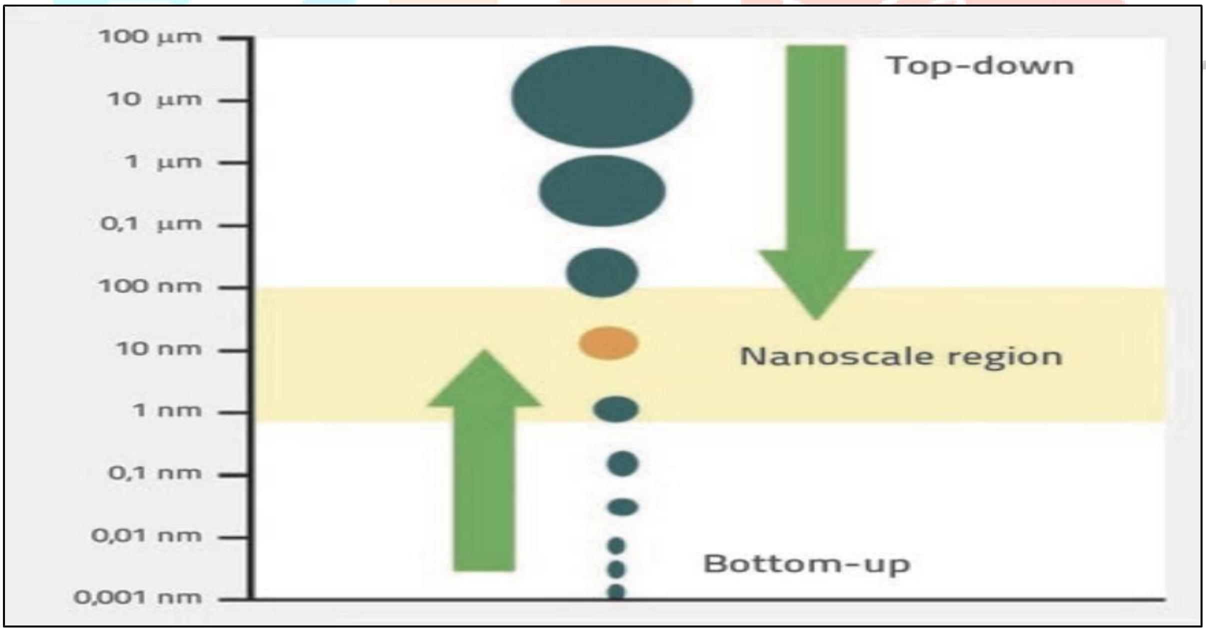


Figure2: Top down and Bottom up synthesis of nanomaterials.

I.2.2. Properties of Nanomaterials

Nanoparticles have many unique properties due to their nano sized and one of the most important is large surface to area ratio which is responsible for other properties such as adsorption, photocatalysis, mechanical strength and all their properties highly suitable for waste water treatment. Nanomaterials have high percentage of atoms or molecules on the surface. There are some semiconductor nanoparticles such as TiO2 which act as good photocatalyst due to high energy band gap structure. Due to their nano size, they have unique chemical and physical properties because the atom percentage at the surface of material becomes significant. Some nanoparticles show magnetic properties which is highly beneficial in waste water treatment. They exhibit optical properties also. They show strong mechanical strength by which nanomaterials can be used as nanomembrane.

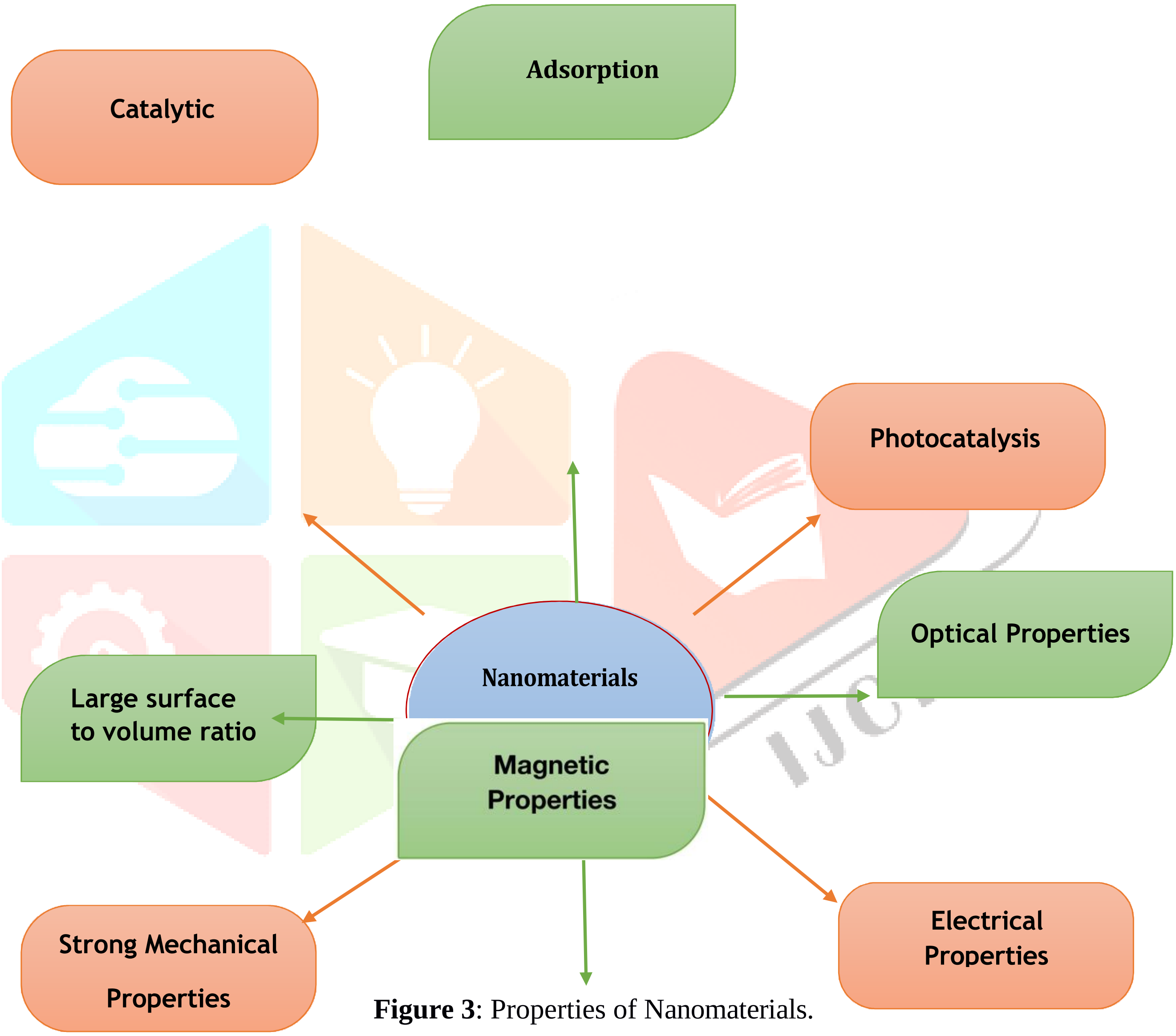


Figure 3: Properties of Nanomaterials.

II. Nano technological processes in waste water treatment

Nanotechnology means a new innovative method fore treatment of waste water and technology assures to reduce the major problems which are coupled with conventional methods. Basically, there are four type of nano based material which we can be use in treatment of waste water or in the water purification, which are as follows (**figure 4**)

- Nano-adsorbent
- Nano-metals and metal oxides
- Nanomembranes
- Nano-Photocatalysis

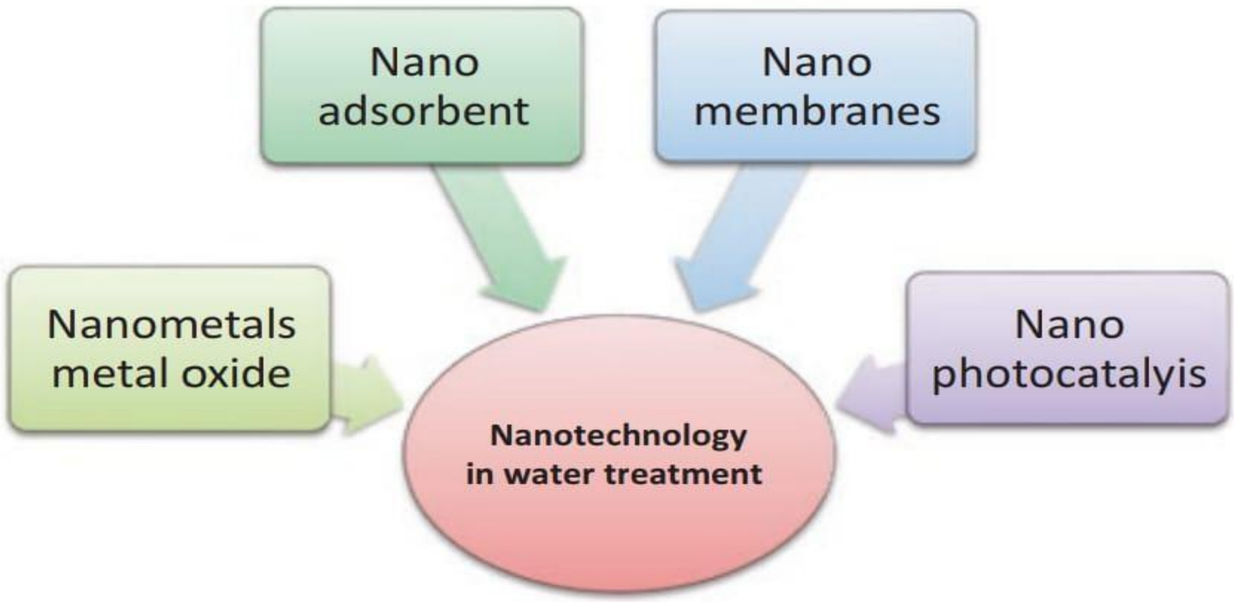


Figure 4: Nanomaterials used in Nanotechnological processes for waste water treatment.

These nanomaterials are classified into different categories because every nanomaterial have its own unique properties and functionality like some can destroy contaminants in the presence of light (photocatalysis) or some can isolate all these contaminants from water (like filteration by nano membrane or passing through a nanotubes).

II.1. Nano-adsorbent

Adsorption is a physio-chemical process that is using for removing contaminants from the waste water. Waste water treatment by adsorption is based on adhesive capacity of absorbent which attract the contaminants on its surface by adsorption technique and basically used to remove and separate of inorganic pollutants mainly heavy metals.

Nano-adsorbents are novel and they have high rate of adsorption for eliminating organic and inorganic pollutants.

There are three types of carbon nano-adsorbents which have high adsorption capacity.

(i) Carbon nano tubes (CNTs)
(ii) Polymeric nano-adsorbents
(iii) Zeolites

Among all the three, in this paper study about carbon nanotubes (CNTs) as a nano adsorbent.

II.1.1. Carbon Nanotubes (CNTs)

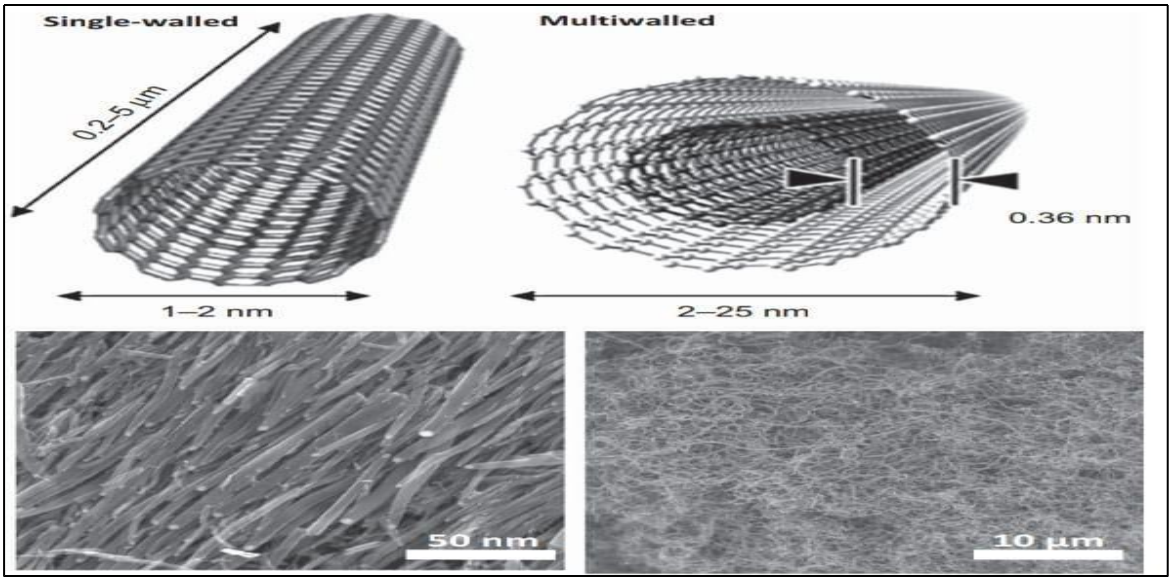
Carbon nanotubes (CNTs) is a type of carbon nanomaterial which act as a great adsorbent due to it's unique properties such as chemical stability, thermal stability and mechanical strength. Nowadays, water is being polluted highly due to industrialization because industry waste contains many heavy toxic metals which dumped into the water, so removal of all these heavy metals is biggest challenge and a serious concern.

To overcome this problem, carbon nanotubes give best solution to remove heavy toxic metals because of it's high adsorption capacity. Even carbon nanotubes show very much high adsorption capacity than that of activated carbon (AC).

Carbon nanotubes shows great potential to remove heavy metals such as zinc (Zn), Cadmium (Cd), lead (Pb), Arsenic (As) and many more. CNTs play an important role to remove of some organic salts, toxic dyes and heavy metals from waste water and make the water clean and safer to drink.

II.1.2. Types of CNT sandit's structure

Carbon nanotubes (CNTs) are man made nanomaterial which is made by rolled up of graphene sheet into cylindrical shape.



ure5: SWCNTs (Top Left) and MWCNTs (Top right) and SEM picture of SWCNTs (Bottom left) and MWCNTs (Bottom right).

cally,on the based of number of layers of graphene sheet there are two types of CNTs

(i) Single-walled carbon nanotubes (SWCNTs)

(ii) Multi-walled carbon nano tubes(MWCNTs)

SWCNTs consist of single graphene sheet wrapped into cylindrical tube with diameter 1-2 nm, where as in MWCNTs consist of array of concentric cylinders with outer diameter 2 -25 nm and inner diameter 0.36 nm (**Figure 5**).

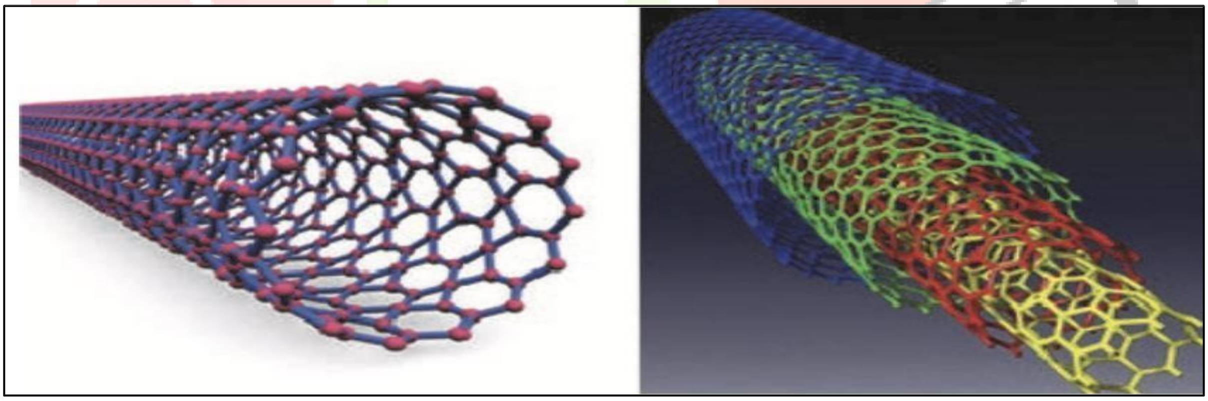


Figure6: SWCNTs (Left) and MWCNTs (Right).

II.1.3. Synthesis methods of Carbon nano tubes (CNTs)

There are basically three commonly used methods for synthesis of CNTS areas follows:

a) Arc discharge
b) Chemical vapour deposition (CVD)
c) Laser Ablation

In all these synthesis methods CNTs produce by using carbon as source and energy.

Laser Ablation and Arc discharge method used to produce only small quantities of CNTs so CVD is most likely method to produce CNTs in bulk and this method prefer globally.

In CVD method, CO & hydrocarbon gases used as carbon sources at 500°C-1000°c temperature and this temperature carbon deposited by decomposition of carbon sources and shaped into CNTs.

Catalyst particle's size also play an important role in deciding CNTs diameter. If particle size small so produce SWCNTs and larger particle so produce MWCNTs.

- **Characterization of CNTs by Fourier Transform IR spectrometer**

FTIR spectra of CNTs and functioned CNTs can see in **Figure 7.** The sample for characterizing passes through Infrared radiation and the sample absorb radiation of specific energy or specific functional group absorb specific energy determine.

CNTs shows a characteristic band at 1600 cm^{-1} correspond to aromatic rings (C=C) bond stretching. Sometimes, peaks at 3800 to 3200 cm^{-1} correspond to O-H bond stretch and 1700 cm^{-1} for O-H bond bending that's how absorb moisture into atmosphere.2910-2940cm^{-1}band correspond to vibration of C-H bond stretching of methylene (CH_2) group (**figure 7a**). A new peak appeared at 1450cm^{-10}

Correspond to bond stretching of CH_2 bending which shows that defect in structure of CNTs (**figure 7b**). A peak appeared near to 1735 cm^{-1}assign to correspond stretching of a carbonyl bond of carboxylic acid and a double bond peak appeared at 2900 cm^{-1}which shows loss in aromaticity due to oxygen functional groups (**figure 7c**).

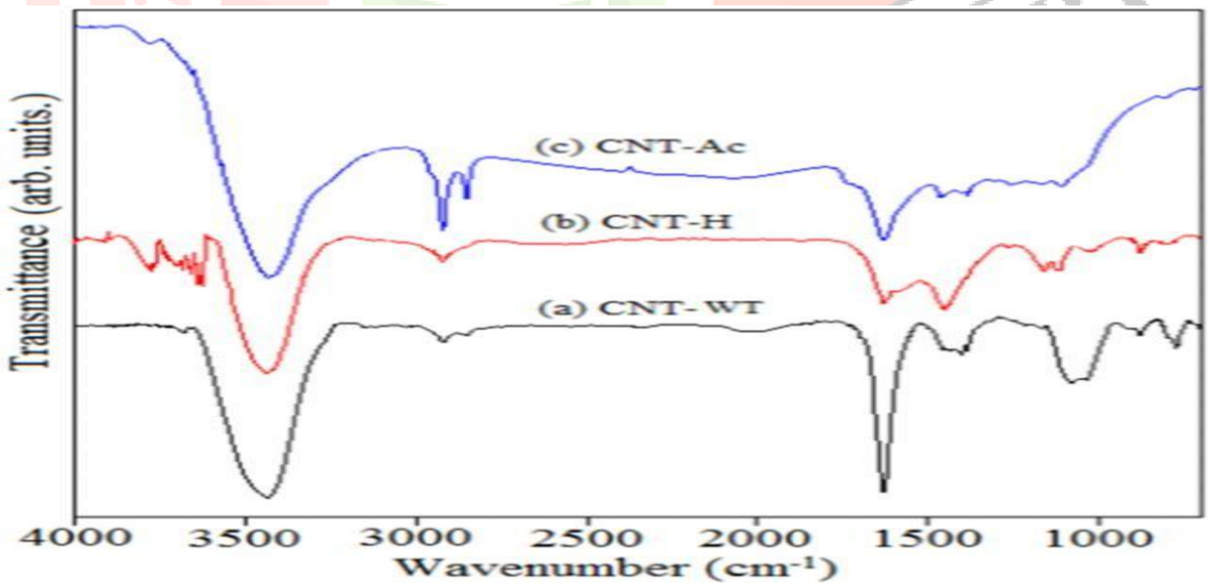


Figure 7:(a) FT-IR Spectra of CNTs (b) and (c) FT – IR Spectra of functionalized CNTs.

II.1.4. Waste water Purification by CNTs

Nowadays, waste water contaminants removal is the major concern became that effect the water quality. The contaminants such as heavy metal ions, organic pollutants (1,2 dichlorobenzene, dioxin) etc. found in waste water which are highly toxic and carcinogenic and non-biodegradable in nature which surely affect to human health and their lifestyle.

A highly effective, adsorbent which is CNT that can effectively remove the contaminants especially heavy metal ions and organic pollutants from waste water compared to powder or granular activated carbon. The use of activated carbon (ACs) for treatment of waste water lacks in some parameters like has poor adsorption capacity and mainly regeneration issues.

CNTs is a third-generation carbonaceous adsorbent. It has a good adsorption capacity because of its layered and hallow flexible structure. CNTs has four adsorption sites for the adsorption of water contaminants (**figure 8**).

(a) Interstitial channel
(b) Inner CNT holes (Internal site)
(c) Grooves site.
(d) Outer surface CNT (External site)

Interstitial channels is help to trap small contaminants depends upon the form of nanotube. SWCNTs generate more interstitial channel, because of aggregation effect and aggregation effect reduce the groove sites. The outermost surface and groove site of CNTs are very useful for adsorption of both organic and inorganic contaminants. SWCNTs has poor volumes of internal site when compared to MWCNTs. Interstitial channels are useful for treatment of waste water contaminant of diameter <1nm such as helpful in adsorption of aromatic hydrocarbons but inner region of CNTs has least adsorption tendency.

Adsorption effect of CNTs depend on the functional group attached with it. CNTs is hydrophobic in nature so if hydrophobic and non polar organic contaminants present in water it show better adsorption capacity but if functionalized the CNTs by different functional groups the hydrophilic nature of CNTs increase by H-bonding and vander walls interaction and now it can interact with contaminants which is polar in waste water.

For any organic molecule (contaminants) to be fit in the distance between the layers of CNTs the distance between layers is so small and due to vander waals interaction CNTs aggregate together that's why the interstitial and inner pores are not available for adsorption and external and groove region is available and show good adsorption for any contaminants present in water.

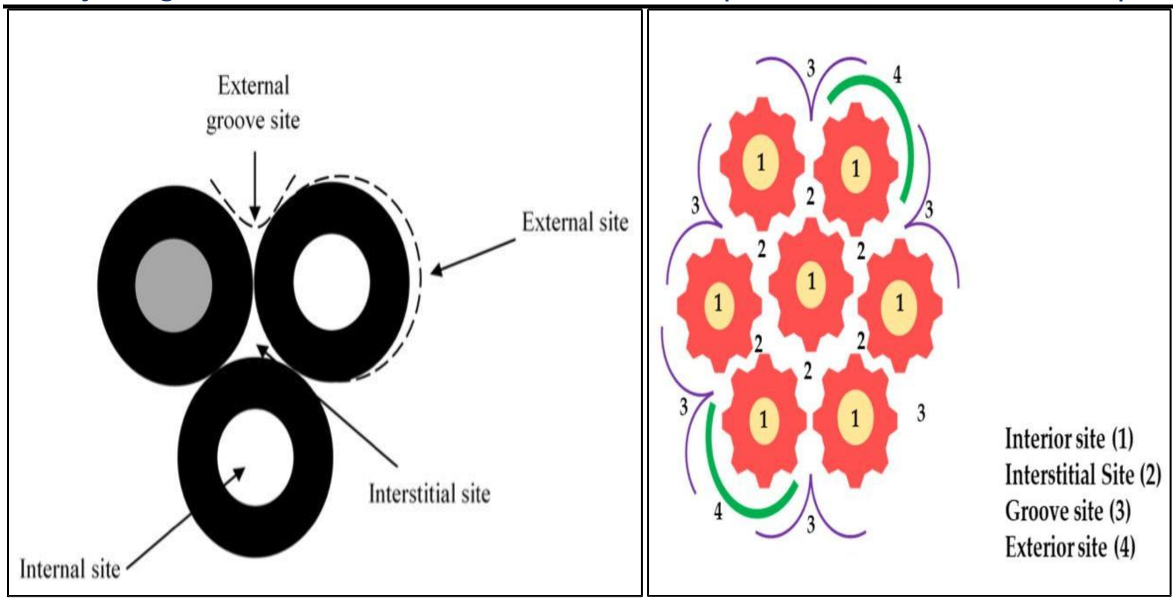


Figure8: Different Adsorbtion sites of CNTs.

There are many types by which we can functionalized CNTs for different waste water system are as follows:1) Oxidation: This is most widely used method if want to introduce hydroxyl, carbonyl or carboxyl groups on CNTS. This method help to increase the hydrophilic properties and adsorption capacity for some contaminants.

MWCNTs effectively oxidized by using of 4M H_2SO_4, 1M H_2O_2 mixture and introduce -OH, -COOH, -C-O, -C-C or -C=O on MWCNTs and make them oxidized MWCNTs which show various properties like H- bonding, vander walls forces and π–π interactions.

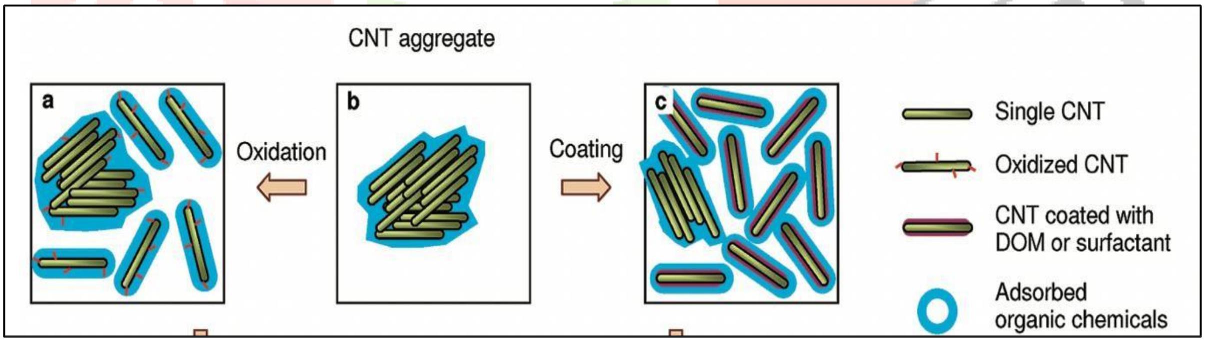


Figure9:(a) CNTs aggregation after oxidation (b) CNTs aggregate (c) CNTs coated with surfactant aggregation.

Table2: Molding process of CNTs as adsorbents

Name	Process	Group introduced onto CNT	Ref
Oxidation	O-MWCNTs oxidised by H_2SO_4/HNO_3 mixed acids. o-MWCNTs oxidised by nitric acid and citric acid.	Oxygen containing functional groups Carboxylic group	[17]
Biologicalization	MWCNTs prepared by decorating. glycine on/ functionized CNTs. MWCNT prepared by amino-functionalizing as made magnetic MWCNTs	Amino group and hydroxyl groups. Carbonyl groups, hydroxyl and amino groups.	[18]

CNTs serve as both organic, and inorganic contaminants adsorbent. CNTs has hydrophobic character due to made up of pure carbon which make it extraordinary water transporters. Due to hydrophobicity nature of CNTs they are weakly interact with water molecule and provide frictionless and high flow rate to water and functionalized CNTs attract to contaminants and allow to water to flow. CNTs functionalized with zwitter ionic groups (positive charge as well as negative charge.) increase the water flux rate from 6.8 to 28.7 GFD because zwitter ions along with CNTs walls create new water transport channel.

Figure10 showing when waste water treated with CNTs, 90% organic waste water meet the standard in just one-stage of adsorption. Then, in second stage of adsorption 9% waste water standard condition meet of waste water. Now, only 1% highly concentrated organic contaminants left which can recycle as product and further oxidise to become a gas. Organic contaminants are the source of carbons can be use to prepare CNTs further by chemical vapour deposition method (CVD).

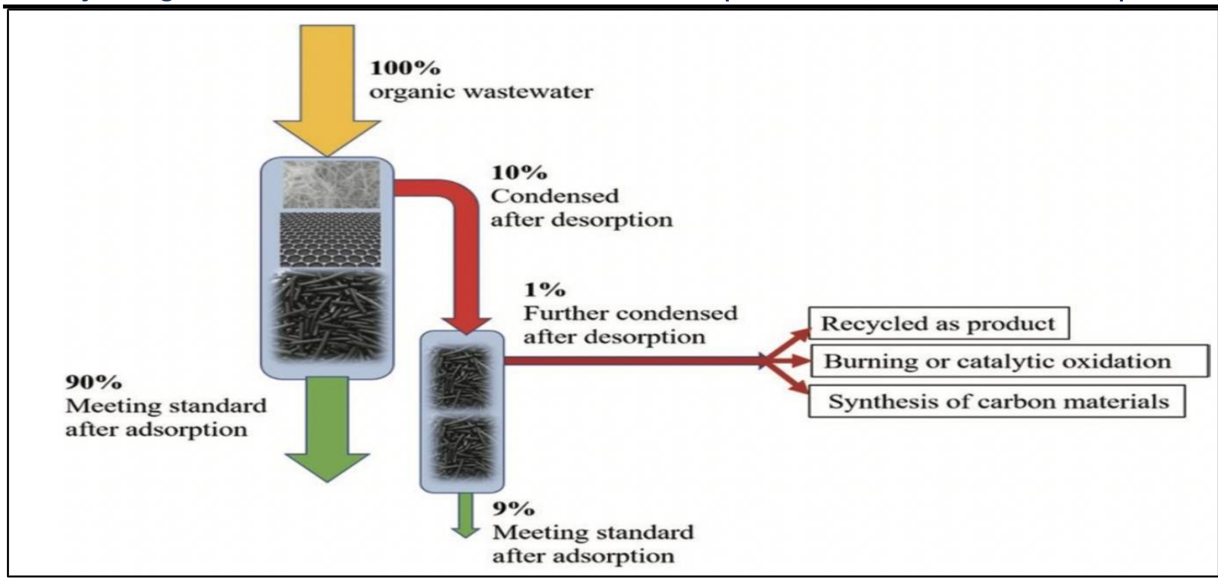


Figure10: Flow direction of organic waste water after being treated with CNTs.

Table3: Removal of heavy metal ions from aqueous samples by functionalized CNTs.

Adsorbate	Absorbent	pH	Removal Meachnism	Comment	Ref
As(III)	MWCNTs	6	Ion exchange	Removal of As(III) was upto 13.5 μg/L	[20]
Pb(II)	Magnetic MWCNTs	6.5	Electrostatic	High removal due to intrinsic properties and porous structure	[21]
Zn(II)	Oxidized MWCNTs	7	Electrostatic Interaction	Small diameter of CNTs greater amount of Hg(II) ions remove	[22]
Ni(II)	MWCNTs Modified	6.5	Electrostatic Interaction	Removal efficiency increase as the mass of MWCNTs increase	[23]

Table4: Removal of organic pollutants dyes from waste water by using functionalized CNTs.

Adsorbent	Dye Pollutants	Removal%	Condition	Ref
Oxidized SWCNTs	Basic red (BR 46)	-	pH-9, 298K Contacttime100 min	[24]
HNO3oxidised MWCNTs	mothymol Blue	**97**	pH=1,293.15K IC=30 mg/L	[25]
Functionalized CNT	Congo red	94	pH=7 Contact time =75min	[26]
Functionalized CNT by TiO2	Methyl orange	100	pH=6.5,298 K Contact time =30min	[27]

II.2. Nano metal oxides

MONPs (metal oxide nanoparticle) there are made up of purely with metal as reactant. The shape and size of metal nanoparticle play an important role in their properties. Metal oxides having nano-sized have many properties like high removal capacity, selective for heavy metals, can act as adsorbent for heavy metals and all these properties are favourable for treatment of waste water. Nanometals oxides show some unique properties which may helpful in the treatment of waste water (**figure 11**). There are lots of nano metal oxides which shows different properties such as magnesium oxide, aluminium oxides, zirconium oxides, iron oxide, zinc oxide and many more.

But, here in this paper we discuss only two types of nano-metal oxides which used in treatment of waste water.

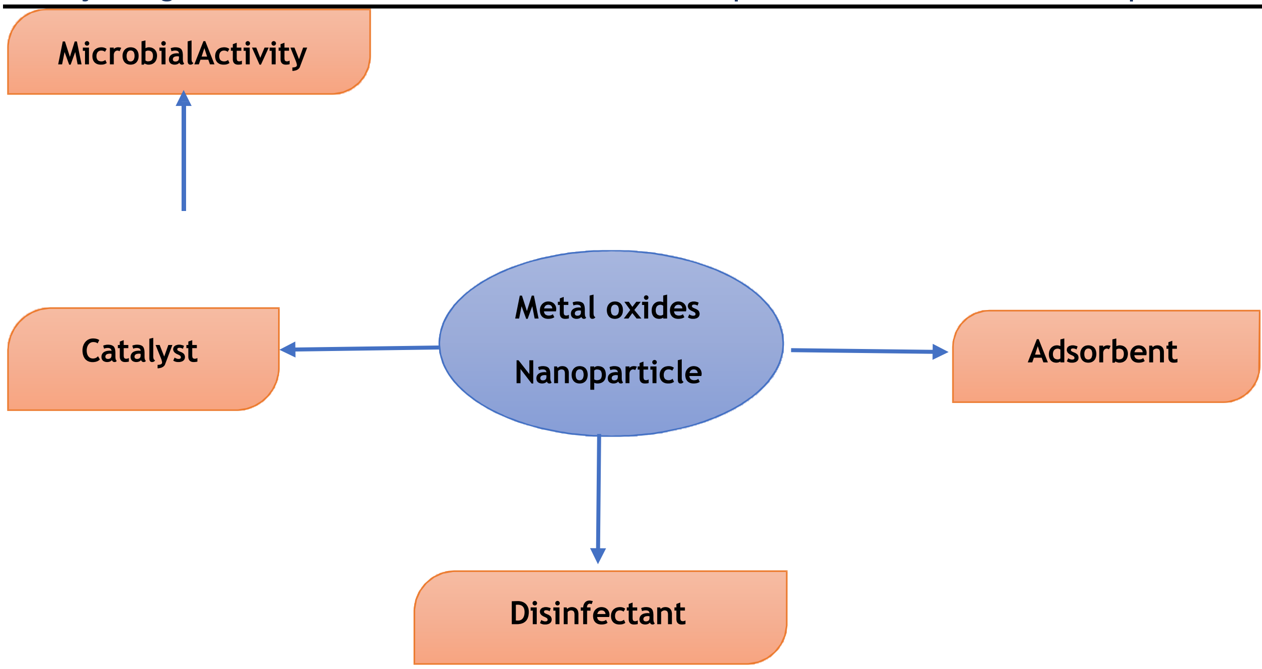


Figure11: Metal oxides nano particles properties useful in waste water treatment.

II.2.1. Iron Oxide Nanomaterials

Iron-oxide nanomaterials have gained a lot of attention in removing various contaminants from waste water because of their special properties like small size, high surface area, high porosity & good magnetic property. Iron oxides are biocompatible and iron oxide nanoparticles also show a super paramagnetic behavior. The super paramagnetic is a type of magnetism which seems in small ferromagnetic nanoparticles.

Iron oxide nanoparticles are easily undergo to agglomeration in aqueous solution. Due to the existence of hydroxyl groups on the surface of iron oxide nanoparticles, hydrophilic interaction takes place between particles and they aggregate which results in the formation of large clusters. This decreases the stability and reactivity of nanoparticles. For the formation of ferrofluids iron oxide nanoparticles should be stable. Basically against aqueous medium. biological medium and magnetic field ferrofluids are being stable. This stability problem could be solved by the surface modification technique. In this technique, coupling agents like silane coupling agents are most familiar attached to the surface of iron oxide nanoparticles gives many functionality on the surface of iron oxide nano particles which creates hydrophobicity around the surface of iron oxide nanoparticles this prevents the aggregation of iron oxide nanoparticles in aqueous solution.[30]

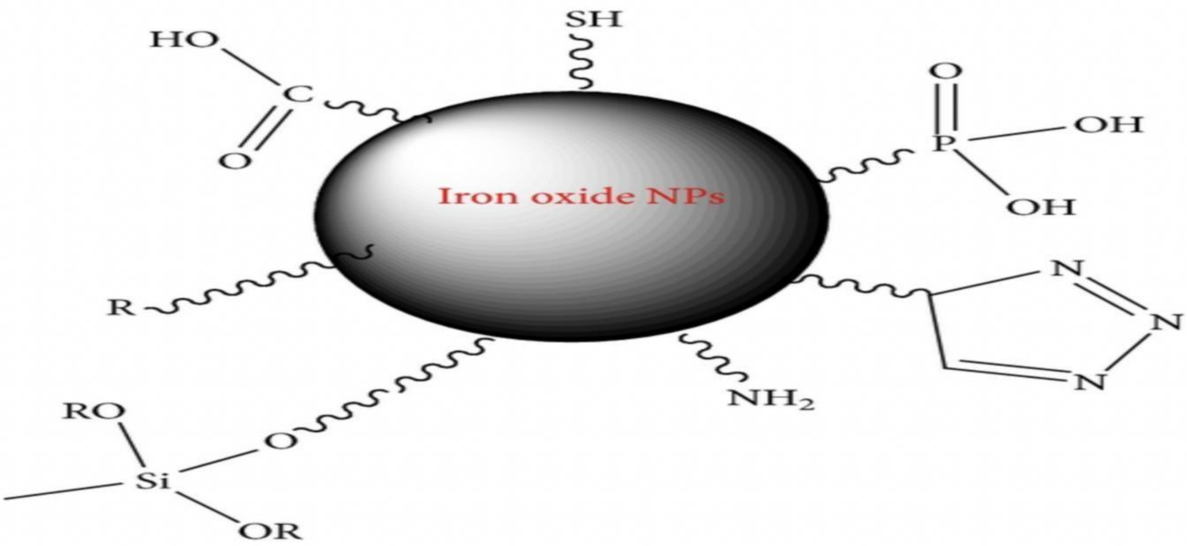


Figure12: Surfacemodification ofironoxidenanoparticles.[30]

Iron oxide nanoparticles exist in many forms such as magnetite (Fe_3O_4), hematite (α-Fe_2O_3)& maghemite (γ-Fe_2O_3). Synthesis of these iron-oxide nanoparticles can be done by three methods such as physical, chemical and biological.[31]

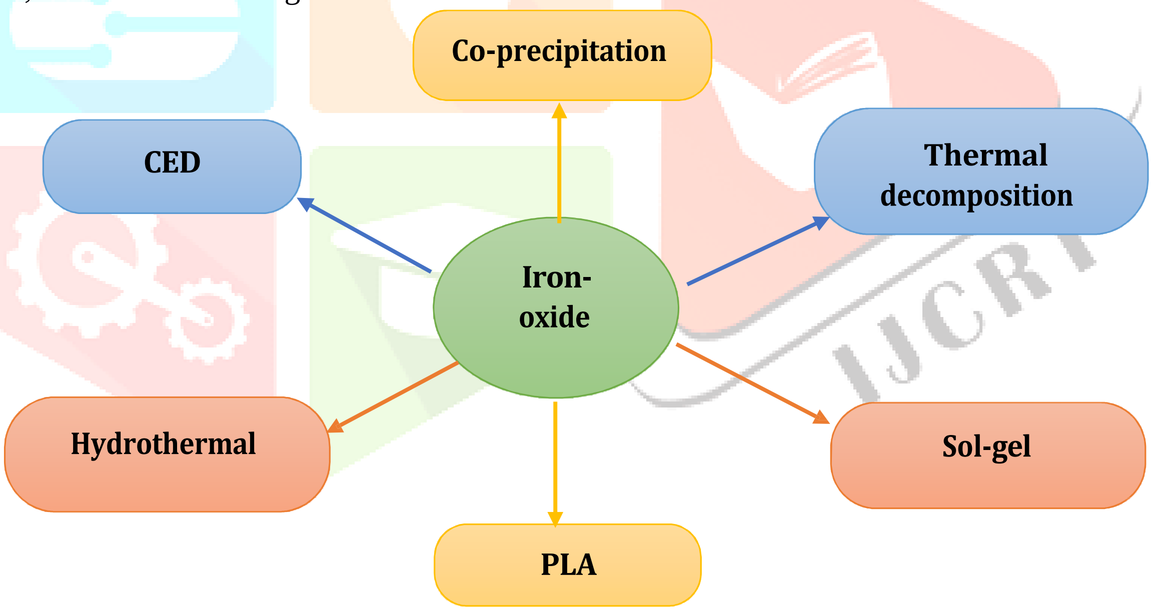


Figure13: Major techniques used for synthesizing iron oxide nanoparticles.

Among all these methods for bulk production of iron oxide nanoparticles chemical methods are being most efficient and from the chemical methods, co-precipitation is most relevant for producing iron oxide nano particles because this method has low cost, produce large amount of material with high purity, control over size particle b/w 2-20 nm and this process doesn't involve the use of any harmful solvent.

In this method, mixture of ferric and ferrous salts are taken in 2:1 stoichiometric ratio in aqueous solution in presence of base.

II.2.2. Ironoxidenanomaterialsin wastewatertreatment

In recent years, iron oxide nanomaterials are the most promising alternative for waste water treatment because of their non-toxicity, chemical inertness, strong adsorption capacity, reusability & easy separation.[30]Iron oxide nanomaterials are capable of removing all the harmful contaminants from water. Iron oxide nanomaterials can be easily separated from the waste water due to having strong magnetic property and they can be reuse for another application. Iron oxide nanomaterials do not harm the human health and environment. Iron oxide nanomaterials possesses all the important properties which is needed for waste water treatment application.

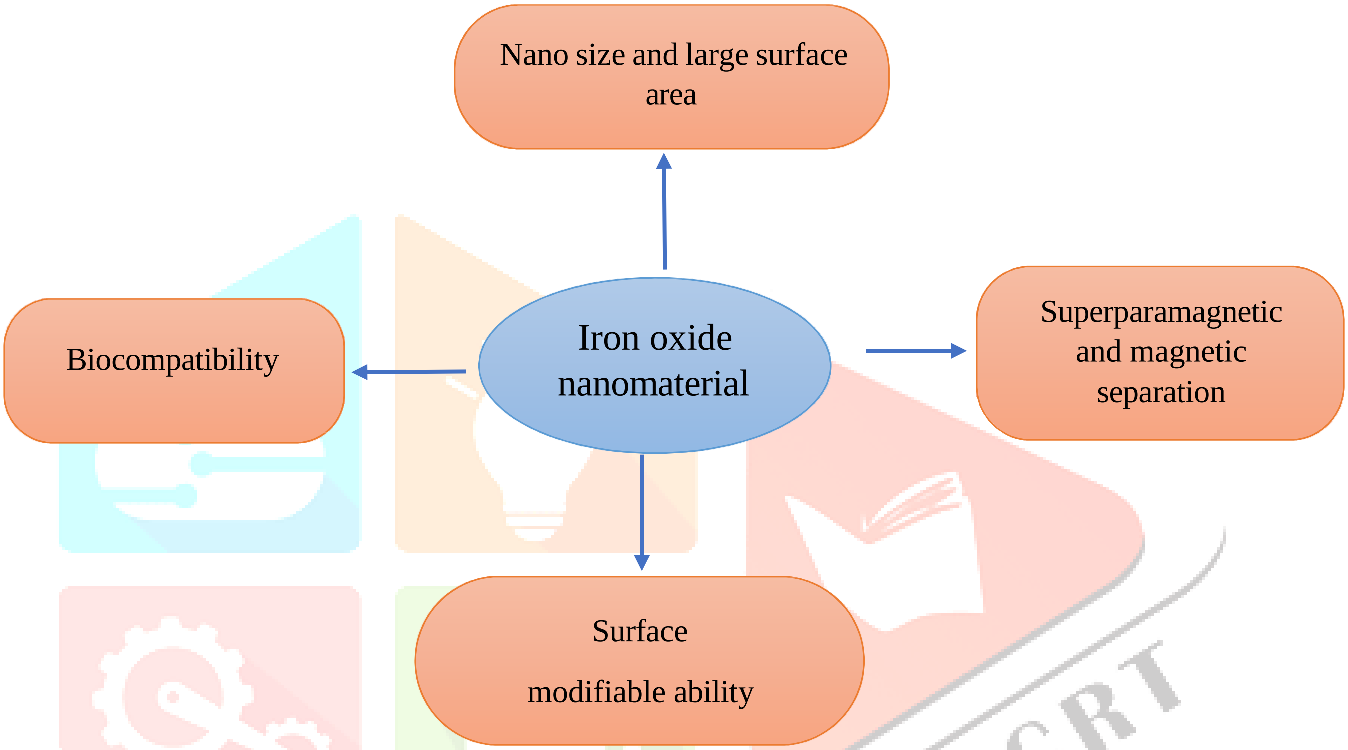


Figure14: Important properties of iron oxide nano particles for waste water treatment application.

For the remediation of water four important characteristics should be possessed by an adsorbent in accordance with research report including 1) high reactivity 2) high porosity 3) capability to remove contaminant 4) no toxicity. Silver nanoparticles effectively remove the contaminants from the wastewater because it shows high reactivity and adsorption efficiency but silver nanoparticles are very expensive. Thus in spite of having these properties cost is considered as another important factor which plays a significant role in applications of the material. These criteria is fulfilled by some of the magnetism is another important physical property that plays a significant role in water purification. Basically, it affects the physical properties of contaminants in water. This property makes the separation simpler. Thus adsorption efficiency combined with magnetic separation widely use in waste water treatment. From the last few years nanomaterials have received a lot of attention in water purification due to its properties which is necessary for water purification. Magnetic nanoparticles can be also used in wastewater treatment because they also possess properties such as small size, large surface area, high porosity and superparamagnetic. Magnetic nanoparticles remove the heavy metals, natural organic matter, inorganic and organic pollutants, nitrates and fluoride from the wastewater.

II.2.2.1. Removal of dyes from water by using iron oxide nano materials Dyes are organic chemicals widely used in textile, pulp, plastic, medicine industries. These dyes are highly toxic and carcinogenic in nature.

When these dyes are thrown into water without proper treatment it can generate a large amount of colored, toxic and carcinogenic waste water that causing a serious risks to aquatic life. This is also harmful for human and animals. Dyes are non-biodegradable means they do not decompose naturally. They are not removed from water by using waste water treatment techniques and traditional methods like ultra filtration, chemical & electro chemical methods. In recent times, iron oxide based nanoparticles have shown extensive adsorption properties for removing dyes and other pollutants from water bodies. Iron oxide. based nanoparticles degrade the organic pollutants by photocatalytic degradation technique. It is a safe and effective technique for the removal of pollutants from water.

For example: **Removal of methylene blue dye from water**

Methylene blue dye is heterocyclic aromatic compound ($C_{16}H_{18}N_3SCl$). It is a dark green colour powder. When this dye is dissolved in aqueous solution it forms a blue colour solution. It is a safe dye at a dose of <2 mg/Kg but when its level exceeds 7 mg/Kg. It can cause serious effects such as when serotonergic agent combines with methylene blue dye at a dose of 5 mg/Kg. It can cause a serious serotonin syndrome. Thus it is necessary to remove this dye from water. For the removal of these dyes from wastewater iron oxide based nanomaterials are used. The photodegradation of methylene blue was done by using iron oxide nanocomposite which were prepared by co-precipitation method using iron oxide, activated charcoal and silver. The optimization of dye degradation property of Fe-AC-Ag nanocomposite is done by photocatalytic degradation technique.

Optimization of methylene blue dye degradation

3 ml of dye sample is taken in 5 test tubes. Iron nanocomposite of different concentrations such as 20, 40, 60, 80, 100 mg are being treated with each of test tubes containing dye sample. Initially at 610 nm, before treatment with iron oxide nanocomposite the optical density of dye sample was found to be 0.316. It was found that the required minimum concentration of iron nanocomposite for the degradation of dye is 40mg. The optical density of dye sample which containing 40 mg concentration of iron nanocomposite is 0.05. After getting the optimum nanocomposite concentration mixture of 4 ml dye sample and 40mg of iron nano composite is taken in a test tube. Then optical density is different time such as 5, 10, 15, 20 & 25 second. After performing this experiment it was found that at 25 second calorimeter shows the lowest value of optical density i.e. 0.018. Before treatment with iron oxide nanocomposite the optical density of dye was 0.316 but after treatment with iron nanocomposite this value decreases due to degradation of dye molecule by photocatalytic degradation technique of iron nanocomposite.[32]

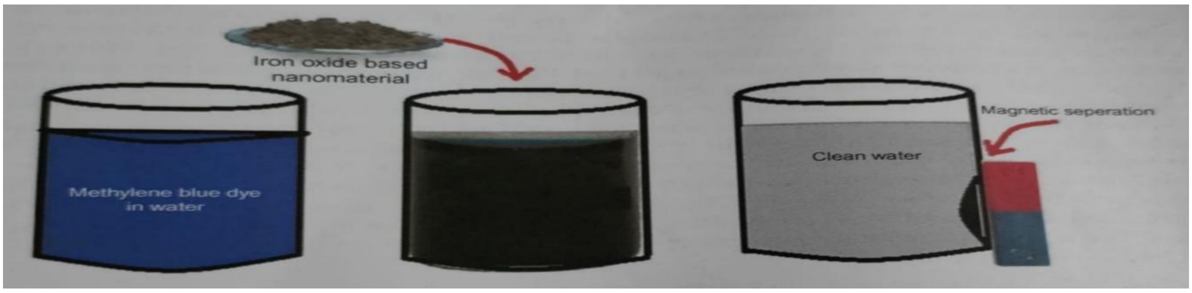


Figure15: Adsorbtion of methylene blue using iron oxide nanomaterials.

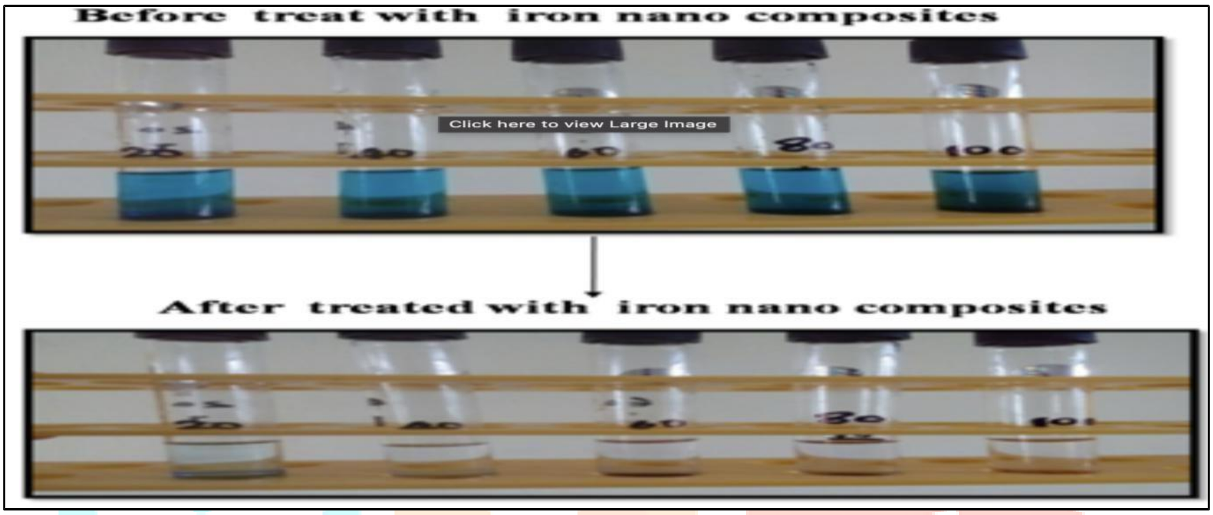


Figure16: Degradation of methylene blue dye by using iron oxide nano composite.

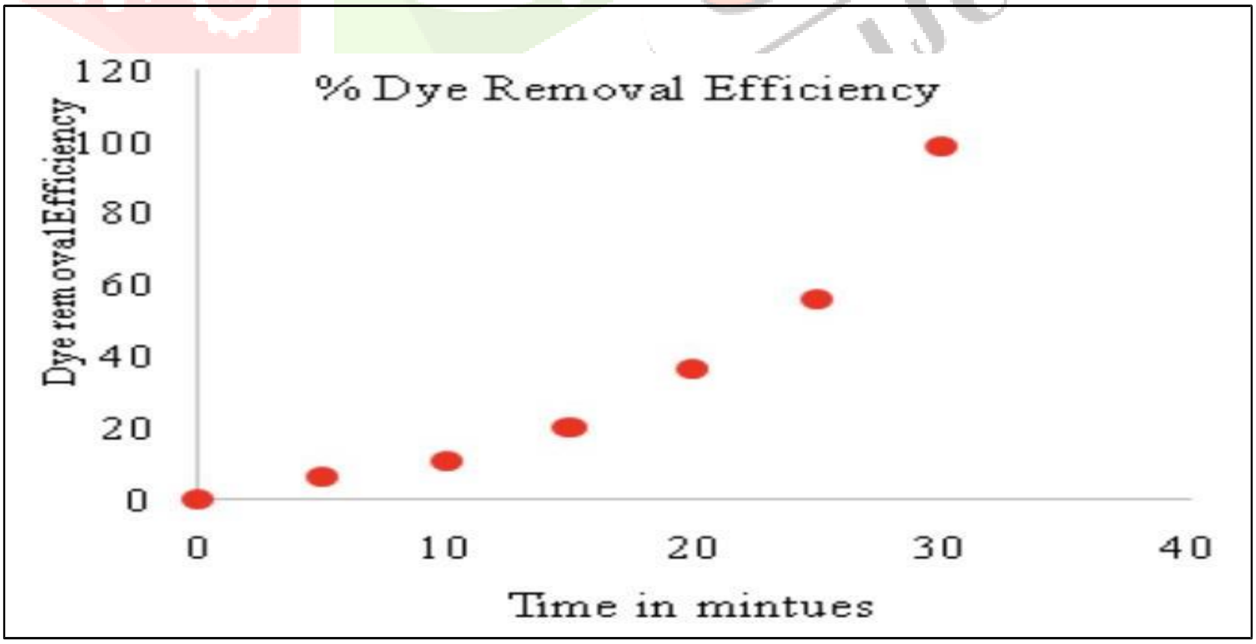


Figure17: Efficiency of decolouration of dyed water with iron oxide nano composite.

Dye removal efficiency (%) = [1-Ct/Co]*100.[33] Co =intial pollutant concentration

Ct= concentration of pollutant after time t

Table5: Removal of dyes by using iron oxide nano materials as nano adsorbents.

Iron oxide nanomaterials as Nano adsorbents	Dyes	Key finding	Reference
ORMOSIL-Fe_3O_4 RGO Composite	Rhodamine dye B	Adsorption capacity was found to be 1339mg/g	[34]
Mn- doped Fe_3O_4nanoparticles coated with activated carbon.	Malachite green& brilliant green	At pH 7 removal efficiency for malachite green and brilliant green was found to be 99% & 99.50%. Highest adsorption capacity was observed 87.566mg/g and 101.215 mg/g for malachite green and brilliant green.	[35]
Flower like iron oxide nanostructures	Orange Dye II	43.5 mg/g removal capacity was achieved	[36]
Iron oxide trapped activated carbon	Methyl orange & methylene blue	10nm nanoparticle size helped to attain 42.2 emu/g saturation magnetization & 99% removal efficiency.	[37]

II.2.2.2. Removal of Organic pollutants by using iron oxide nanomaterials

From the last few years, Water pollution is becoming one of the serious problem. Many harmful pollutants such as inorganic and organic pollutants, Dyes and heavy metals are present in water therefore treatment water is so important. Recently, mesoporous iron oxide carbon nano composite used fast adsorption for removing 2, 4-dichlorophenoxyacetic acid showed the removal efficiency upto 97% in a period of 5 min of treatment. Iron oxide- graphene nanocomposite used for removing 1-naphthol and 1-naphthyl amine. It showed maximum adsorption capacity of 625 mg/g and 528 mg/g for 1-

naphthylamine and 1-naphthol.

Using iron oxide nanomaterials as nano adsorbents has gained a lot of attention in the removal of organic pollutants. This is the research summary of removal of organic pollutants by using iron oxide based nanomaterials.

Table 6: Removal of organic pollutants from waste water by using iron oxide nanoparticles.

Iron-oxide based nanomaterials	Organic pollutants	Key finding	Reference
Iron oxide/sodium dodecyl sulphate nanocomposite	Safranin dye	Highest removal capacity obtained was 769.23 mg/g	[39]
Iron oxide – graphene nanocomposite	1-naphthylamine&1 naphthol	Maximum adsorption capacityof625&528mg/g for 1- naphthylamine and 1-naphthol were obtained	[40]
Fe3O4/C magnetic nanoparticles	Crestline red & methylene blue	Adsorption capacity of 11.22 & 44.38 mg/g for cresol red & methylene blue were obtained	[41]
Mesoporous iron oxide carbon nanocomposite	2,4-Di chlorophenoxyacetic acid	97% removal efficiency was obtained in a period of 5 minor treatment	[42]

Immobilization of biomass on the surface of iron-oxide nanomaterials have shown the great potential in the removal of various pollutants. Because macro and microbial biomass showed an extensive adsorption capacity. Immobilization of biomass on the surface of iron oxide nanoparticles increases the activity and properties of iron oxide nanoparticles. These adsorbents have shown the efficient removal efficiency for example- Immobilization of Saccharomyces cerevisiae on the surface of magnetic nanoparticles coated with chitosan have been used for the removal of Cu (II) from waste water. 90% removal efficiency was obtained within 20 min & the 134 mg/g adsorption capacity was achieved.

II.3. Nano-photocatalysis

Metal nanoparticles and metal oxides are act as good catalyst in oxidation reacting Metal oxides show strong catalytic activities by which a highly complex pollutants molecules in waste water oxidised and form less toxic as simpler products. Nanoparticles exhibit all their types of behaviour because of this some unique properties like: (i)Large surface to volume ratio due to very small particle size. (ii) Due to nano size exhibit high reactivity· [4,5]Photocatalysis is the process that occur when a photon adsorb a ultraviolet light where energy is greater than the energy required to overcome the interstitial of two electrons shells that is (Valence Band and Conduction Band) of a semiconductor. It is an oxidation process. In this process, a "hole" created in the valence Band (VB) when a photon brighten on catalytic surface an electron which is of negatively charge excited to empty conduction Band (CB) and create a hole with positive charge. This "e-h" pair (election- hole) responsible for a creating highly reactive radicals and easily react with pollutants molecules and thus break down the contaminants. This process involve the advanced oxidation process (AOP) of organic and inorganic pollutants that are present in waste water.

In **figure 19**, Stage 1 and 2 induce when electron excited from VB to CB shell by absorb photon light. Stage 3 and 4 occur when charge are separated and migration occur from bulk of semiconductor surface and react with adsorb species and Stage 4 and 5 generate when dissipation of energy occur. All these steps occurrence depend on the characteristic of photo catalyst.

There are a wide variety of photo catalytic materials present such as metal oxides like ZnO, TiO_2, CeO_2, Nb_2O_5 etc. In this paper, TiO_2 is discussed which shows best photo catalytic activity in aqueous medium for waste water treatment.

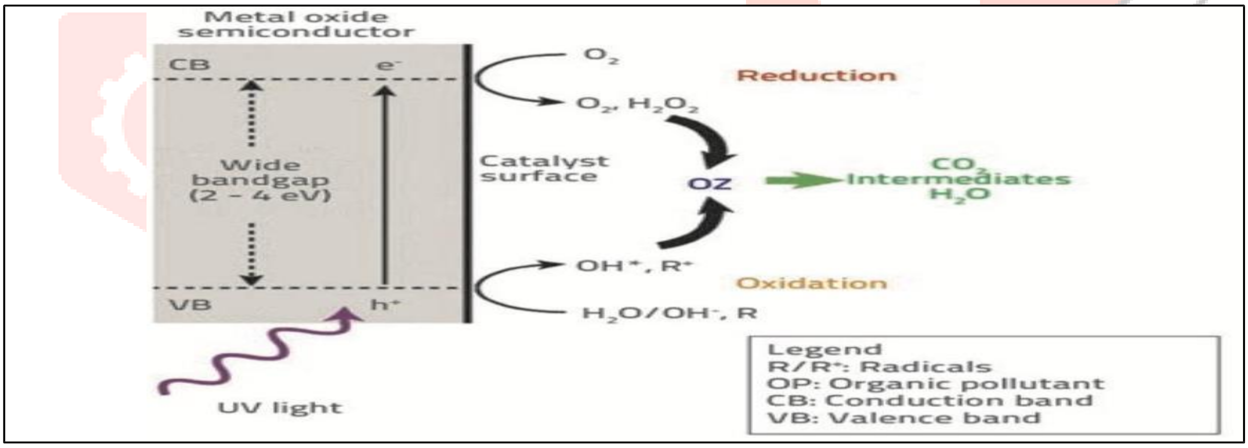


Figure18: Photocatalysis on the surface of nano catalyst semiconductor.

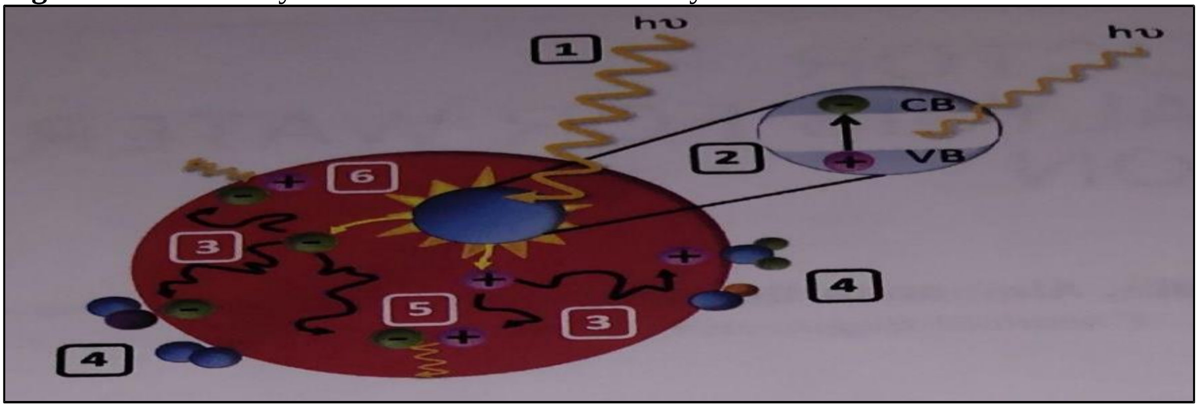


Figure19: Simplified diagram of irradiated photocatalyst particle.

II.3.1. Titanium dioxide (TiO_2) nanoparticles

Nowadays, TiO2 act as a good photo catalyst because of large band gap energy (3.2 eV) and UV excitation change separation between the particles induced, TiO2 as a nano metal oxides has vast use because photostability, high photocatalytic activity, chemical stability and most important is resonable price. las comparable to other metal oxides and having low human toxicity. TiO2 exist in three different crystalline which are as follows:

(i) Anatase

(ii) Rutile (iii)Brookite

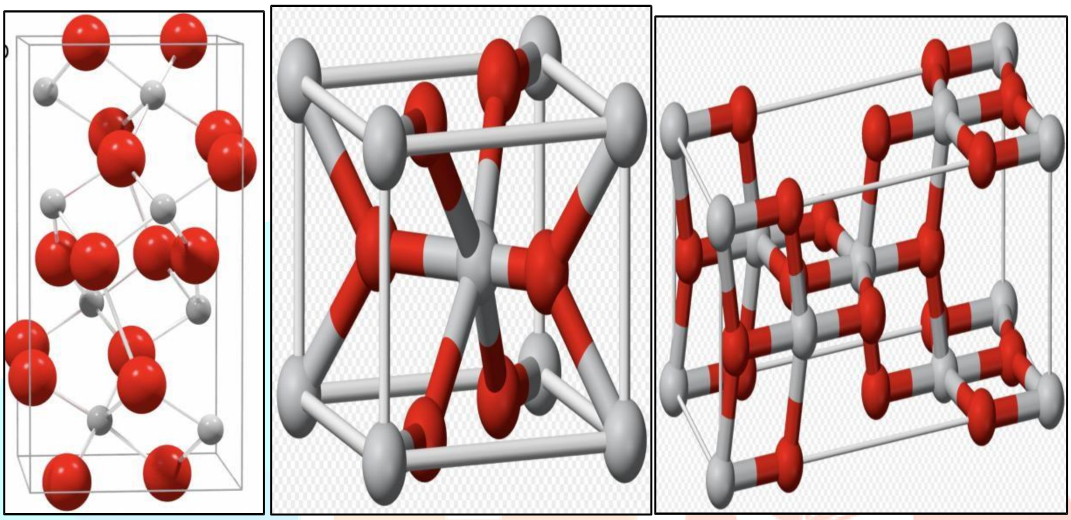


Figure20: Brookite, Rutile and Anatase (from left to right)

Rutile and anatase are the purest from of titanium dioxide which can be synthesized at low temperatures and these two crystalline form preferred for the photocatalytic process. TiO2 nanoparticles can be synthesized by using various different methods (**figure 21**). Due to photocatalytic activities of titanium dioxide, it can be used as in waste water purification. The most important application of titanium dioxide is in the treatment of waste water because they have endless lifetime and on degradation of microorganisms and organic compounds it remains unchanged. The another main importance of titanium dioxide, it has photo – induced hydrophilicity and has high oxidative power which make TiO2 as membrane attractive material.

Synthesizing of Titanium oxide nanoparticles

TiO2 NPs, can produce by using sol gel technique in which take 20 milliliters of titanium tetra isopropoxide added into 240 milliliters of ethanol in bath containers with volume, 1000 milliliters. Solution agitated for approx 30min by magnetic stirrer and for making hydrolysis mixture,10milliliters of distilled water and 8millilitersof HCl mixed by adding dropwise of mixture. Then, reaction mixture stirred and make a homogeneous solution. Solution pH should maintain in acidic medium (pH~5) and allow the reaction. to occur for approx 20 hours, and then gels generated was heated in oven at 300°for dehydration and TiO2 powder form.

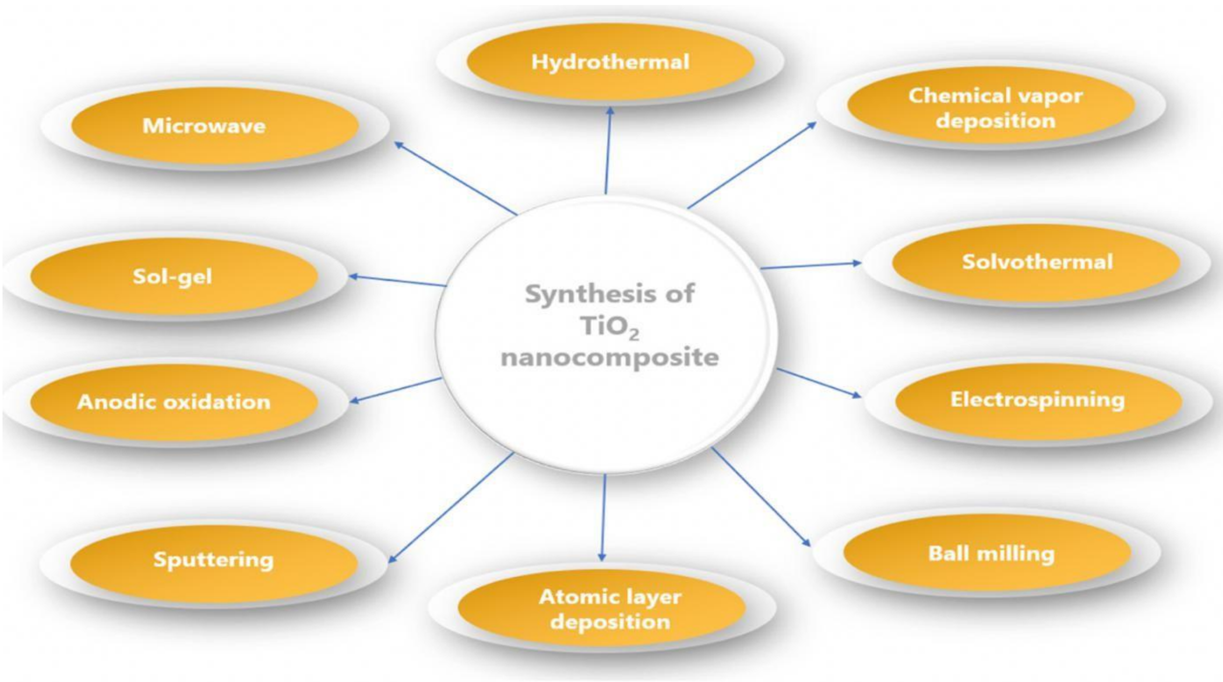


Figure21: Various methods for synthesizing TiO2 nanoparticles.

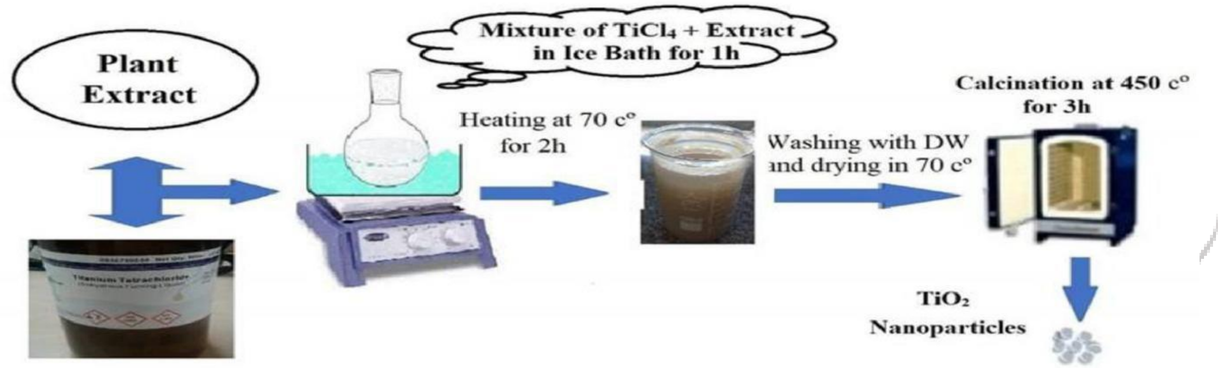


Figure22: Greener way to synthesize TiO2 by using plant extract.

2.3.2Titanium dioxide (TiO2) as photocatalyst in waste water purification

Photocatalysis use an oxygen as its primary reagent at mild conditions. It is a most researchable technology among AOPs (advanced oxidation process). This photocatalytic reaction based on free radical generation in situ by using different methods and techniques such as UV or photocatalysis or both combinations. Photocatalysis can treat many water pollutants such as contaminants of emerging concern(CECs), Endocrine Disrupting compounds (EDCs) and pathogenic gems etc.

Photocatalysis process occur when photon or light with suitable wavelength depends on the energy gap of VB and CB interact with the solid material or semiconductor. After the interaction from the bulk of material charge carriers migrate. If this process occur in aqueous medium the dissolved oxygen present in water can adsorb on the photocatalyst surface and reduced in the form of superoxide free radicals O2- on the other hand holes oxidise to water and hydroxyl anions and produce hydroxyl radical. By protonation superoxide free radical can form hydroperoxyl radicals. These produced oxidant free radical allow to set a pollutants present in waste water as shown in equations below.[33]

$(O_2)_{ads} + e^- \rightarrow O_2^{\bullet -}$ $H_2O + h^+ \rightarrow HO^{\bullet} + H^+$

$OH^- + h^+ \rightarrow HO^{\bullet}$

$O_2^{\bullet -} + H^+ \rightarrow HOO^{\bullet}$

$HO^{\bullet} / HOO^{\bullet} / O_2^{\bullet -} + P \rightarrow$ Oxidized Intermediate $\rightarrow CO_2 + H_2O$ $HO^{\bullet} + H^+ + e^- \rightarrow H_2O$

$HOO^{\bullet} + HOO^{\bullet} \rightarrow H_2O_2 + O_2$ $HOO^{\bullet} + H^+ + e^- \rightarrow H_2O_2$

$e^- + h^+ \rightarrow$ **hv** (heat)

where P: Pollutants

The generation of the oxidant radicals occur when the potential of reactions fall within the band gap between the VB and the CB of the photocatalyst.

TiO_2 act as a best photocatalyst because of its band gap energy & this band gap energy depend on its crystalline phases like for anatase and brookite 3.2 eV whereas for rutile the energy gap is 3.0 eV. Anatase mesoporous show higher photocatalytic activity when compared with TiO_2 thin films.

TiO_2 play a very important role in removing the various impurities from the surface of waste water. For the waste water treatment by TiO_2, just add the TiO_2 powder in the waste water and allow to pass the UV light through it so on the photocatalysis process it work and degrade the contaminants into $CO_2$and H_2O. The treatment of waste water by TiO_2 is very useful because firstly method is highly efficient and contaminants treatment does not produce harmful products and it has photo stability, high photo catalytic activity and no toxicity.

But if TiO_2 use in the powder form difficulty arises that can not recover to it from the water and it has limited adsorbtion capacity which may be the drawback of use of TiO_2. To overcome this drawback of TiO_2 instead of using powder TiO_2 modified TiO_2 used such as if TiO_2 mixed with ferric oxide nanomaterials, the ferric oxide magnetic property provide the magnetic behaviour to TiO_2 and then TiO_2 can be removed or recover from the waster easily by applying strong magnetic field.

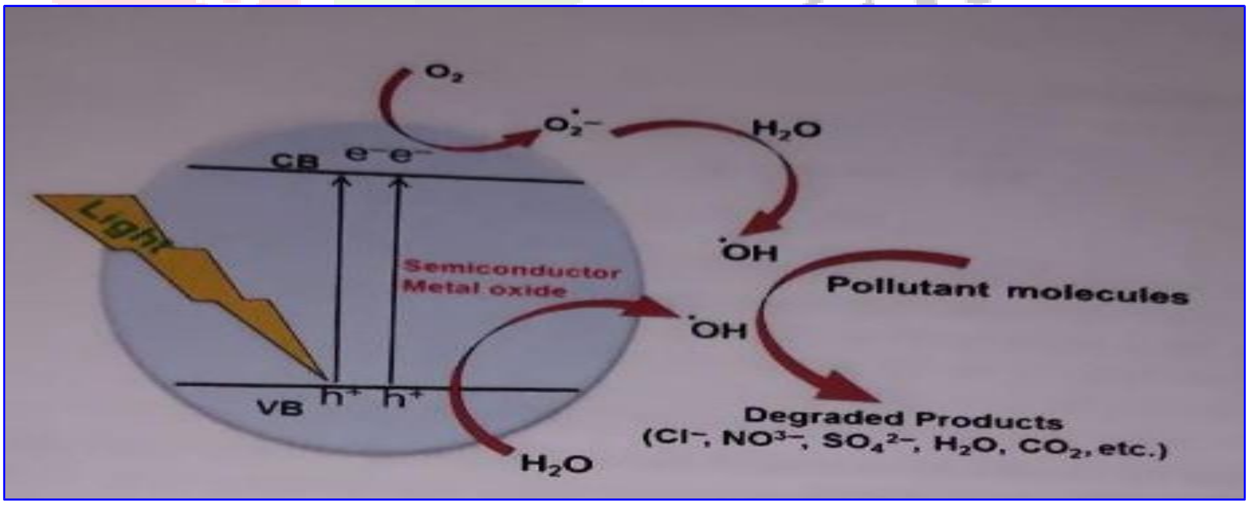
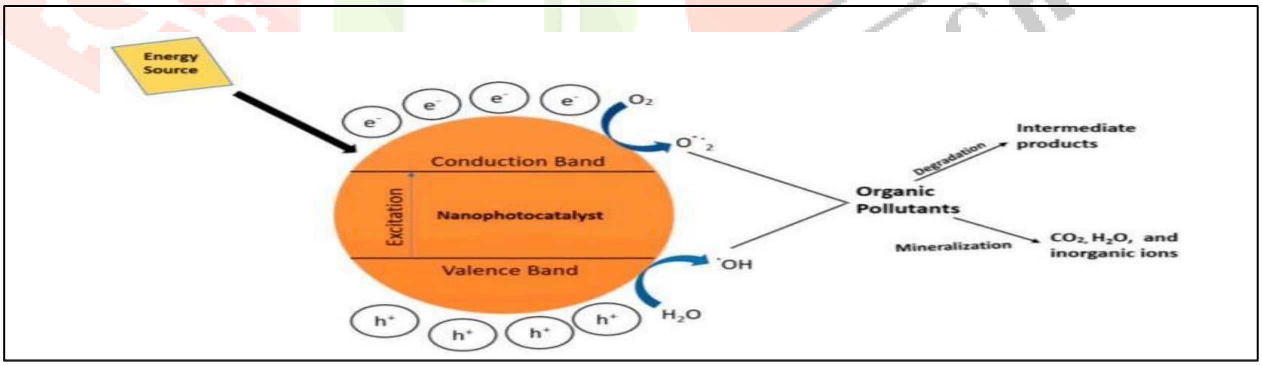


Figure23: Photocatalytic degradation by nanometal oxides.

TiO_2 can use as a waste water contaminants removal substrate. These nanoparticles remove multiples of metals like (Ni, Cd, Cu, Zn, Pb and many more) and also use to remove heavy metals such as(Pb^{2+},Cu^{2+},Fe^{3+},$Cd^{2+}$and Zn^{2+}) from the waste water in the form of residue.

Table7 : TiO2 applications in waste water treatment and its existing methods.

S.No	Application	Characteristics	Reference
1.	Antibacterial activity	Synthesized TiO2 nanoparticles act as disinfection of Eco bacteria and Human pathogens.	[46]
2.	Removal of heavy metal	Absorbtion efficiency of TiO2 for Pb^{2+}=97.6, for Cu^{2+}=75.24andfor Fe^{3+}=79.77	[47]
3.	Removal of Zn(II) and Sr(II) ions	Highest absorption efficiency acheived At pH-8 and if particle size 25nm	[48]
4.	Photocatalytic activity	After UVradiationfor60 min,98% Of 10ppm MO (methylene orange) degraded	[49]
5.	Photodegradation of 4-chlorophenol and phenol	Maximum degradation of chlorophenol 99% for 0.5mM and 97% for 0.5mM for phenol	[50]
6.	Removal of Cr (IV)	Max Cr(total) removal efficiency 99.02% in 60min under sunlight radiation.	[51]



re 24: Mechanism of degradation of toxic organic compounds through nano photocatalysis.

III. Conclusion And Future Prospects

Water is an essential natural resource on this planet. All living things including plants and animals are dependent upon water. Water is necessary for the survival of all living things. From the last few years, water pollution is becoming the critical problem. Many harmful contaminants such as heavy metals, dyes and organic contaminants are present in water that pollutes the water. Polluted water is not appropriate for use. As a result supply of clean and portable water has become a matter of concern. Therefore waste water treatment is very important to improve the quality of water. This research has been done to solve this problem. To improve the water quality, nanomaterials gives best solution like carbon nano tubes act as good adsorbent of heavy metal ions. Iron oxide based nanomaterials effectively removes the heavy metals, dyes and organic pollutants from the water. It can be easily separated from the system due to having strong magnetic property. Therefore it can be reuse for further applications. TiO2 which use for treatment of waste water as photocatalyst degrade most of the contaminants from water and produce non toxic products. All these nanomaterials clean the water effectively in effective cost and these are reusable thus nanomaterials have gain lots of attention by various scientists and governments in recent time. Nanoparticles use in waste water treatment produce less toxic products, environmental friendly can be produce by greener method and mainly cost effective methods due to all these reasons nanoparticles use and development in upcoming years.

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