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Green Synthesis of Metal Oxides Nanoparticles and Their Applications in the Removal of Dyes from Aqua Solutions - A Review

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Abstract: Progressions in nanotechnology have empowered analysts to create and blend different nanomaterials with unmistakable properties, making them ideal for various biomedical purposes. Metal oxide nanoparticles (MONPs) certainly stand out because of their uncommon attributes, which are notably not the same as those of their mass counterparts. Recognizing the meaning of metal oxide nanoparticles as key mechanical materials, the writers present a broad survey of examination on these nanoparticles, including their synthetic techniques, nanoscale physicochemical properties, and explicit modern applications inside applied nanotechnology. This review looks at recent researches on the synthesis of metal oxide nanoparticles and their viability in removal of dyes from aqueous solutions.

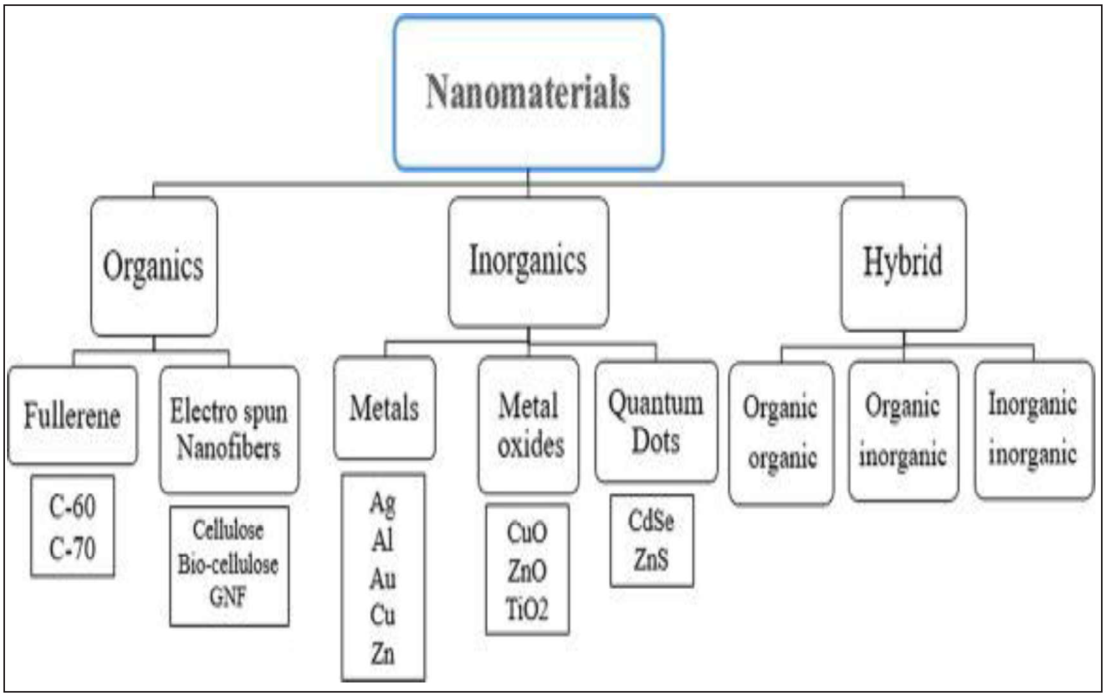
Keywords: Biomedical applications, Metal oxide nanoparticles, Nanotechnology, Physicochemical properties.

I. INTRODUCTION

Metal oxide nanoparticles (MONPs) are produced from different metal-containing solutions, leading to the formation of nanoparticles made of metal oxides. There are various types of MONPs with a wide range of applications, such as in purification systems, photocatalysis, optical devices, and biomedical systems. Some examples of MONPs include iron oxide (Fe_2O_3), zinc oxide (ZnO), titanium oxide (TiO_2), silver oxide (Ag_2O), and copper oxide (CuO). Nanoparticles (NPs), and MONPs in particular, have attracted considerable interest because of their small size and large surface area [1] which offer researchers new ways to diagnose and treat diseases previously deemed untreatable due to size constraints. MONPs are highly valued in the drug and health-related industries because of their high stability, simple preparation methods, excellent engineering control over size, shape, and porosity, and their ability to penetrate cells [2]. The advancement of engineered MONPs has enabled researchers to surpass the limitations of bulk materials, resulting in significant progress in targeted drug delivery, bio-imaging, biomolecule sensing, and other areas. Today, different types of MONPs are being used in clinical settings for purposes such as antibacterial and wound healing dressings, biosensors, anticancer treatments, and image contrast agents [3]. MONPs have a large surface area due to their small size, which allows them to adsorb dye molecules from aqueous solutions effectively. This adsorption brings the dye molecules closer to the catalytic sites on the nanoparticle's surface, facilitating their subsequent degradation [4]. During the photocatalytic process, MONPs can generate active intermediate species that aid in breaking down dye molecules. These intermediates can interact with the dye molecules, resulting in their conversion into water, carbon dioxide, and other harmless substances [5]. This review paper is focusing on the water remediation application.

A. Nanomaterials

Materials with at least one dimension in the nanoscale rangetypically between 1 and 100 nanometers (nm) are known to as *nanomaterials* [6]. These materials have special qualities that set them apart from their bulk equivalents, such as enhanced chemical reactivity, improved mechanical strength, and distinctive optical and electrical behavior. These characteristics are a result of their nanoscale size. The enhanced surface area to volume ratio and quantum effects, which become more pronounced at the nanoscale, are primarily responsible for these characteristics. There are many different types of nanomaterials, such as nanoparticles, nanowires, nanotubes, nanofilms, and nanocomposites [7].



Source: ScienceDirect.com

Fig. 1

B. Metal Based Nanomaterials

These are made up of metal oxides such as zinc oxide and titanium dioxide and metal nanoparticles (like gold, silver, and platinum). The catalytic, antimicrobial, and optical properties of metal nanoparticles are well recognized. For example, due to their unique optical properties, gold nanoparticles are applied in biosensing and imaging, while silver nanoparticles are widely used in medicinal applications for their antibacterial qualities [8].

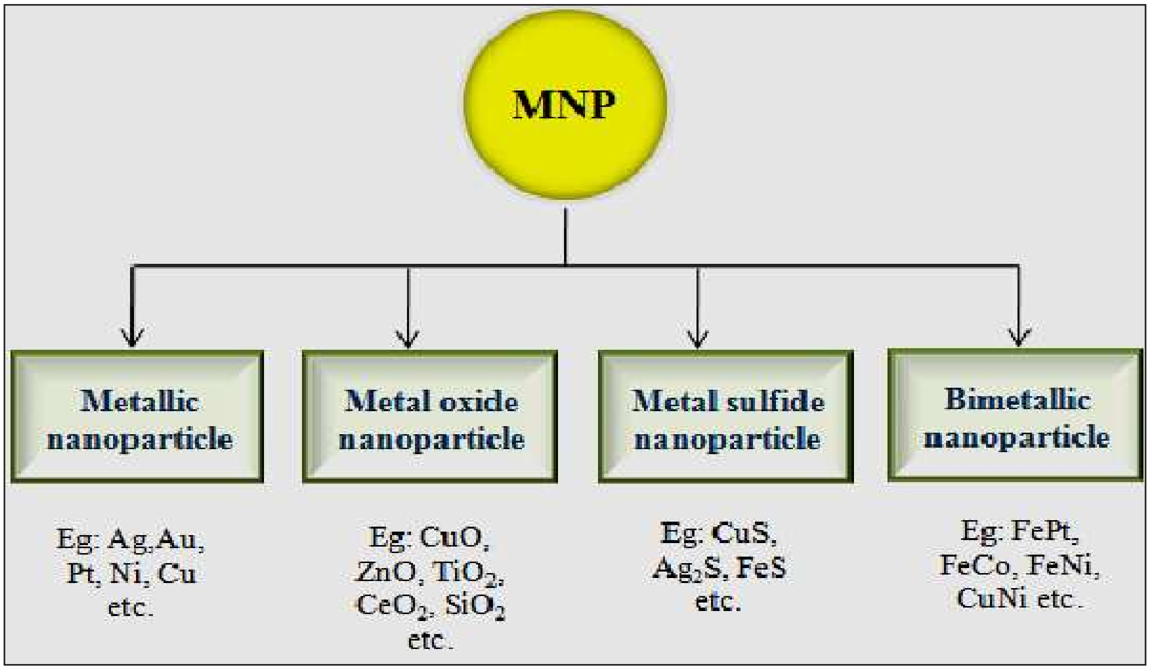


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Fig. 2: Metal Based Nanoparticles

C. Carbon Based Nanomaterials

These include carbon nanotubes (CNTs), fullerenes, and graphene. Carbon nanotubes are cylindrical structures that have remarkable mechanical strength and electrical conductivity, making them very useful for applications in electronics, composites, and drug delivery systems. Graphene, a single layer of carbon atoms arranged in a hexagonal lattice, has excellent thermal conductivity, mechanical strength, and electron mobility, which makes it a promising material for use in flexible electronics, sensors, and energy storage devices [9].

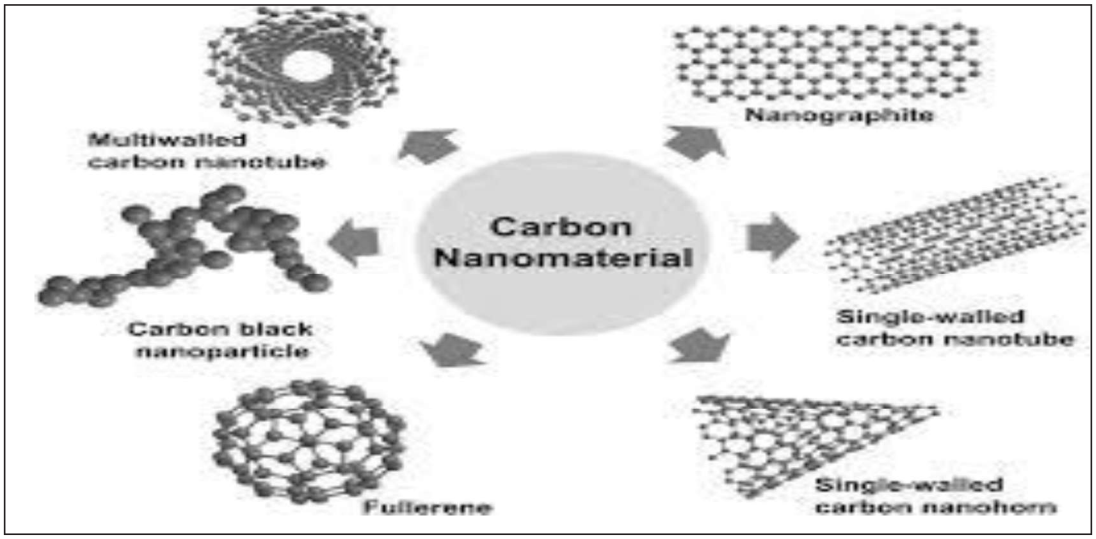

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Fig. 3: Carbon Based Nanoparticles

D. Polymeric Nanomaterials

These are made up of nanoparticles of polymers and nanocomposites, which blend polymers with nanoparticles to improve their mechanical, thermal, and electrical properties. Because of their high value in regulated drug release and biocompatibility, polymeric nanoparticles are widely used in drug delivery systems [10].

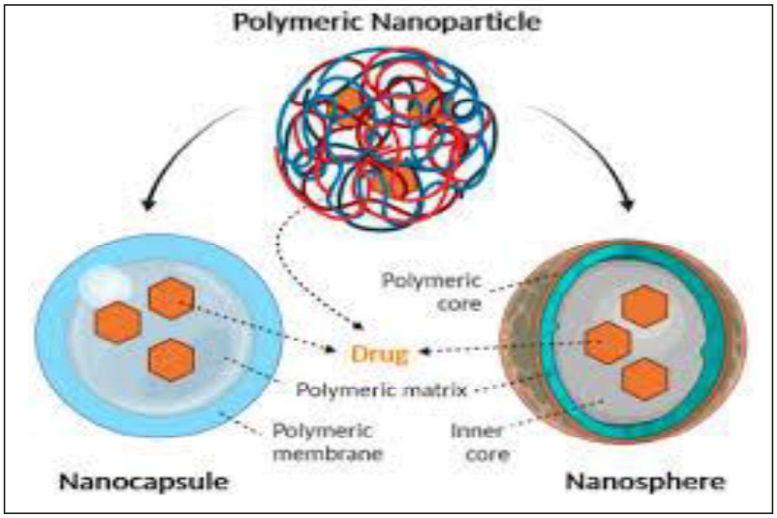

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Fig. 4: Polymeric Nanomaterials

E. Nanocomposites

These are materials that integrate nanoparticles into a matrix of another material (metal, polymer, or ceramic) to improve the composite's properties. For example, adding carbon nanotubes to a polymer matrix can greatly improve the mechanical strength and electrical conductivity of the composite. Nanocomposites are used in automotive, aerospace, and construction industries for their high durability and performance [11].

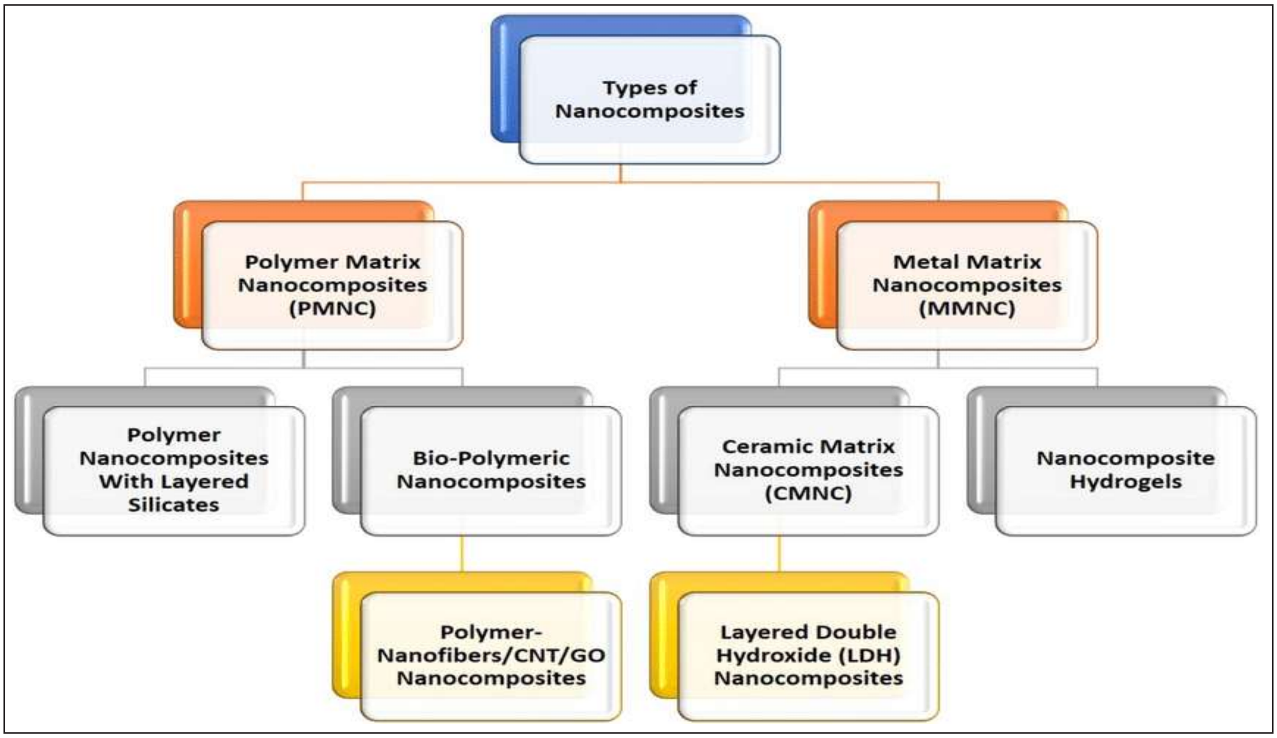

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Fig. 5: Types of Nanocomposites

II. GREEN SYNTHESIS OF NANOMATERIALS

Green synthesis of nanomaterials is an eco-friendly approach that focuses on the use of non-toxic materials and sustainable processes. This techniquereduced biological entities such as plant extracts, microorganisms, and natural polymers to synthesize nanoparticles, eliminating the need for hazardous chemicals and reducing environmental impact [12]. Plants, bacteria, fungi, and algae are used in green synthesis as a reducing and stabilizing agents. For example, plant extracts contain bioactive compounds that can reduce metal ions to nanoparticles while also capping them to prevent aggregation [13]. Green synthesized nanomaterials are used in remediation of the environment, health, and agriculture, among other domains. Green-synthesized nanoparticles, for example, are effective in antibacterial and water pollution removal applications [14].

A. Advantages of Green Synthesis Techniques

These techniques have more advantages compared to other existing techniques of nanoparticle synthesis due to some certain discovered evidences, among which include;

- *Eco-Friendliness:* Hazardous chemicals that are bad for the environment and people's health are frequently used in traditional nanoparticle manufacturing. By using natural sources like fungi, bacteria, and plant extracts, green synthesis minimizes the need for harmful solvents and poisonous chemicals. This lowers the risks related to one's health and the contamination of the environment [15].
- *Cost-Effectiveness:* As at now, green synthesis involves less complicated, more affordable procedures. It reduces the need for expensive, energy-intensive machinery and frequently utilizes biological waste as its raw material. This makes it a more economical and environmentally friendly choice [16].
- *Biocompatibility and Safety:* Greenly produced nanoparticles are frequently more biocompatible, making them safer for use in biomedical applications including antibacterial therapies and drug delivery. This is due to the fact that the biological agents, such as plant compounds or microbial enzymes that are used in their synthesis produce more stable and non-toxic nanoparticles [17].

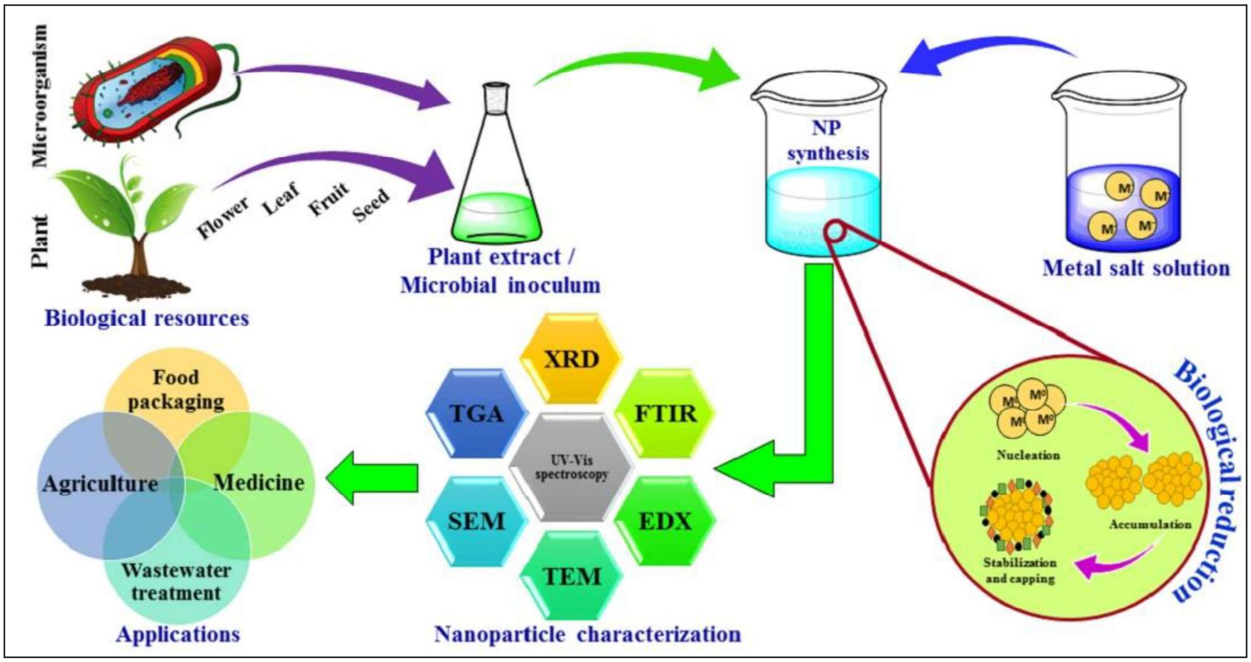

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Fig. 6: Green Synthesis Route

III. Characterization of Nano Materials

Characterization of nanomaterials refers to the process of analyzing and determining various physical, chemical, and structural properties of nanoparticles, such as their shape, size, composition, surface area, and crystallinity [18]. It is essential for understanding how these materials behave at the nanoscale, which is crucial for their applications in fields like medicine, electronics, and energy. Characterization methods can be grouped into various categories based on the properties being studied: This review aimed to study the following techniques:

a) Microscopic Techniques

- *Transmission Electron Microscopy (TEM):* This offers high-resolution images so that the morphology and internal structure of nanomaterials can be studied [19].
- *Scanning Electron Microscopy (SEM):* This provides, morphological, topographical and compositional information by scanning the surface of the material with a focused beam of electrons [20].

b) Spectroscopic Techniques

- *X-Ray Diffraction (XRD):* It is a technique that provides information about the crystal structure, phase, and grain size of nanomaterials [21].
- *Fourier Transform Infrared Spectroscopy (FTIR):* It is used for identification of chemical bonds in nanomaterials by measuring absorption of infrared light [22].
- *Raman Spectroscopy:* This is used for studying vibrational modes to provide molecular and chemical structure details of the molecule [23].

c) Particle Size Analysis

- *Dynamic Light Scattering (DLS):* This technique is also known as photon correlation spectroscopy it measures the size distribution of particles in suspension by analyzing fluctuations in the scattering of light, it is based on the principle of Brownian motion [24].
- *Nanoparticle Tracking Analysis (NTA):* This method tracks individual particles in solution to determine their size and concentration using high speed camera and image analysis software, it is also based on Brownian motion principle [25].

d) Surface Area and Porosity Analysis

- *Brunauer-Emmett-Teller (BET) Analysis:* This technique measures specific surface area and porosity of material based on adsorption of gas at specific temperature and pressure. It is important in determining reactivity, especially for catalytic materials [26].

e) Zeta Potential Measurement

This technique measures the surface charge of nanomaterials in a colloidal suspension, providing information on the stability and aggregation characteristics of the nanomaterials [27].

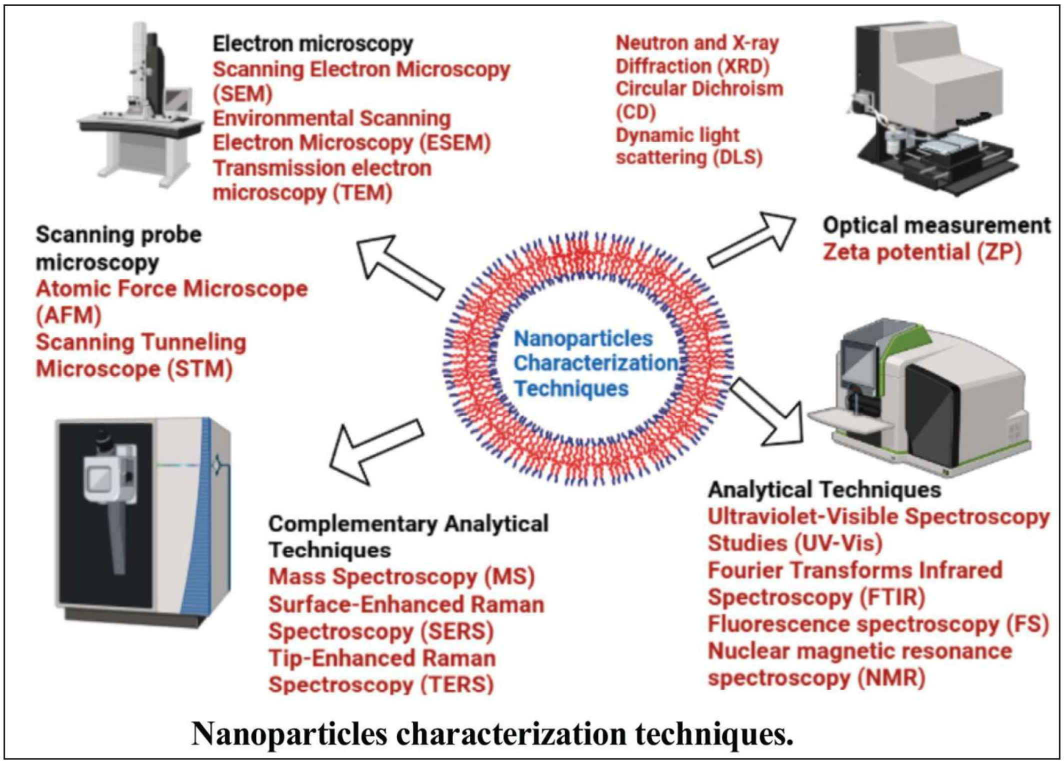


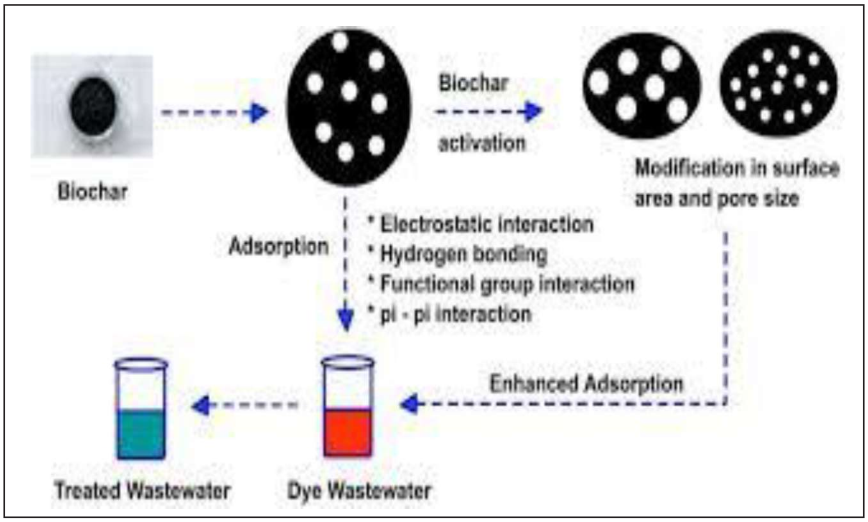
Fig. 7: Characterization Techniques

IV. Removal of Dyes from Aqueous Solutions by Adsorption

As explain earlier this review focused on environmental remediation, we can further explain that, in addition to their many applications in agriculture, medicine, and the environment, nanoparticles are widely used in the surface-based process of adsorption, which causes dye molecules to adhere to the surface of nanoparticles through chemical or physical interactions. These techniques make use of the large surface area of nanoparticles, high surface energy, and modifiable surface chemistry.

a) Mechanism of Adsorption

- *Surface Area:* Because of their large surface area and porous structures, such as those observed in metal oxides or carbon-based nanoparticles, more dye molecules can bind to the particles and this enhance the adsorption [28].



Source: Researchgate.net

Fig. 8: Adsorption Mechanism

- *Surface Chemistry:* The surface of nanoparticles can be functionalized to enhance specific interactions with dye molecules, such as electrostatic attractions, hydrogen bonding, or van der Waals forces [29].
- *pH-Sensitivity:* Numerous nanoparticles, including metal oxides (Fe_2O_4 and TiO_3), have pH-sensitive surface charges that affect how they interact with different dyes, which can be anionic or cationic [30]. For instance, positively charged nanoparticles are capable to adsorb an ionic dyes effectively (e.g., Congo Red) through electrostatic interactions.
- *Pore Structure:* The known high porosity nanoparticles that enable dye molecules to penetrate into interior pores and boost adsorption capacity are mesoporous silica and activated carbon [31].
- *Kinetics and Thermodynamics of Adsorption:* Numerous fields of studies, including environmental science, materials science, and catalysis, gain an understanding of the energy involved in the adsorption process (thermodynamics) and the rate at which adsorption happens (kinetics) [32].

b) Kinetics of Adsorption

The term “kinetic of adsorption” describes the rate at which molecules adhere to a surface. Typically, it gets affected by some factors such as:

- *Concentration:* Higher concentrations often lead to faster adsorption.
- *Temperature:* Generally, higher temperatures increase the rate of adsorption.
- *Surface Area:* A larger surface area provides more sites for adsorption.
- *Adsorbent-Adsorbate Interactions:* The strength of the interactions between the adsorbent and adsorbate affects the rate.

There are some other kinetic models that describe the rate of adsorption, which include:

- *Pseudo-First-Order:* This assumes that the rate is proportionate to the concentration of the adsorbate [33].
- *Pseudo-Second-Order:* Assumes that the rate is proportional to the square of the adsorbate concentration [33].
- *Intraparticle Diffusion:* This is the diffusion within the pores of the adsorbent [34].

c) Thermodynamics of Adsorption

Thermodynamics can predict whether an adsorption process will occur spontaneously. This is determined by analyzing the *Gibbs free energy change* (ΔG), which considers the *enthalpy change (ΔH)* and *entropy change (ΔS).* Adsorption processes often follow either the *Langmuir* or *Freundlich isotherm models.* These models describe how dyes are distributed between the liquid phase and the solid surface at equilibrium. The rate of adsorption is influenced by the surface properties of the nanoparticles and the molecular size of the dyes [35].

V. Factors Affecting Adsorption of Dye by Nanomaterials

Adsorption of dyes by nanomaterials is a complex process influenced by several parameters, which can be summarized and explain as follows:

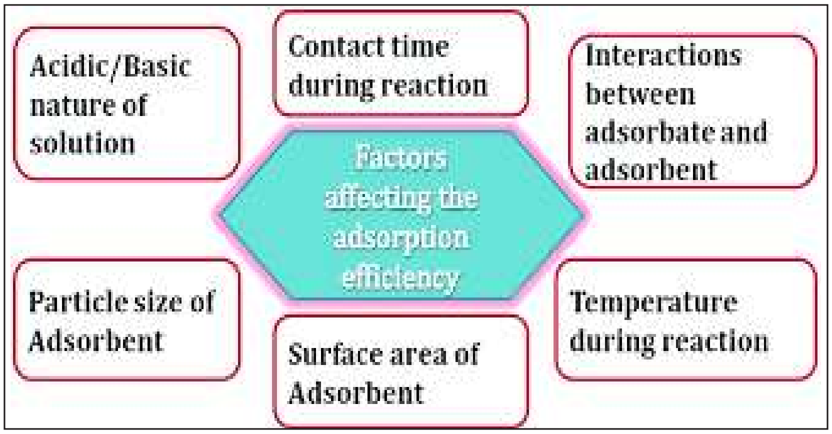


Fig. 9: Factors Affecting Adsorption Efficiency

a) Surface Area of Adsorbent

Nanomaterials frequently have a large ratio of surface area to volume. An increased surface area gives dye molecules additional places to cling to, increasing the ability of the nanomaterials to adsorb dyes [36]. For instance, studies have shown that because of their huge surface area, nanoparticle-based adsorbents, such as graphene oxide, have shown great dye removal effectiveness [37].

b) Surface Charge and Functional Groups

The surface charge of nanomaterials and the presence of functional groups which influence chemical properties of the nanomaterials and their interaction with dye molecules. Dyes can be cationic, anionic, or neutral, and the surface charge of the nanomaterials can enhance or reduce electrostatic interactions. For example, Silver nanoparticles with different surface functional groups have been used to adsorb anionic dyes like Congo Red, demonstrating the role of surface chemistry [38].

c) pH of the Solution

The pH affects the ionization of both the dye and the adsorbent surface. It can affect the degree of ionization of the dye molecules and the surface charge of nanomaterials, thus impacting adsorption processes. Some studies have shown that the removal efficiency of dyes like methylene blue using iron oxide nanoparticles varies with pH [39].

d) Temperature

The adsorption rate and capacity are dependent on temperature variations. Elevated temperatures typically accelerate the adsorption process because of their increased kinetic energy; however, they can also modify the stability and solubility of the adsorbent and dye. According to certain research, heated carbon nanotubes can adsorb more dyes, such as rhodamine B, because of faster diffusion rates [39].

e) Initial Dye Concentration

The starting concentration of the dye affects the adsorption driving force. The adsorption capacity often increases with increasing concentrations until equilibrium is reached. When starting with varying quantities of dyes, such as malachite green, nanomaterials like TiO_2 have demonstrated variable dye removal efficiency [40].

f) Contact Time

The amount of dye eliminated depends on the adsorption time. Dye usually absorbs quickly at the beginning, but as the sites fill up, the adsorption slows down. According to Zhao *et al.* (2011), adsorption experiments involving dyes on silica nanoparticles generally exhibit a rapid initial adsorption, which is succeeded by a gradual approach to equilibrium [41].

A. Adsorption Models

Nanoparticle adsorption models explain the interactions and binding mechanisms between substances and the surfaces of nanoparticles. These models are important for predicting and understanding adsorption behavior for various applications, including catalysis and environmental cleanup [42]. Below is a detailed overview of important adsorption models and recent developments in the field:

i) Langmuir Adsorption Model

The Langmuir model is based on the idea that adsorption takes place on a surface with a limited number of uniform sites, where each site can accommodate only one molecule [43]. Its key assumptions include:

- Adsorption sites are evenly distributed across the surface.
- Adsorption is a reversible process, with an equilibrium between the molecules that are adsorbed and those that remain free.
- There are no interactions between molecules once they are adsorbed.

This model is mathematically represented as:

$$q_{e}= \frac{q_m K_l C_e}{1 + K_l C_e}$$

Where:

- q_e is the amount of dye adsorbed per unit mass of adsorbent at equilibrium.
- q_m is the maximum adsorption capacity.
- K_l is the Langmuir constant related to the adsorption affinity.
- C_e is the equilibrium concentration of dye.

Mathematical Application of the Model

Consider the following example, A study was conducted to investigate the adsorption of methylene blue dye onto a nanomaterial. The experimental data shows that at a dye concentration (C_e) 50 mg/L. The nanomaterial adsorbed (qe) is 30 mg/g. The maximum adsorption capacity (q_m) is 45 mg/g and the Langmuir constant (K_l) is 0.02 L/mg were determined experimentally, using Langmuir isotherm. calculate the theoretical amount of dye adsorbed (q_e) at an equilibrium concentration (C_e) 50 mg/L.

Using formula:

$$q_{e}= \frac{q_m K_l C_e}{1 + K_l C_e}$$

When substituting the values, then we get

$$q_{e}= \frac{45 \times 0.025 \times 50}{1 + 0.02 \times 50}$$

The value of q_e then can be determined as:

$$q_e = \frac{45}{2} = 22.5 \frac{mg}{g}$$

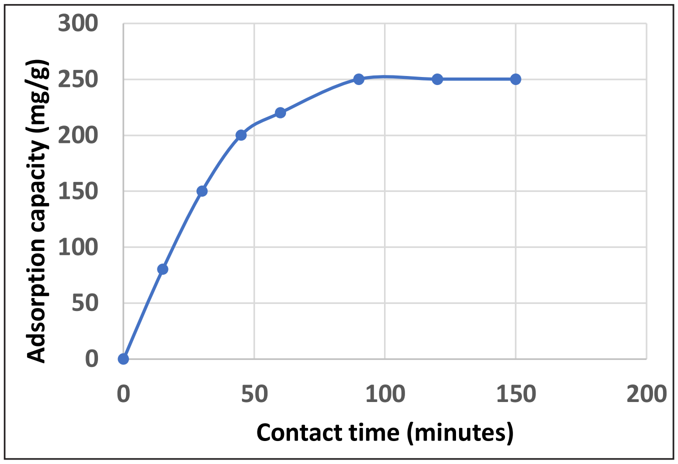
The theoretical adsorption of methylene blue dye on nanomaterial at an equilibrium concentration (C_e) i.e. 50 mg/g is equal to 22.5 mg/g.

Adsorption can equally be recorded graphically using Langmuir model, when data on contact time and adsorption capacity of the dye is gathered, for example: Adsorption of Methylene blue (MB) dye by ZnO nanoparticles was observed and recorded as follows:

Table I

Contact Time (Minutes)	*Adsorption Capacity (mg/g)*
0	0
15	80
30	150
45	200
60	220
90	250
120	250
150	250

Using Langmuir adsorption isotherm, the data can be represented graphically as follows:



The graph illustrates monolayer adsorption, which aligns with the Langmuir model. This linearity results from the model's assumptions and offers an easy method to calculate the Langmuir constant, helping to evaluate whether the model accurately represents a specific adsorption system.

ii) Freundlich Adsorption Model

The Freundlich adsorption isotherm is an empirical equation that describes the relationship between the amount of a gas adsorbed on a solid surface and the gas pressure at a constant temperature [44]. It was proposed by Herbert Freundlich in 1909.

Equation

$$\frac{\boldsymbol{x}}{\boldsymbol{m}} = \boldsymbol{K} \times \boldsymbol{p}^{\frac{1}{n}}$$

where:

- x is the mass of the adsorbed gas.
- m is the mass of the adsorbent.
- p is the equilibrium pressure of the gas.
- K and n are constants specific to the adsorbent-adsorbate system.

Interpretation

- K is a constant related to the adsorbent and adsorbate. A higher value of K indicates stronger adsorption.
- n is a constant related to the intensity of adsorption. It is usually a value between 0 and 1.

If n is less than 1, it indicates that adsorption is more favorable at lower pressures.

If n is equal to 1, it indicates linear adsorption.

If n is greater than 1, it indicates that adsorption is more favorable at higher pressures.

This isotherm is widely applied to model adsorption in various fields, such as:

Environmental Science: To investigate the adsorption of pollutants from air or water onto adsorbent materials.

Chemical Engineering: To design adsorption processes used in separation or purification.

Materials Science: To analyze the adsorption behavior of materials like activated carbon or zeolites.

While the Freundlich isotherm offers a practical empirical model, it lacks a strong theoretical foundation. For more complex systems or when a deeper understanding of adsorption mechanisms is necessary, models like the Langmuir isotherm may be more appropriate [45].

iii) Redlich-Peterson Isotherm Model

This is a hybrid adsorption isotherm model which describes the adsorption process on heterogeneous surfaces by combining elements from both the Langmuir and Freundlich isotherms. It offers a more generalized approach to modeling adsorption equilibria, particularly when the data cannot be accurately captured by either the Langmuir or Freundlich models alone [46]. The Redlich-Peterson Adsorption isotherm is a semi-empirical equation used to represent the adsorption of gases onto solid surfaces, incorporating aspects from both the Langmuir and Freundlich isotherms [47].

The equation is given by:

$$P = \frac{(K \times n)}{\left(1 + (K \times P)^{\frac{1}{n}}\right)}$$

where:

- P is the pressure of the gas.

- K is a constant related to the affinity of the gas for the solid surface.
- n is a constant related to the heterogeneity of the surface.

The Redlich-Adsorption isotherm has the following properties:

- It reduces to the Langmuir isotherm when n = 1.
- It reduces to the Freundlich isotherm when n approaches infinity.
- It can be used to model adsorption on both homogeneous and heterogeneous surfaces.

The Redlich-Adsorption isotherm is a model used to analyze how gases stick to solid surfaces. It can help us figure out how much gas a solid can hold and how much the gas likes to be on the surface. The Redlich-Peterson model is another model that mixes parts of two other models, Langmuir and Freundlich, to give a more accurate picture of how gases stick to uneven surfaces [48].

iv) Temkin Adsorption Model

The Temkin isotherm is a mathematical model used to represent how gases stick to solid surfaces. It assumes that the energy required to make a gas molecule stick to the surface gets smaller as more molecules already stick there. This happens because the molecules that are already on the surface can push on each other, making it difficult for new ones to stick [49].

Equation:

The Temkin isotherm equation is given by:

$$q = RT \times \ln(K \times P)$$

where:

- q is the amount of gas adsorbed per unit mass of adsorbent.
- R is the gas constant.
- T is the absolute temperature.
- K is a constant related to the adsorbent-adsorbate interactions.
- P is the pressure of the gas.

Kinetic Phenomena in Adsorption Techniques. Temkin model assumes that the energy required for a gas molecule to stick to a surface decrease as more molecules already adhere there. It also assumes a single layer of molecules can stick and there is no interaction between them [50]. This model is often used to explain how gases stick to surfaces that vary, like catalysts and activated carbons. It's also used to study pollutant removal from water and air. The model can be used to describe adsorption on uneven surfaces and determine the energy involved in adsorption. However, it doesn't account for interactions between adsorbed molecules and might not be as accurate as other models. In conclusion, the Temkin model is a valuable tool for understanding gas adsorption on solid surfaces, especially for uneven surfaces, and can help determine the energy involved [51].

v) Elovich Model of Adsorption

The Elovich equation is a model used to explain how gases or dissolved substances stick to solid surfaces. It is often used to study data from experiments where surfaces are uneven or the sticking process is complicated [52].

Equation:

The Elovich equation is given by:

$$\log(q) = \log(q_m) - \frac{(k \times t)}{2.303}$$

where:

- q is the amount of adsorbate adsorbed per unit mass of adsorbent at time t.
- q_m is the maximum adsorption capacity.
- k is the rate constant of adsorption**.**

The Elovich equation can be linearized by plotting log(q) versus time (t), where the slope of the line is given by -k/2.303, and the intercept corresponds to $\log(q_m)$. The rate constant k is associated with the activation energy of adsorption, with a higher k value indicating a faster adsorption rate. The maximum adsorption capacity (q_m) can be determined from the plot's intercept [53]. Elovich equation is often employed to analyze adsorption data from various experimental techniques like batch adsorption, column adsorption, and gas chromatography. It is especially useful for studying adsorption on heterogeneous surfaces or examining complex adsorption mechanisms. As a kinetic model, the Elovich equation offers valuable insights into the adsorption behavior of gases or solutes on solid surfaces, making it an important tool for analyzing experimental data and understanding the mechanisms behind adsorption processes [54].

This model assumes that the sticking process involves the formation of chemical bonds between the sticking substance and the surface. The surface is uneven, with different spots having different energy levels for sticking. As more of the substance sticks, the rate of adsorption process exponentially slows down.

vi) Dubinin-Radushkevich (DR) Model

The Dubinin-Radushkevich (DR) model is a mathematical framework used to explain the adsorption of gases or vapors onto solid surfaces. It relies on the volume filling theory, which assumes that adsorbent pores are gradually filled with adsorbate molecules until saturation is reached [55].

Equation:

The DR equation is given by:

$$\log(q) = \log(q_m) - B \times (A \times \log(P))^2$$

where:

- q is the amount of adsorbate adsorbed per unit mass of adsorbent.
- q_m is the maximum adsorption capacity.
- B is a constant related to the adsorbent-adsorbate interactions.
- A is a constant related to the characteristic energy of adsorption.
- P is the pressure of the gas or vapor.

The DR equation can be linearized by plotting log(q) against, where the slope of the line is -B, and the intercept corresponds to $\log(q_m)$ [56]. The constant B is associated with the micropore volume of the adsorbent, with higher B values indicating larger micropore volumes. The constant A relates to the characteristic energy of adsorption, where a higher a value signifies stronger interactions between the adsorbent and adsorbate.

The DR model is frequently used to analyze adsorption data from techniques such as gas chromatography, breakthrough curves, and isotherms [57]. It is especially useful for studying the adsorption of gases or vapors on microporous materials like activated carbons and zeolites [58].

The DR model is straightforward and user-friendly. It offers insights into the micropore volume and the characteristic energy of adsorption, and it can be applied to a wide variety of adsorbents and adsorbates [59].

The main limitation of the DR model is that it may not be precise for adsorbents with a broad range of pore sizes, and it does not consider interactions between adsorbed molecules. Despite this, the Dubinin-Radushkevich model remains a valuable tool for analyzing adsorption data and understanding the behavior of adsorbents and adsorbates. It offers insights into the micropore structure and adsorption characteristics of materials, making it a widely applied model in both research and industrial settings.

Understanding these adsorption models is crucial for assessing the efficiency and capacity of nanomaterials in various applications. Recent research offers new perspectives on how these models apply to emerging nanomaterial systems and their interactions with various dyes. For more detailed studies, the referenced articles provide further data and experimental validation of these models.

B. Kinetics and Thermodynamics Adsorption Models

The adsorption models discussed above can be classified into kinetic and thermodynamic models, both of which are essential for understanding the interactions between adsorbates and adsorbents. Kinetic models emphasize the rate of adsorption and how it evolves over time, providing insights into how quickly a system reaches equilibrium [60]. In contrast, thermodynamic models focus on the equilibrium state and the associated energy changes, helping to determine whether adsorption is favorable and the maximum amount of a substance that can be adsorbed at equilibrium [61]. The key differences between these two models can be summarized in a table as follows:

TABLE II: COMPARISON BETWEEN ADSORPTION MODELS

Model	*Focus Point*	*Usability*	*Important Variables*	*Examples*
Kinetic adsorption model	Rate of Adsorption	Predicting rate of Adsorption	Time, concentration and temperature	Pseudo-first-order, pseudo-second-order, intraparticle diffusion
Thermodynamic adsorption model	Equilibrium state	Determining equilibrium capacity and thermodynamics properties	Concentration/ pressure and temperature	Freundlich, Langmuir, Temkin, Brunauer-Emmett-Teller (BET)

These models are both essential tools for predicting and understanding the adsorption processes and Mathematical applications of the models [62].

VI. CONCLUSION

This review highlights the important advancements reached in green synthesis of metal oxide nanoparticles and their promising applications in dye removal from aqueous solutions. The use of organic (biological) resources as stabilizing and reducing agents provides a sustainable and eco-friendly alternative to conventional chemical methods. Metal oxide nanoparticles, with their high surface area, catalytic activity, and adsorption capacity, are highly effective adsorbents for various dyes.

Future research should focus on advancing green synthesis techniques to enhance the efficiency of nanoparticle production while also controlling their size, shape, and surface properties. Furthermore, it is crucial to investigate the long-term stability and reusability of these nanoparticles for practical applications. By overcoming these challenges, green-synthesized metal oxide nanoparticles can offer sustainable water treatment solutions and help reduce the environmental impact of dye pollution.

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