

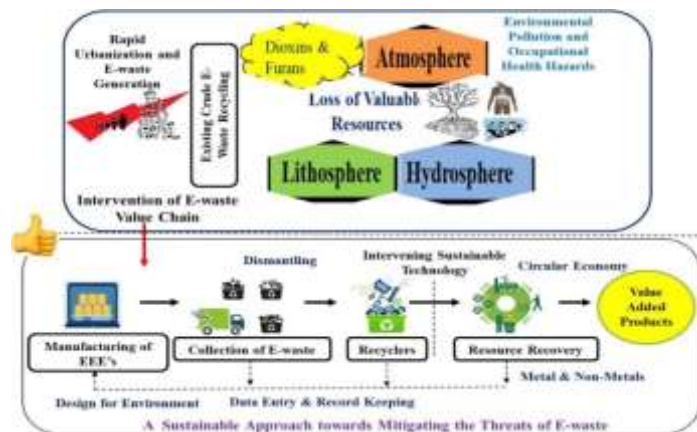
Module 3

E-Waste Management, Water and Nano-technology

E-waste management

Introduction

E-Waste refers to unwanted or unused material generated from the waste of Electronic and Electrical Equipment (WEEE). Alternately, all items of electrical and electronic equipment and its parts that have been discarded by the user as waste without the purpose of re-use or re-cycle is called Electronic Waste.



Sources of E-waste:

E-waste in India is estimated to generate from the following sources

- Large household appliances like refrigerators/freezers, washing machines, dishwashers, televisions.
- Small household appliances which include toasters, coffee makers, irons, hairdryers.
- Telecommunication equipment such as personal computers, telephones, mobile phones, laptops, printers, scanners, photocopiers, headphone etc.
- Electrical apparatus tools i.e. handheld drills, saws, screwdrivers etc.
- Toys, leisure and sports equipment.
- Lighting equipment such as fluorescent lamps, CFL lamps, LED lamps.
- Industrial Laboratory equipment

Types of E-Waste:

E-Waste has been categorised into following types.

Type 1- Major appliances (refrigerators, washing machines, dryers etc.)

Type 2 – Small appliances (vacuum cleaners, irons, blenders, fryers etc.)

Type 3 – Computer and telecommunication appliances (laptops, telephones, mobile etc.)

Type 4 – Consumer electronics (video and audio equipment, musical instruments)

Type 5 – Lighting devices (incandescent light bulbs, fluorescent tubes, gas-discharge lamps)

Type 6 – Electronic tools (drills, saws, gardening devices etc.)

Type 7 – Electronic toys, sports equipment

Type 8 – Medical devices (all medical equipment)

Type 9 – Monitoring devices (detectors, thermostats, laboratory equipment etc.)

Type 10 – Vending machines

Effects of e-waste on environment and human health

The electrical and electronic equipment (EEE) manufacturing sector is rapidly expanding around the world. The dependency on EEE has increased with industrialization, economic expansion, technological development, and luxurious lifestyles.

Effect on Environment

1. E-Waste Negatively Impacts the Soil: First, e-waste can have a damaging effect on the soil of a region. As e-waste breaks down, it releases toxic heavy metals. Such heavy metals include lead, arsenic, and cadmium. When these toxins leach into the soil, they influence the plants and trees that are growing from this soil. Thus, these toxins can enter the human food supply, which can lead to birth defects as well as a number of other health complications.

2. E-Waste Negatively Impacts the Water

E-waste that is improperly disposed of by residents or businesses also leads to toxins entering groundwater. This groundwater is what underlies many surface streams, ponds, and lakes. Many animals rely on these channels of water for nourishment. E-waste can also impact humans that rely on this water. Toxins like lead, barium, mercury, and lithium are also considered carcinogenic.

3. E-Waste Negatively Impacts the Air

When e-waste is disposed of at the landfill, it's usually burned by incinerators on site. This process can release hydrocarbons in the atmosphere, which pollutes the air that many animals and humans rely on. Furthermore, these gases lead to global warming.

Effect on Human health

1. Exposure to Harmful Substances

Every year, over 50 million metric tons of e-waste are produced throughout the world. Workers take whatever measures possible to get rid of that waste, including burning or recovering valuable materials that are still useful, like copper and gold. This exposes those people to harmful substances. Many electronics contain toxic materials like nickel, zinc, lead, chromium, barium and flame retardants. These can all cause damage to the human body. Lead may get into the blood, kidneys and even the nervous system.

2. Affects Development of Unborn Children

When a pregnant woman is exposed to those harmful substances, it can affect the development and health of her unborn child both in and out of the womb. Adverse health effects to the child include stillbirth, premature birth and low birth weight. Further, any exposure the woman

has to lead could reduce neonatal behavioural scores, an increased risk of mental health disorders, behavioural problems and reduced cognitive abilities. It can also affect a child's lung function, respiratory system and chronic diseases later in their lives.

3. Air and Water Pollution effects

Another way e-waste affects humans is through air pollution. Often, the electronics that are sent away to other countries end up in the incinerator. This process releases harmful chemicals and pollutants into the air. Humans rely on air to breathe, so when that air fills with toxins, it can affect a person's respiratory system. The toxins from electronics enter the groundwater, which is what feeds into streams, ponds and lakes. Humans rely on these freshwater sources, and if they ingest it, it could lead to serious health problems.

E-waste sources	Constituents	Health effects
Solder in printed circuit boards, glass panels, and gaskets in computer monitors	Lead	Damage to central and peripheral nervous systems, blood systems, and kidney damage
		Adverse effects on brain development of children; causes damage to the circulatory system and kidney
Chip resistors and semi-conductors	Cadmium	Toxic irreversible effects on human health
		Accumulates in kidney and liver
		Causes neural damage
Relays and switches, and printed circuit boards	Mercury	Chronic damage to the brain
		Respiratory and skin disorders due to bioaccumulation in fishes
Galvanized steel plates and decorator or hardener for steel housing	Chromium	Causes bronchitis
Cabling and computer housing	Plastics and PVC	Burning produces dioxin that causes reproductive and developmental problem

Methods of disposal

Non-biodegradable and toxic wastes like radioactive remnants can potentially cause irreparable damage to the environment and human health if not strategically disposed of. Waste disposal has been a matter of concern, the main problem growth in population and industrialization. Here are a few methods of waste disposal.

Disposal of E-waste are mainly done in 5 types.

1. Recycling
2. Reuse
3. Metal recovery by acid
4. Insinuation
5. Secured land-filling

1. Recycling: Devices such as electronic waste, monitors, picture tubes, laptops, keyboards, telephones, hard drives, CD drives, fax machines, printers, CPUs, modem cables etc. can be recycled. In this process, various metals and plastics are sabotaged separately and preserved for reuse.

2. Reuse: The metals from the old electronic devices can be extracted and reused. Such as from computers, mobiles, laptops etc.

3. Metal recovery by acid: Different types of parts like ferrous and nonferrous metal and printed circuit board are separated by electronic waste. Different types of metals like lead, copper, aluminium, silver, gold, platinum etc. are recovered and reused.

4. Incineration: In this process the e-waste is lit in a fully closed chamber inside the insulator at a temperature of 900 to 1000 degree centigrade. Due to which the quantity of e-waste is reduced considerably and the toxicity of the organic substance present in it is reduced significantly. The smoke and gas coming out of the chimney in the injector is passed through the Air Pollution Control System (APCS) and the various types of metals present in the smoke are separated by chemical action and the gases are treated.

5. Secured land-filling: The e-waste is built on the flat land and the pits are pressed into the soil by putting the e-waste in it. Residues from waste incineration or waste that is not suitable for material recycling or thermal treatment are deposited in landfills that are compliant with the legal requirements. If the waste does not fulfil the requirements for landfilling, it must be pre-treated.

Advantages of Recycling E-Waste

Adopting a healthy habit of recycling e-waste by every individual makes a large difference in the longer run. We should be responsible and protect the environment by recycling e-waste. To save our future generations from an unhealthy environment or before completely losing natural habitats.

1. Save Landfill Space: Electronic waste is being thrown into landfills at an increasing rate each year. By recycling of E-waste, the amount of waste getting landfilled will reduce and thereby reduced the landfill space.

2. Save Natural Resources: The components in an electronic device are recyclable. Metals extracted through mining require much difficulty and effort. Apart from mining, the cost to refine metals and transform them to a usable form is also very high. Through the extraction and reuse of metal from old electronic gadgets, the need to manufacture and refine raw metals decreases. Hence, recycling save natural resources

3. Increase in Employment: Only experts can deal with electronic waste properly. Distinguishing between reusable and non-reusable materials is a task that requires a sharp eye and a lot of product knowledge. There are a lot of jobs in the field of recycling. There are many experts out there that have professional degrees regarding the recycling of electronic waste. Increased education about electronics recycling means more people recycle and more jobs are creating. Eventually, it results in the prosperity of the whole nation.

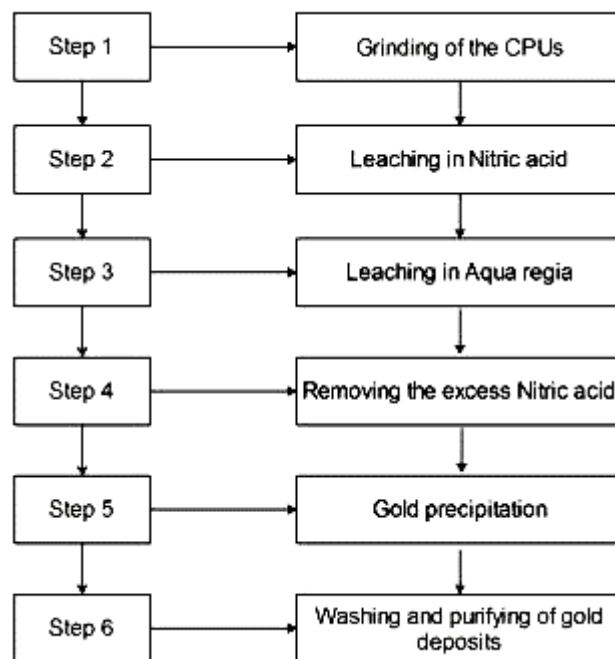
4. Increases Affordability: In many cases, people want to get rid of an electronic device not because it has stopped working, but because they want to buy one with the latest technology. If

they give their old gadgets to charity or sell them in a second-hand-shop, other people who cannot afford to buy new electronic devices can easily buy them. Recycling e-waste increases the opportunity for people who do not have access to such devices to use and own them.

5. Saves the Environment: Earth gives millions of resources to us every day. To prevent the environment from the toxicity, we should take a few simple steps while getting rid of e-waste. Toxic and harmful poisons are reduced because green gas emissions are decreased and plastic is not thrown into the sea thereby improving marine life. These toxins from e-waste are partially responsible for diseases such as cancer in human beings as well as animals. Thus, environmentalists repeatedly inform us about the importance of recycling e-waste so that future generations are safe.

Extraction of Gold from e-waste

Recovering precious metals from e-waste through hydrometallurgical processes is more attractive economically than other methods. A hydrometallurgical process consists of first a set of operations including acidic or alkaline dissolution (leaching) of solids. The resulting solutions are then exposed to separation and purification methods including deposition, solvent extraction, adsorption, and ion exchange in order to isolate and concentrate the intended metals.



Step 1: (grinding of the CPUs): First, any dust or other particles were removed from the CPUs. The size of the grind pieces was 1 mm.

Step 2: (leaching in nitric acid): Concentrated nitric acid (65%) was added. Leaching time in this stage was 1 hour.

Step 3: (leaching in aqua regia): The aqua regia solution was obtained using three volumes of HCl plus one volume of HNO₃ (under the hood). Typically, the gold of composite CPU-containing boards is easily dissolved in 4-to-1 aqua regia. The solution was decanted, and the pieces were subsequently washed with 10 mL of concentrated HCl so that all of the gold content was fed into the solution.

Step 4: (removing the excess nitric acid): Sulfuric acid was added to the solution to accelerate the removal of nitric acid and sedimentation of the lead as lead sulphate (if present). The time required for the complete removal of nitric acid from this solution was 45 minutes.

Step 5: (precipitation of gold): A certain amount of iron sulphate (per one gram of gold: 4.2 g of iron sulphate) was dissolved in warm water and gradually added to the gold-containing solution. For better dissolution of iron sulphate, some drops of HCl can be used.

Step 6: (washing and purifying gold deposits): The deposit was coated with HCl and then boiled (to dissolve the excess copper sulphate). Following boiling, the acid was removed and the deposit was re-washed in HCl to ensure the cleanness of the gold powder. Eventually, the deposit was filtered and washed with large amounts of warm water. At this stage, the deposit was placed in an oven at a temperature of 100°C to dry. Sampling and measuring of precious metals were performed following the first and second stages of leaching, after the stage of gold extraction, and finally following the purification of deposits.

Water technology

Sources of water: The various sources of water found on earth are:

1. Surface water:
 - a) Rain water: Purest form of water
 - b) River water: Rivers are fed by rain and spring waters.
 - c) Lake water: Has constant chemical composition.
 - d) Sea water: Most impure form of natural water
2. Underground water: Spring and well water.

Water Parameters

Hardness of Water

The hardness of water is due to the presence of soluble bicarbonates, chlorides and sulfates of calcium and magnesium. Water which does not give lather with soap is hard water.

Water can be classified as hard water and soft water.

- **Soft water:** It lathers with soap. Water which is obtained from the rains is soft water. This water is suitable for household purposes for example laundry and cleaning.
- **Hard water:** It is known as hard water because of the presence of salts of calcium and magnesium. Hard water does not lather with soap but instead forms a precipitate.

Difference between Hard water and Soft water	
HARD WATER	SOFT WATER
It is rich in minerals	Contains very few elements
Soap is not so effective	Soap is easily effective
Less foam/lather from soaps	Bubbly lather from soaps
Leaves spots on the washed dishes after they are dried	Does not leave any spots on dishes after they are dried
Contains minerals like magnesium and calcium	Contains sodium ion
Preferred drinking water	It is not preferred drinking water
Example: Groundwater like deep wells	Example: Rainwater
Hair and skin become dry	Hair and skin become soft

Types of hardness of water

The total hardness of water is the sum of temporary and permanent hardness.

$$\text{Total Hardness} = \text{Temporary hardness} + \text{Permanent hardness}$$

1. Temporary Hardness of Water:

It is due to presence of bicarbonate of magnesium and calcium salt. It can be removed by boiling. While boiling water soluble metal bicarbonates become insoluble metal carbonates. Hence gets precipitated and is removed.



2. Permanent Hardness of Water:

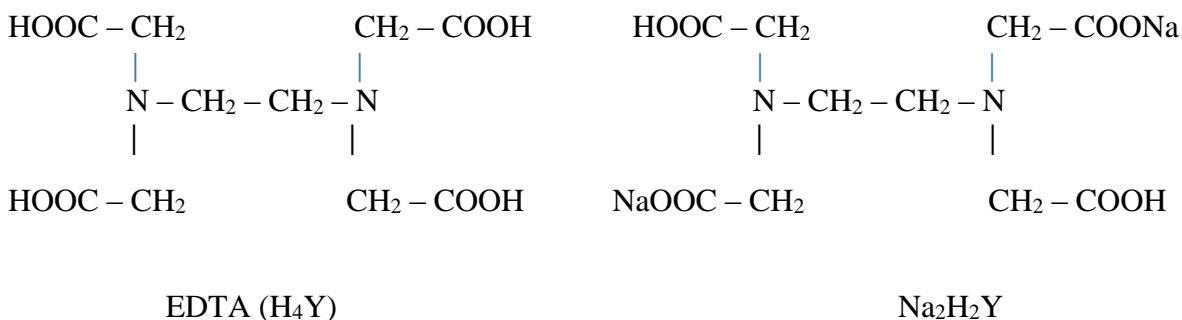
It is due to presence of chlorides, sulphates magnesium and calcium salt. These can be removed by chemical treatment such as reverse osmosis, ion exchange method etc.

ESTIMATION OF HARDNESS BY EDTA METHOD

DETERMINATION OF TOTAL HARDNESS OF WATER SAMPLE USING DISODIUM SALT OF EDTA

Principle:

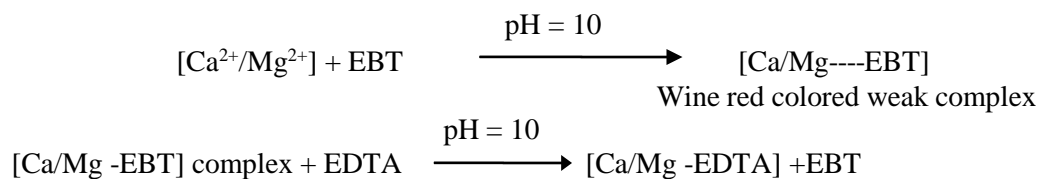
Hardness of water is due to the presence of calcium and magnesium salts in water. Ethylene diamine tetra acetic acid (EDTA) forms complexes with a large number of cations including Ca^{2+} and Mg^{2+} ions. So it is possible to determine the total hardness of water using EDTA reagent.



The disodium salt of EDTA molecule (H_2Y) has two easily replaceable hydrogen atoms and after ionization it is represented as H_2Y^{2-} . The later forms complexes with metal ions as follows.



where M^{2+} is Ca^{2+} and Mg^{2+} in water. Reaction (1) can be carried out quantitatively at a pH of 10 using Eriochrome Black-T indicator. Since the reaction involves the liberation of H^+ ions, buffer mixture has to be used to maintain a pH of 10. The buffer mixture used in the titration is $\text{NH}_3 - \text{NH}_4\text{Cl}$. The hardness of water is usually expressed in terms of ppm (parts per million) of CaCO_3 . Since EDTA (free acid) is sparingly soluble, its disodium salt, $\text{Na}_2\text{H}_2\text{Y}$ is used for preparing the reagent.



When this solution is titrated against EDTA, it replaces the indicator from the weak complex form stable EDTA complex. When all the hardness causing ions are complexed by EDTA, the indicator is set free. The color of the free indicator is steel blue. Thus the end point is the change of color from wine red to steel blue.

Procedure:

Part A- Preparation of standard solution of disodium salt of EDTA – Weigh accurately the given disodium salt of EDTA crystals using an electronic weighing balance. Note the weight, transfer the crystals carefully into a funnel placed over a 250 cm³ volumetric flask and note down the empty weight of the weighing bottle. Add small amount of water allowing all the crystals to run down into the flask and then ½ test tube of ammonia. Dissolve the crystals by swirling the flask gently. Dilute the solution up to the mark with ion exchange water, stopper the flask and mix the solution thoroughly by inverting the flask several times so that a homogeneous solution results. Calculate the molarity of EDTA.

Part B - Determination of total hardness of water sample - Pipette out 25 cm³ of the given water sample into a clean conical flask. Add 5 cm³ of NH₃ – NH₄Cl buffer and a pinch of Eriochrome Black – T indicator. Titrate against standard EDTA solution till the colour of the solution changes from wine red to clear blue. Repeat the titration for concordant values.

OBSERVATION & CALCULATIONS

Weight of weighing bottle + EDTA salt =g

Weight of empty weighing bottle = g

Weight of EDTA salt = g

Molarity of EDTA Solution = $\frac{\text{Weight of EDTA} \times 4}{\text{Molecular weight of EDTA} \times 1000}$ = $\frac{\text{.....} \times 4}{372.24}$ =M

Burette readings	Trial I	Trial II	Trial III
Final burette reading (cm ³)			
Initial burette reading (cm ³)			
Volume of EDTA solution run down in (cm ³)			

Volume of EDTA consumed = cm³

(M×V)_{Hard water} = (M×V)_{EDTA}

$$\begin{array}{c}
 (M \times V)_{\text{EDTA}} \\
 M_{\text{Hard water}} = \frac{\dots\dots\dots}{25} = \frac{\dots\dots\dots}{25} = \dots\dots\dots M
 \end{array}$$

$$\begin{aligned}
 \text{Weight per liter of CaCO}_3 \text{ equivalent hardness} &= M_{\text{Hard water}} \times \text{Mol. Wt. of CaCO}_3 (100) \\
 &= \dots\dots\dots \times 100 = \dots\dots\dots \text{g/liter (Z)}
 \end{aligned}$$

$$\begin{aligned}
 \text{Hardness of water sample} &= \frac{Z \times 10^6}{1000} = \frac{\dots\dots\dots \times 10^6}{1000} \text{ mg/litre of CaCO}_3 = \dots\dots\dots \text{mg/liter of CaCO}_3
 \end{aligned}$$

Result: The total hardness of the given water sample = $\dots\dots\dots$ mg/liter or ppm of CaCO_3

Disadvantages of hard water

- When hard water is heated, lime scale forms and is deposited in particular places. Appliances for heating water and water pipes both have clogging.
- The buildup of deposits in pipes and appliances can result in blockages, and in appliances, it can reduce energy efficiency and shorten life.
- Can make garments appear dull and grey, losing all of their colours.
- With soap or detergents, lathering is challenging. Additionally, using hard water increases the likelihood of scum buildup, which wastes soap.
- Hard water can cause dry skin and hair in people, among other effects.

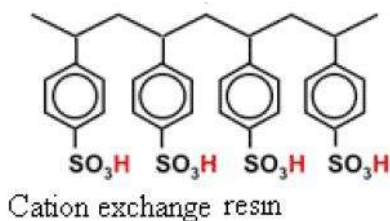
DEMINERALISATION (OR) ION-EXCHANGE PROCESS

The process of removing of salts from water is known as softening of water.

Ion exchange or de-mineralization:

Ion exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure.

The functional groups present in the resins are capable of exchanging their ions with cations (acidic functional groups like $-\text{COOH}$, $-\text{SO}_3\text{H}$ (RH)).



The anions (basic functional groups like $-\text{R}_4\text{NOH}$ (ROH)) present in water.

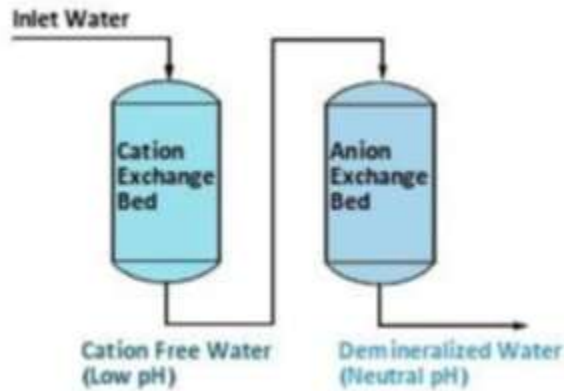
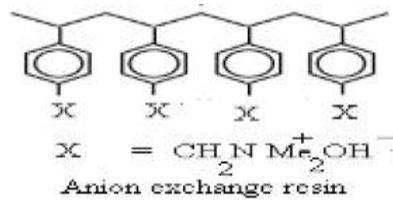
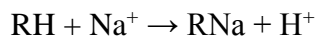
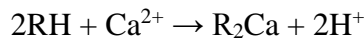
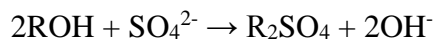
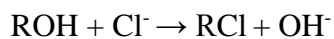


Figure: Schematic of ion-exchange process. Courtesy: <http://cleanboiler.org/>.

Cation exchange Process: The hard water is passed first through cation exchange column which removes all the cations like Ca^{2+} , Mg^{2+} etc. from it and equivalent amount of H^+ ions are released to water.



Anion exchange Process: Then hard water is passed through anion exchange column which removes all the anions like SO_4^{2-} , Cl^- etc. from it and equivalent amount of OH^- ions are released to water.



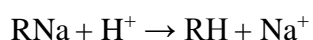
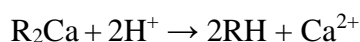
In this process, H^+ and OH^- ions are combined to produce water.



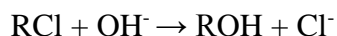
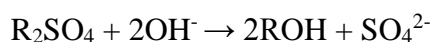
Water coming out from the exchanger is free from cations as well as anions and is known as deionized or demineralized water.

Regeneration Process: when the resins are exhausted and lose their capacity to exchange ions, hence they are regenerated.

Cation exchange resin: It is regenerated by adding dil.HCl/ H_2SO_4



Anion exchange resin: It is regenerated by adding dil.NaOH/ NH_4OH



Finally, the columns are washed with deionized water and can be used for ion-exchange process.

ADVANTAGES OF ION-EXCHANGE PROCESS:

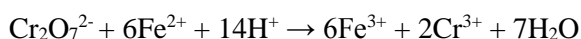
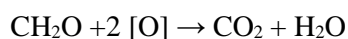
- This method produces soft water of very low residual hardness
- Highly acidic and alkaline water can be treated by this process.
- Regeneration of ion-exchange resin is possible.
- Maintenance cost is less.
- No sludge disposal problem arises.

Chemical Oxygen Demand (COD):

Chemical oxygen demand is the amount of oxygen required for the complete chemical oxidation of both organic and inorganic matter present in the sample of water by a strong chemical oxidizing agent such as acidified potassium dichromate.

Principle:

COD determination is based on refluxing with dichromate because of higher oxidizing ability of dichromate. The organic matter gets oxidized completely by dichromate with silver sulphate as catalyst in the presence of concentrated H_2SO_4 to produce CO_2 and H_2O . The excess $K_2Cr_2O_7$ is titrated against ferrous ammonium sulphate (FAS). The dichromate consumed gives the oxygen required for oxidation of the organic matter. The chemical reactions involved in the method are:



The oxidisable constituent of waste water includes straight chain aliphatic compounds, aromatic hydrocarbons, straight chain alcohols, acids, pyridine and other oxidisable materials. Straight chain compounds and acetic acid are oxidized more effectively in presence of silver ions (added as silver sulphate) as catalyst. However, the silver ions become ineffective in presence of halide. This difficulty is overcome by treating the waste water with mercuric sulphate before the analysis for COD. Mercuric sulphate binds the halide ions and makes them unavailable.

A known volume of waste water sample is treated with excess of acidified dichromate. The unreacted dichromate is titrated with standard ferrous ammonium sulphate solution using ferroin indicator. A blank titration without the waste water sample is performed. COD of the water sample is determined from the difference in the titre value. This method can be used to estimate COD values of 50mg or more.

Procedure:

a. Preparation of standard Mohr's salt solution (FAS solution)

Weigh about 9.8 g of Mohr's salt accurately into a 250 cm³ volumetric flask. Add half test tube of 1:1 sulphuric acid and dissolve the crystals. Dilute the solution with ion exchange water upto the mark and shake well.

b. Titration

Back Titration:

Pipette out 25cm³ of the waste water sample into a conical flask. Add 5 ml of Hg₂SO₄, 10 ml of Ag₂SO₄/H₂SO₄ followed by 10 cm³ of standard potassium dichromate solution with constant shaking. The contents of the conical flask are refluxed for about 30 min on a water bath and it is cooled to room temperature. Add 2-3 drops of ferroin indicator and titrate against standard Mohr's salt solution until the solution turns from bluish green to reddish brown. Repeat for agreeing values.

Blank Titration:

Repeat the above procedure without sewage water or with 25 ml of distilled water.

From the difference in the titre values, calculate the COD of the given waste water sample.

OBSERVATION & CALCULATIONS

Part A: Preparation of standard Ferrous Ammonium Sulphate (Mohr's Salt) solution

1. Weight of bottle + FAS crystals = _____ g
2. Weight of empty bottle = _____ g
3. Weight of FAS crystals = _____ g

$$\text{Normality of FAS solution} = \frac{\text{Weight of FAS} \times 4}{\text{Equivalent weight of FAS}} \times 4 = \frac{\text{Weight of FAS} \times 4}{392} = \dots\dots\dots \text{N (a)}$$

Burette reading	I	II	III
Final Reading			
Initial Reading			
Vol. of FAS run down in cm ³			

Concordant burette reading-----

Calculation:

Vol. of FAS Consumed by K₂Cr₂O₇ needed to oxidize impurities (oxidizable) present in water
(V_{FAS}) = Blank titre value - Back titre value

$$(\text{NV})_{\text{H}_2\text{O}} = (\text{NV})_{\text{FAS}}$$

$$(N) \text{ oxidizable matter in water} = \frac{(NV)FAS}{V_{H_2O}} = \dots\dots\dots N$$

Weight of oxidizable matter in 1 litre of water sample = N × Equivalent weight of oxygen (8)

$$W = N \times 8 \text{ g/litre}$$

$$W = \dots\dots\dots \text{g/litre}$$

$$\text{Amount of oxidizable matter in } 10^6 \text{ ml of the given water sample} = \frac{W \times 10^6}{1000} = \dots \text{mg/litre}$$

Result: The COD of given waste water sample =mg of O₂/litre or ppm

Significance of COD

1. It measures the effect of pollutants on dissolve oxygen.
2. It helps in designing & calculation of efficiency of the water treatment plants.
3. It helps in deciding the disposal of domestic & industrial effluents in various types of water streams

Problems on COD

1. Solve the COD of the effluent sample when 25ml of effluent sample requires 8.5ml of 0.5M K₂Cr₂O₇ solution for complete oxidation.

$$(M) \text{ oxidizable matter in water} = \frac{(MV)FAS}{V_{H_2O}} = \frac{8.5 \times 0.5}{25} = 0.17M$$

Weight of oxidizable matter in 1 litre of water sample = M ×Molecular weight of oxygen (16)



$$W = M \times 48 \text{ g/litre}$$

$$= 0.17 \times 48 = 8.16 \text{ g/litre}$$

$$\text{Amount of oxidizable matter in } 10^6 \text{ ml of the given water sample} = \frac{8.16 \times 10^6}{1000} = 8160 \text{ mg/litre}$$

2. In a COD experiment, 29.5 cm³ and 20 cm³ of 0.025 N FAS solution were required for blank and back titrations respectively. Solve for the COD of the sample, given volume of the test sample used is 25 cm³.

Vol.of FAS Consumed by K₂Cr₂O₇ needed to oxidize impurities (oxidizable) present in water
(V_{FAS}) = Blank titre value - Back titre value = 29.5-20 = 9.5 ml.

$$(N) \text{ oxidizable matter in water} = \frac{(NV)FAS}{V_{H_2O}} = \frac{9.5 \times 0.025}{25} = 0.0095 \text{ N}$$

$$V_{H_2O} = \frac{25}{25}$$

Weight of oxidizable matter in 1 litre of water sample = $N \times$ Equivalent weight of oxygen (8)

$$W = 0.0095 \times 8 \text{ g/litre} \\ = 0.076 \text{ g/litre}$$

$$\text{Amount of oxidizable matter in } 10^6 \text{ ml of the given water sample} = \frac{W \times 10^6}{1000} \dots \text{mg/litre} \\ \frac{0.076 \times 10^6}{1000} = 76 \text{ mg/litre}$$

Biological oxygen demand [BOD]

“Biological oxygen demand is the amount of oxygen required for the oxidation of organic matter present in the sample of water by a microorganism”.

BOD is determined by measuring DO of water in the beginning [DO_1] and after the period of 5 days [DO_2]. The amount of DO consumed for oxidation over the period of 5 days is BOD of water.

$$BOD = \frac{D_1 - D_2}{A} \times B \text{ mg dm}^{-3}$$

- DO \longrightarrow Dissolved oxygen in the blank solution.
D1 \longrightarrow Dissolved oxygen in sample solution before incubation.
D2 \longrightarrow Dissolved oxygen in sample solution after 5 days.
A \longrightarrow Volume of sample in ml before dilution
B \longrightarrow Volume of sample in ml after dilution.

Significance of BOD

1. It is useful in designing of treatment plants & calculation of waster load.
2. The higher the BOD of a sample the higher will be pollution.
3. It helps in pollution control.

Nano materials

One nanometer is defined as one thousand-millionth/one billionth of a meter (10^{-9} m).

Nanomaterials possess size from one nanometer to hundred nanometers at least in one dimension.

Classification of nanomaterials

The classification of nanomaterials is based on the number of dimensions According to Siegel, nanostructured materials are classified as: zerodimensional (0D), one-dimensional (1D), two-dimensional (2D) and threedimensional (3D) nanomaterials.

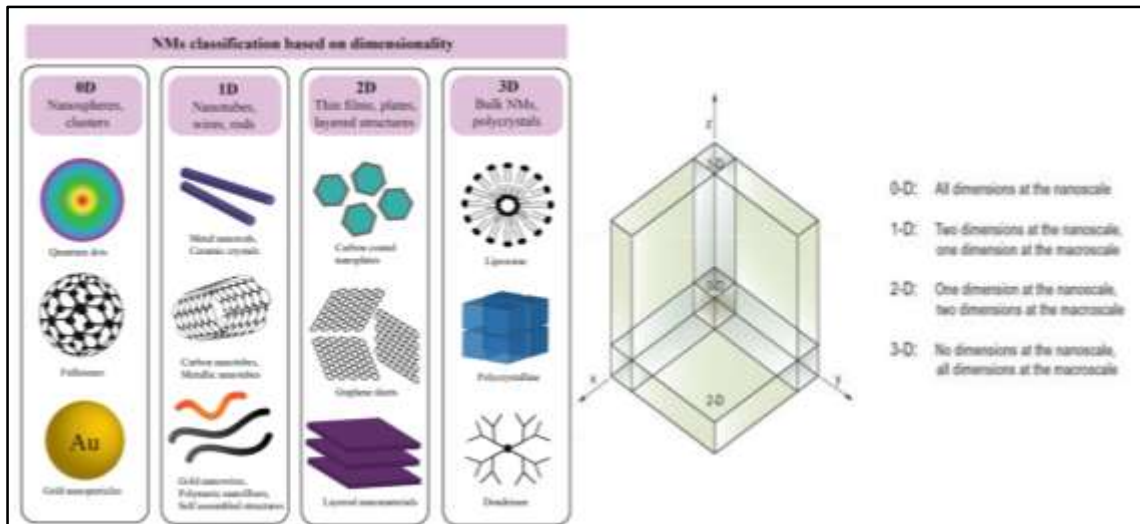


Fig 1: Nanomaterial classification

Zero-dimensional (0D) nanomaterials: Here all the dimensions are measured within the nanoscale (no dimensions are larger than 100 nm). Most commonly, 0D nanomaterials are nanoparticles such as quantum dots and nanospheres.

One-dimensional nanomaterials (1D): Here one dimension is outside the nanoscale. This class includes nanotubes, nanorods, and nanowires.

Two-dimensional nanomaterials (2D): In this nanomaterial, two dimensions are outside the nanoscale. This class exhibits plate-like shapes and includes graphene, nanofilms, nanolayers, and nanocoatings.

Three-dimensional nanomaterials (3D): The materials that are not confined to the nanoscale in any dimension. This class can contain bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers. Example: nanoprisms & nanoflowers

Types of nanomaterials

Nanomaterials can be categorized into four types.

✓ **Inorganic-based nanomaterials:** An inorganic nanomaterial (NM) can comprise a metal or non-metal element, or take the form of an oxide, hydroxide, chalcogenide or phosphate compound. Example: Examples of metal-based and metal oxide based inorganic nanomaterials are silver (Ag), gold (Au), zinc oxide (ZnO), and copper oxide (CuO).

✓ **Carbon-based nanomaterials:** Carbon-based are amazing technological advancement with unique properties (high mechanical strength, high conductivity, attractive optical properties, chemical versatility, etc.). Carbon-based nanomaterials include graphene, fullerene, single-walled carbon nanotube, multiwalled carbon nanotube, carbon fiber, an activated carbon, and carbon black.

✓ **Organic-based nanomaterials:** The organic-based nanomaterials are formed from organic materials excluding carbon materials. For example, dendrimers, cyclodextrin, liposome, and micelle.

✓ **Composite-based nanomaterials:** Composite nanoparticles are defined as the nanomaterials with composite structure which are constituted by two or more components of nanoscale with special physical and chemical properties. The composite nanomaterials are any combination of metal-based, metal oxide-based, carbon-based, and/or organic-based

nanomaterials, and these nanomaterials have complicated structures like a metal-organic framework. For example, ZnO-Cu₂O, BiOBr-CoWO₄ composites.

Size dependent properties of nano materials:

i) **Surface area:** The physical and chemical properties of a material depend on its surface area. Surface area is increased on moving from bulk to nano scale. Nanomaterials have a significant fraction of atoms residing on the surface. Properties like **catalytic activity, gas adsorption and chemical reactivity** depends on surface area.

For example: Finely divided nickel acts as an effective catalyst in hydrogenation of oils than bulk Ni.

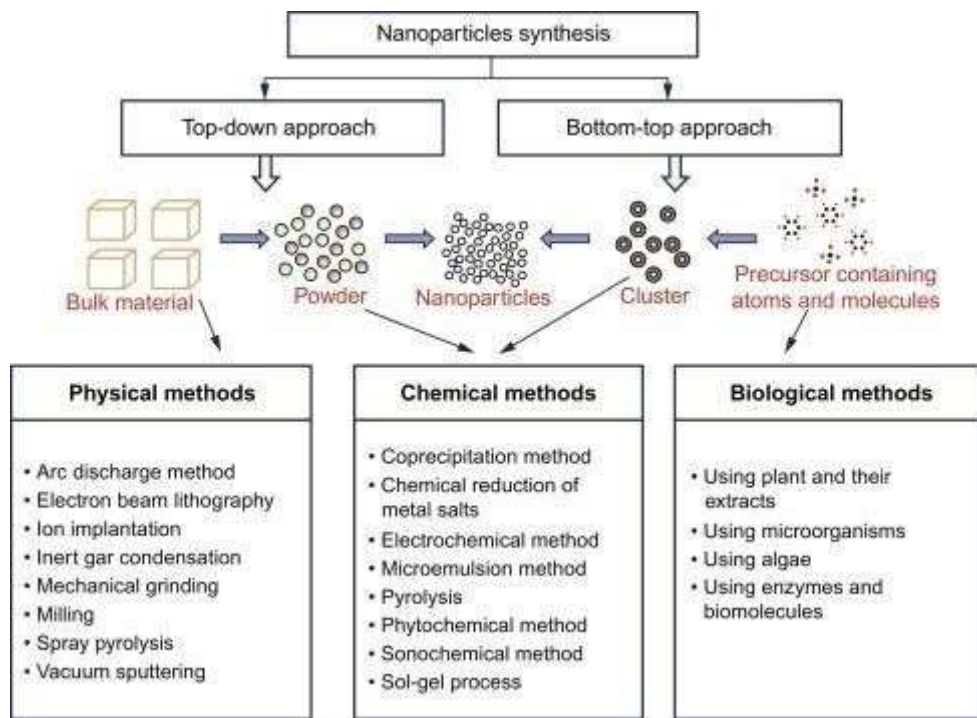
ii) **Electrical properties:** The electronic bands in bulk material are continuous due to overlapping of orbitals of billions of atoms. But in the nano size materials, very few atoms or molecules are present so the electronic bands become discrete. Hence, metals which are good conductors in bulk become semiconductors and/or insulators at nano level.

iii) **Optical properties:** The nanoparticles of different sizes can scatter radiation of different wavelengths. For example, different colours exhibited by colloidal solutions. Nanoparticles of metals exhibit unique optical property called as surface plasmon resonance. When light falls on the surface of metal, electrons start oscillating back and forth in a synchronized way in a small space and the effect is called as plasmon resonance.

Methods to Synthesis of Nanomaterials

In general, top-down and bottom-up are the two main approaches for nanomaterials synthesis.

- a. **Top-down:** size reduction from bulk materials.
- b. **Bottom-up:** material synthesis from atomic level.



Top-down routes are included in the typical solid –state processing of the materials. This route is based with the bulk material and makes it smaller, thus breaking up larger particles by the use of physical processes like crushing, milling or grinding. Usually this route is not suitable for preparing uniformly shaped materials, and it is very difficult to realize very small particles even with high energy consumption. The biggest problem with top-down approach is the imperfection of the surface structure. Such imperfection would have a significant impact on physical properties and surface chemistry of nanostructures and nanomaterials. It is well known that the conventional top-down technique can cause significant crystallographic damage to the processed patterns.

Bottom –up approach refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule or cluster-by-cluster. This route is more often used for preparing most of the nano-scale materials with the ability to generate a uniform size, shape and distribution. It effectively covers chemical synthesis and precisely controlled the reaction to inhibit further particle growth. Although the bottom-up approach is nothing new, it plays an important role in the fabrication and processing of nanostructures and nanomaterials.

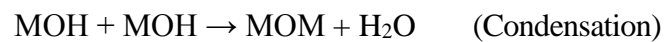
Sol-gel method to synthesis of nano materials

Sol-gel process: Sol-gel process has been used in the synthesis of nanoparticles of metal oxides and temperature sensitive organic-inorganic hybrid materials. It consists of following steps:

i) **Preparation of sol:** Sol is prepared by dispersing metal oxide or metal alkoxide (precursor)

in a solvent.

ii) **Conversion of sol to gel:** Sol is then converted into gel by hydrolysis and condensation of precursors. Hydrolysis and condensation reactions are initiated by addition of an acid or a base as catalyst.



iii) **Aging of gel:** Gel on aging for a known period of time which facilitates the formation of nanoclusters.

iv) **Removal of solvent:** The encapsulated liquid from gel can be removed by evaporation.

v) **Heat treatment:** The sample is then calcined to obtain nanoparticles (1 to 100 nm).

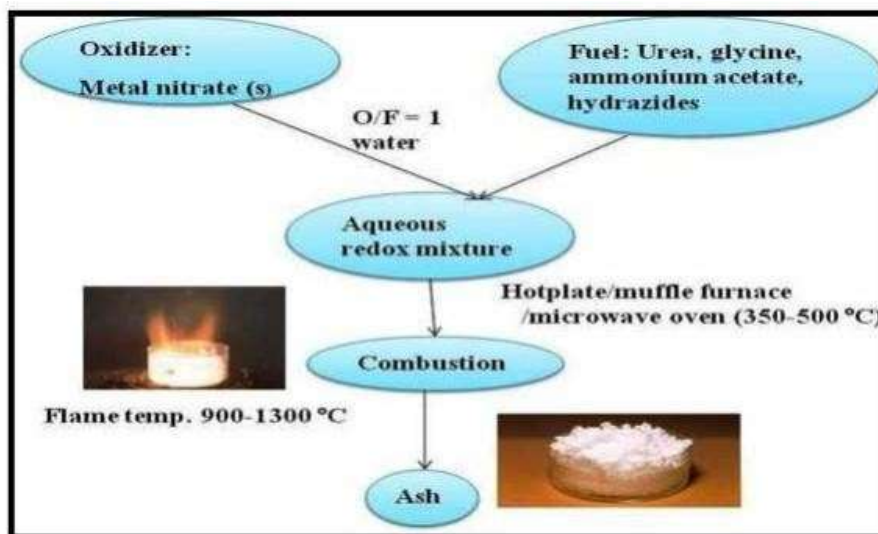
Advantages

1. Nanomaterials of high purity with good homogeneity can be obtained.
2. Samples can be prepared at lower temperature.
3. Easy to control synthesis parameters to control physical shape and size of nanomaterials.

Solution Combustion process for synthesis of nanomaterials

- Solution combustion (SC) is an effective method for synthesis of nano-size materials and it has been used for the production of a variety of more than 1000. It is a traditional method. e.g: ZnO, CuO, Fe₂O₃ nano particles.
- The oxidizer (usually metal nitrates such as copper nitrate, zinc nitrate etc.) and fuel (containing carbon and hydrogen as main components include urea, citric acid, glycine, ascorbic acid etc.) are taken in a stoichiometric ratio.
- Dissolve the oxidizer and fuel in distilled water and mix up on a magnetic stirrer to get homogeneous solution.
- Put the container on muffle furnace at 400 °C so that first dehydration of solvent takes place.
- After the dehydration, starts the combustion of mixture since it is exothermic process reach the temperature about 900-1200°C.

- Calcination at combustion temperature gives pure nanomaterials and by products is let off from the furnace.



Flow chart of the steps of solution combustion synthesis (SCS)

Advantages

1. The synthesis temperature is low.
2. Short reaction/process time
3. The products are high purity
4. The use of relatively simple equipment
5. Formation of desired size and shape of products [depends on nature of reactants and exothermicity]

Descriptive type

1. Outline the effects of e-waste on environment and human health.
2. Summarize the various methods of disposal.
3. Outline the steps with a flow diagram for extraction of gold from e-waste.
4. List the advantages of recycling of e-waste.
5. List the sources of e-waste.
6. Define hardness of water. Distinguish between hardwater and soft water.
7. Outline the procedure for determination of hardness of water.
8. Define COD. Elaborate the experimental determination of COD of waste water.
9. Define BOD with its mathematical equation.
10. List the types of nanomaterials with examples.
11. Summarize the size dependent properties of nanomaterial.
12. Sol-gel method of synthesizing nanomaterial's is very popular. Elaborate the synthesis steps.
13. Illustrate the Solution Combustion Method of synthesis for nanomaterials.

MCQs

1. Major appliances of home are categorised as
 - a. **Type 1,**
 - b. Type 2
 - c. Type 3.
 - d. Type 4
2. Incineration is
 - a. **Waste disposal method,**
 - b. source of e-Waste,
 - c. toxic waste
 - d. Recycling method.
3. The process used for extraction of gold from e-waste
 - a. Pyrolysis,
 - b. **Hydrometallurgy,**
 - c. Reduction,
 - d. None
4. The indicator used to measure the hardness of water is
 - a. **EBT,**
 - b. phenolphthalein,
 - c. Ferroin
 - d. None
5. To determine the COD of water, the oxidising agent used is
 - a. **Pottasium dichromate,**
 - b. hydrochloric acid
 - c. Formic acid
 - d. None
6. Cation-exchange resins are capable of exchanging
 - a. anions,
 - b. **cations**
 - c. Both
 - d. None
7. The amount of oxygen (in mg/L) required by bacteria to oxidize the organic molecules aerobically is known as
 - a. COD, b. TDS, c. BDS, d. **BOD**
8. The number of milligrams of oxygen required to oxidize the impurities present in 1000 ml of waste water using strong oxidizing agent like acidified $K_2Cr_2O_7$ is known as
 - a. DO, b. **COD,** c. TDS, d. BOD
9. In COD determination, silver sulphate is used because
 - a. **It acts as a catalyst,**
 - b. it acts as a oxidizing agent
 - c. it acts as a reducing agent
 - d. No effect
10. Nanometer refers to
 - a. 10^9 cm, b. 10^9 m, c. 10^{-9} cm, d. **10^{-9} m**
11. Which approach is involved in sol-gel technique for the synthesis of nanomaterials?
 - a. **Bottom up approach,**
 - b. Top-down approach,
 - c. Backward approach,
 - d. Sidewise approach
12. Catalytic property of nanomaterials is related to
 - a. **Surface area,**
 - b. Optical properties,
 - c. Electrical properties
 - d. none of these
13. Sol is then converted into a gel by
 - a. Hydrolysis reaction of precursor
 - b. Condensation reaction of precursor
 - c. Aging reaction of precursor

d. Hydrolysis and condensation reaction of precursor

14. Identify the size dependent properties of nanomaterials

- a. Surface area b. electrical properties c. Optical properties d. **All the above**

15. Identify the oxidizer used in solution combustion method

- a. Metal nitrates** b. Metal oxides c. Metal hydroxides d. Metal hydrides

16. Find the fuel used in solution combustion method is

- a. Urea b. Citric acid c. Glycine d. **All of these**

15. Ca/Mg-EBT complex is

- a. Colorless, b. Blue, c. **Wine red,** d. None