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Preparation of Bimetallic and Trimetallic Nanomaterials and their Role in Waste Water Treatment: A Review

Rangnath Ravi*[1] and Abhijeet Mishra[2]

[1]Department of Chemistry, Sri Aurobindo College, University of Delhi, India.

[2]School of Life Sciences, Jawaharlal Nehru University, New Delhi, India

ABSTRACT

Multimetallic nanoparticles (NPs) have extraordinary properties and therefore, drew the attention regarding their synthesis and applications in the form of bi and tri metallic nanoparticles. Bimetallic (BNPs) and trimetallic nanoparticles (TNPs) are gaining enormous attention than that of monometallic nanoparticles. Both NPs can be synthesized by different methods such as microwave, selective catalytic reduction, micro-emulsion, co-precipitation and hydrothermal etc. Using physical and chemical methods have more disadvantages such as production of toxic byproduct, use of excess energy and additional use of stabilizer. In addition, nanocomposites of bimetallic and trimetallic can be synthesized with inorganic and organic compounds such as: carbon, graphene, gelatin, cellulose, starch, chitosan, alginate, etc. The combination of two or more phases in these nanoscale materials provide them high surface area to volume ratio and possess higher degree of porosity that help in enhancing their adsorption and reusability found more helpful in removing the toxic pollutants from the environment. Further these nanomaterials can also be fabricated in such a way that reduces the electron hole recombination, which induces synergetic effect between the constituent moieties that help in the degradation of pollutants. For instance the synthesis of trimetallic nanostructures with defined design along with the required morphology as well as mesoporous and magnetic characteristics have shown their versatile properties find applications in many industries such as conducting magnetic inks, memory devices, catalysis, bio-medical and especially in water treatment. Although, to obtain the nanoparticles with desired morphology and size is relatively difficult, which involves expensive non-eco-friendly reagents. In this review, we discussed in detail about the synthesis and role of Bimetallic and Trimetallic NPs as an adsorbent.

KEY WORDS: NANOPARTICLES, BIMETALLIC, TRIMETALLIC, WASTE WATER TREATMENT AND ADSORPTION.

INTRODUCTION

The significance of nanotechnology and nanoscience has been mainly associated with fabrication, characterization and applications of nanoscale materials in the form of nanorods, nanotubes, nanoparticles, nanosheets and nanoporous structures. They have been developed through the association of atomic and molecular clusters (Pitkethly 2004). Nanoparticles (NPs) may be defined as they possess at least one of the dimensions of nanosize. They are lying in the nanoregime i.e. in between 1nm to 100nm range (Jain et al., 2006). They act as the bridge between the bulk and their atomic structures (Luo et al., 2006). Bulk materials exhibit regular physiochemical properties regardless of their size. However, when the same materials acquire the nano-size, they start to show highly enhanced useful physico-chemical, electronic, electrical, magnetic, optical, catalytic properties etc. as compared to their conventional counterparts (Jiang et al., 2008; Sonkusare et al. 2020).

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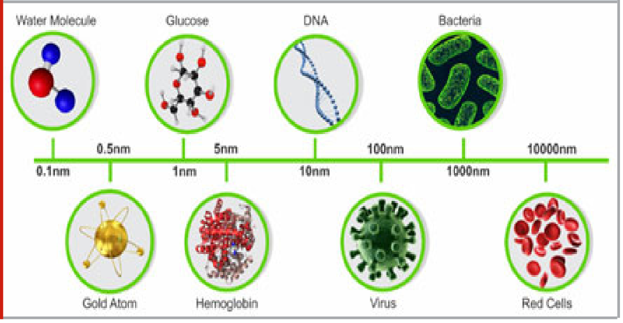
This can be attributed to the high surface area to volume ratio (Schrand et al., 2010). Because of these characteristic properties NPs have shown tremendous potential for their applications in the field of engineering, environmental, biological sciences as well as in biotechnology (Mishra et al.,2015). NPs also play a pivotal role in many catalytic and biochemical processes (Guildford et al. 2009; Wang et al. 2019). The concept of nanoparticle and their application in biological systems also has advantages over other materials because their size is very much close to the size of cellular components (Yang et al. 2019). For instance, the size of a DNA molecule is about 2.5 nm, thickness of biological membrane is 6 nm and a protein is approximately 50 nm wide (Liu et al. 2018). Besides this, NPs plays significant role to analyze toxic dye removal from industrial wastewater (Leite et al. 2018; Sonkusare et al. 2020). The NPs classification, synthetic procedures and their applications in dye removal and cancer treatment are discussed in the proceeding units.

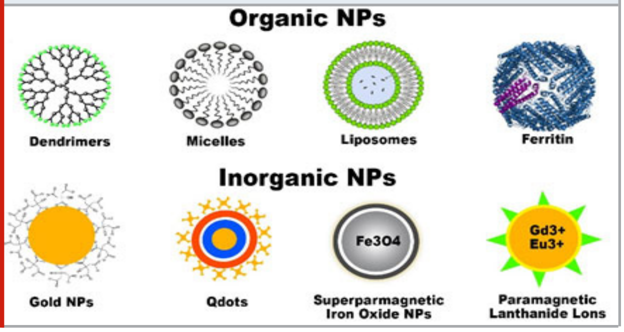
Background and Purpose of Review: The classification of NPs based on structure, morphology and size, the NPs of various shapes are presented in fig 1 a-b and further discussed as follows.

Figure 1a: Comparison of size in nanoparticles. (Brar et al., 2010)



Based on dimensions: Based on their dimensions and aspect ratio, NPs can be classified into four classes. The general characteristics of these nanoparticles are discussed in Table1.1, covering their definitions and area of applications, while their two- and three-dimensional structures are given in Fig. 2.

Figure 1b: Examples of nanoparticles based on constituents and structures (Silva et al., 2019)



Based on uniformity: NPs can be classified in the forms of their states such as distributed aerosols, nanoclusters, colloidal solution and suspension (Kumar et al., 2018). These behaviors are based on the notion of dispersed phase and nature of dispersion medium along with their chemical and electromagnetic properties. Effectively, slightly loaded particles and magnetic particles display aggregation unless some stabilizing agent, like polymers are added and covers their surface. Agglomerated NPs act as macromolecules and loses the specific characteristics of NPs. NPs like nanocubes and spherical NPs are isometric due to their equal sizes (Adamiano et al., 2018, Saleh et al., 2020). There are some anisometric NPs like nano-stars, nanorods and nano-plates etc (Bansal et al., 2020).

Table 1.1 Types of NPs, their definition along with examples and their uses.

Types of NPs	Definition	Examples	Uses	Ref
Zero Dimension (0D)	NPs having each of three dimensions limited in the nanoscale.	Fullerenes Composite NPs Core Shell NPs	In various biomedical applications	(Barnakov et al. 2019)
One Dimension (1D)	NPs have two dimensions in the nanoscale.	Nanotubes Nanorods	Energy harvesting, Storage efficiency	(Linfeng et al. 2019)
Two dimensional (2D)	NPs having one dimension in nanoscale	Nano films, Nanosheets	Biochemical sensors, Catalysis	(Yola et al. 2018)
Three dimensional (3D)	NPs which no dimension are confined to the nanoscale	Bulk powders, Nanowire bundles	Biomedical	(Yang et al. 2019)

Metal Oxides NPs: For the last several decades, metal oxides have gained a considerable interest for the maximum numbers of nanomaterials due to their different promising constituents and versatile nature. Metal oxides are most easily available, fast and effective materials for their application in water treatment without the involvement of undesirable by-products. It can also be applied for many other applications including biomedical sciences because of their nontoxic and anti-microbial behavior. They can provide the oxygenated sites for the surface complexation with foreign elements thus can be most suitable for water remediation technology. Moreover, metal oxides due to their high surface area are expected to be more suitable for water treatment under the water quality constraints. For this, the separation of adsorbent and post adsorption is necessary; therefore, the use of magnetic metal oxide NPs in the field of water treatment technology has more pronouncedly emerged, with these characteristics the metal oxide NPs are further classified as follows:

Figure 2: Nanoparticles based on dimensions. (Pal et al., 2011)

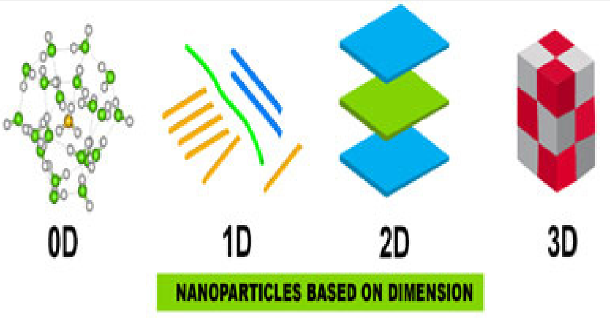
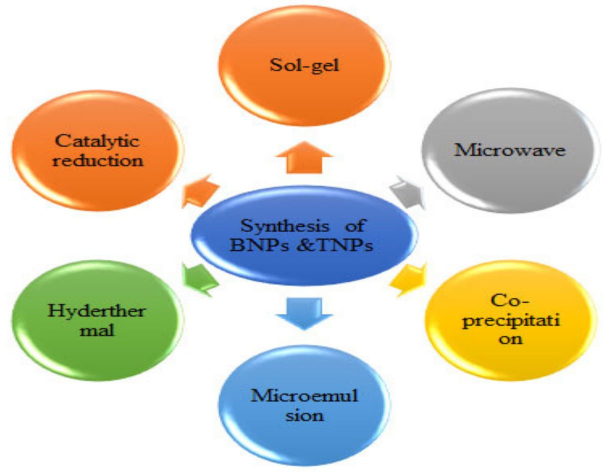


Figure 3: Different approaches of synthesis for Bimetallic and Trimetallic NPs.



Monometallic NPs: As the name suggests monometallic NPs (MNPs) consist of single metal atoms, which alone determines the properties of these NPs. They can be prepared by many methods, out of which chemical method is the most common. From the past few decades, MNPs have attained greater interest owing to their enhanced physical and chemical properties (Pantidos et al., 2014). The most important examples of monometallic oxides are: Iron oxide (FeO, Fe_2O_3 and Fe_3O_4), titanium oxide (TiO_2), aluminium oxide (Al_2O_3), zirconium oxide (ZrO_2), manganese dioxide (MnO, MnO_2 and Mn_2O_3), copper oxide (CuO and Cu_2O) and zinc oxide (ZnO). These NPs have been widely used for several applications such as in electronic, dye adsorption (Zhang et al., 2016), catalysis (Gawande et al., 2016), optical (Maruthupandy et al., 2017), and as antimicrobial agents against a few microorganisms such as Escherichia coli (Ribeiro et al., 2018) and *Streptococcus mutans* (Ramar et al., 2015, Lima et al., 2020).

Bimetallic NPs and Trimetallic NPs: Bimetallic nanoparticle (BNPs) are the mixture of two different metals. BNPs can be formulated by using two inorganic materials in order to enhance the desired properties, which cannot be achieved by single metal atom. Furthermore, by the virtue of tiny size and greater volume to surface area ratio, these are significantly used in adsorption of various dyes for water purification, anticancer properties, catalyst etc. (Nasrabadi et al., 2016, Sharma et al., 2017). In addition to magnetic adsorptive property, adsorbent used in removal of pollutants like arsenite As(III), preoxidation of As(III) to As(V) is also necessary, which can be achieved by the doping of oxidants like chlorine. However, they can also increase the risk of the formation of un-healthy by-products by reacts with natural organic matter present in water.

Trimetallic NPs (TNPs) are the blend of three different metals and have advantage over MNPs. The volume to surface area ratio of TNPs is reasonably unstable, which can be stabilized by using different stabilizers such as organic ligands and surfactants leads (Martinez et al., 2018). TNPs as well as BNPs have acquired more interest than the MNPs in terms of scientific and technological point of view (Ravi et al., 2019). The properties of BNPs and TNPs can be same or differ from the pure elemental particles and may acquire unique size, and extra optical, electronic, thermal and catalytic properties (Sharma et al., 2017, Ali et al., 2020). In past few years, extensive studies in the field of BNPs and TNPs have recorded.

Preparation of Bimetallic and Trimetallic NPs: BNPs and TNPs can be synthesized by various important methods such as sol-gel, microwave radiation, co-precipitation, catalytic reduction and hydrothermal etc. These methods are important to prepare nanoparticles of different size, shape and composition. Some of the methods used for the synthesis of the nanoparticles are discussed below (Table 1.2 and Fig.3).

Applications of Bimetallic and Trimetallic nanoparticles: NPs because of their versatile properties and many folds enhanced chemical, catalytic, structural, magnetic and electrical characteristics, they find wide applications in the field of electronic, optical, energy, biological, medicinal and environmental industries (Fig.4). Among these applications, our review discusses the use of these BNPs and TNPs in the field of environmental pollution (water treatment) and nanomedicine for the treatment of lethal diseases (Chen et al. 2016).

Application of BNPs and TNPs in Water treatment: Industrial wastewater is the major source of water pollution. As per the WHO report (WHO), thousands of pollutants are present in environment in the form of air and water pollutants, some of these pollutants have severe thread for living organisms specially for aquatic systems, besides these pollutants are also responsible for various types of deadly diseases like cancer. Globally 9.6 million deaths per annum due to cancer in 2018 (WHO 2018). The alarming death rate due to cancer has become a worldwide challenge to the bio scientists and physicians. Literature reports that the toxic dyes used in textile industries is one of the main sources of pollutants causing cancer and danger for aquatic life (Mishra et al. 2015). The effects of textile dyes on the wealth of society and aquatic systems have been shown in Fig. 5 (Sha et al. 2016). Thus, the water pollution acts as the biggest challenge to the mankind (Carolin et al. 2017).

Table 1.2. Fabrication, mode of synthesis and significant applications of some important inorganic and organic nanoparticles.

Sr. No.	Inorganic/ organic NPs	Mode of synthesis	Significant applications	Ref.
1	Titanium dioxide	Sol gel, Hydrothermal, sonochemical, solvothermal, reverse micelles	Photo-catalysis, antimicrobial applications, gas and humid sensor, sunscreen products, wastewater treatment etc.	(Morshed et al., 2018, Baranowska-Wójcik et al., 2020)
2	Zinc oxide	Homogeneous precipitation, microwave method, thermal evaporation, Sol–gel, and chemical synthesis	Gas and humid sensor, photocatalytic degradation of toxic pollutants from wastewater, skin care products, biomedical applications such as anticancer, antifungal and antibacterial etc.	(Rajabi et al., 2017)
3	Aluminium oxide	Sol–gel, flame spray pyrolysis, reverse micro emulsion	Removal of heavy metal ions from waste water treatment, antimicrobial applications, separation chamber, catalysis, biomedical applications etc.	(Su et al. 2018)
4	Silica	Flame synthesis, sol-gel, micro emulsion	Gene and drug delivery, biosensor, enzyme immobilization etc.	(Sodipo et al.2016)
5	Magnetic	Sol–gel, Co-precipitation, solvothermal, and sonochemical method	Bio-separation, dye and arsenic removal from wastewater, MRI, Immobilization of enzymes	(Srikar et al.2016)
6	Silver	Chemical reduction, photochemical method, Microwave and gamma irradiation, Biological synthesis by plant extract, enzymes, carbohydrate etc.	Antimicrobial, anticancer, catalysis, biosensor, water purification	(Natsuki et al.2015)
7	Gold	Reduction by chemicals, photochemical reaction, microwave irradiation	Biosensors, catalysis, drug delivery, anticancer etc.	(De souza et al. 2019, Priyadarshini et al. 2017)
8	Starch	Acid Hydrolysis, Ultrasonication, Gamma Irradiation	Drug carrier, wastewater treatment, tire making, fat replacers and emulsion stabilizers	(Kim et al. 2016)
9	Chitosan	Ionic gelation method, Reverse micelles method	Delivery system for vaccines, prevent infection in wounds and wound-healing process by enhancing the growth of skin cells, antibacterial agent	(Chandra et al. 2016)

Figure 4: Various applications of metallic NPs.

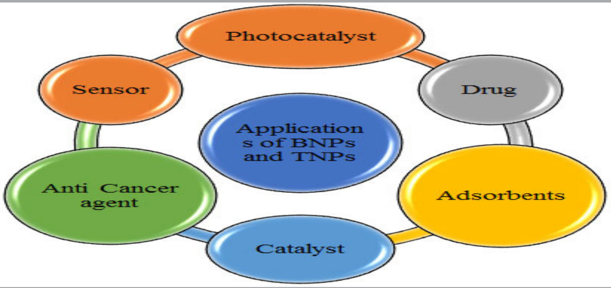


Figure 5: Pictorial representation of the effect of textile dyes in health and aquatic system.

Table 1.3. List of adsorbents used against the removal of various dyes

S.N.	Adsorbent	Dyes	Ref.
1	Fe–Ni bimetallic NPs	Reactive Blue 21	(Kale et al. 2019)
2	ZnO NPs	Methyl orange Amaranth	(Zafar et al. 2019)
3	Partially oxidized graphite nanoparticles (POG-NPs)	Congo red Malachite green	(Mahmoud et al. 2019)
4	Fe_3O_4@SiO_2@PIL nanocomposite	Acid orange II Thionin acetate	(Yang et al. 2019)
5	ZnO	Malachite Green Congo Red	(Zhang et al. 2019)
6	$FexCo_3$-xO_4 NPs	Congo Red	(Liu et al. 2019)
7	Ni-Ag bimetallic NPs	Sunset Yellow Tartrazine	(Mirzajani et al. 2019)
8	Agar@Fe/Pd Bimetallic NPs	Methylene blue Rhodamine B	(Patra et al. 2019)
9	ZnO NPs stabilized on MWCNTs	Reactive blue 203	(Bagheri et al. 2019)
10	Ag-NPs using Albizia procera leaf extract	Methylene blue	(Rafique et al. 2019)
11	Fe_3O_4@Tb/AMP core-shell NPs	Alizarin Red Congo Red	(Huang et al. 2018)
12	CeO2 NPs	Reactive Green 19 Reactive Orange 84 Reactive violet 1 Reactive Yellow 81	(Sane et al. 2018)
13	WOx NPs	Rhodamine B	(Ying et al. 2018)
14	Alginate/γ-Fe_3O_4	Methylene Blue	(Talbot et al. 2018)
15	ZnO NPs using alginate	Methylene Blue	(Tamer et al. 2018)
16	Iron oxide NPs	Reactive Black 5	(Chang et al. 2018)
17	Nickel ferrite	Methyl orange Congo red	(Moghaddam et al. 2018)
18	carbon dots/$ZnFe_2O_4$ (CDs/ZFO)	Methyl orange	(Shi et al. 2018)
19	Zr-based magnetic Metal-Organic Frameworks composites	Methylene Blue	(Huang et al. 2018)
20	$SrFe_2O_4$	Erichrome black T	(Zafar et al. 2018)
21	ZnO	Methylene blue Congo red	(Kataria et al. 2017)
22	ZnO loaded activated carbon	Brilliant green Orange G	(Nasrollahzadeh et al. 2018)
23	$NiFe_2O_4$@AlMCM-41-Cu_2O	Rhodamine B Methylene blue	(Sohrabnezhad et al. 2017)
24	$MnFe_2O_4$/diatomite nanocomposite	Methylene blue	(Sun et al. 2017)
25	Ag NPs	Methylene blue	(Saha et al. 2017)

Adsorption technique is found to be more suitable, simple and cost effective, which has been efficiently used for the removal of wide range of water pollutants (Lata et al. 2016). These adsorbents maybe of organic (Cellulose, organic fibers, agricultural wastes and their fibers etc.) and inorganic (sands, metallic ferrites, metal sulphides, oxides etc.) nature (Soltani et al. 2015). Among these various types of magnetic metal ferrites have been successfully used for the removal of toxic dyes and other pollutants due to their easy reusability high absorbance capacity and more simple mode of application and rechargeability (Chang et al.,2020). The use of various types of metal NPs as adsorbents for the removal of different types of dyes are highlighted in Table 1.3.

Moreover, the literature on the application of various types of NPs in removal of dyes is highlighted in Table 1.3.

CONCLUSION

Bimetallic and Trimetallic nanoparticles are more important than that of the monometallic nanoaprticles. The bimetallic and trimetallic nanoparticles are synthesized by various method such as sol-gel, microemulsion, sputtering, co-precipitation etc. Different shape and size of the BNPs and TNPs can be obtained by the various methods. Bimetallic and Trimetallic NPs are used as an excellent adsorbent due to their high adsorbing capacity and shown outstanding results for reusability purpose.

Future Application: Bimetallic and trimetallic are very promising nanomaterials for waste water treatment as compared to other types of NPs. To get the best result further experiments and research should be carried out. Further, these NPs could be used for other applications including biomedical application and catalysis.

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