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# A Review on the Synthesis and Application of Nanomaterials for the Removal of Emerging Contaminants from Industrial Wastewater

**Comfort M. Ngwu, *Steven A. Odoemelam and Jude C. Nnaji**

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***Abstract*** *The removal of emerging contaminants from the environment has been an issue of top priority in recent times due to their adverse ecological effects. Nanomaterials have proven their worth in the search for effective and efficient remediation materials for wastewaters. The chemical methods of nanomaterial synthesis with co-precipitation being the simplest and the biological methods using plants provide ease of fabrication and make them economical too. Characterizations are done using different techniques such as powder XRD, electronic microscopy, atomic force microscopy and thermogravimetric analysis and these give information about the morphology, particle size, impurities, roughness, thermal stability and degradation pattern of nanomaterials. Nanomaterials often find application in adsorption, photocatalysis, catalytic ozonation, membrane process and nanoremediation of environmental pollution.*

**Key Words**: *Nanomaterials, emerging contaminants, industrial wastewater, nanoremediation, environmental pollution.*

**Comfort Ngwu**
Department of Chemistry,
Michael Okpara University of Agriculture
Umudike, P.M.B 7267, Umuahia, Abia State, Nigeria
**Email:**
**Orcid id**

**Steven S. Odoemelam**
Department of Chemistry,
Michael Okpara University of Agriculture
Umudike, P.M.B 7267, Umuahia, Abia State, Nigeria
**Email:** saodoemelam@gmail.com
**Orcid id**

**Jude C. Nnanji**
Department of Chemistry,
Michael Okpara University of Agriculture
Umudike, P.M.B 7267 Umuahia, Abia State, Nigeria
**Email:** judennaji30@gmail.com
**Orcid id:**0000- 0002-5569-4818

## 1.0 Introduction

The discharge of contaminants (ECs) such as pharmaceutical and personal care products (PPCPs), disinfectants, surfactants, pesticides, dyes, paints, preservatives and food additives into the aquatic environment by industries has attracted serious environmental concern because of their impact on aquatic and other components of the environment. Emerging contaminants (also known as organic contaminants) are synthetic or naturally occurring chemicals or any microorganisms that are not commonly monitored in the environment but have the potential to enter the environment and cause known environmental damages and suspected detrimental impact on the ecosystem and human health (Rosenfeild & Fengm 2011). The different classes of ECs that are currently known are listed in Table 1.

As at 2015, Geissen *et al*. (2015) stated that none of the emerging contaminants are included in any international monitoring programme indicating that insight knowledge about the life of emerging contaminants and their impact is significant in providing a guide to the health of the environment. In the twentieth century, scientific awareness of the existent and future danger has been reported for several components of the ecosystem. The progress has been enhanced by documented researches (Adeleye *et al.,* 2016; Grey *et al.,* 2013). Staurt *et al.* (2012) however detected new emerging organic ground water contaminants that were not previously found in the UK and attributed their source to agriculture, urban and rural point sources. Most of the reported emerging contaminants were polar molecules that may not be easily removed by conventional drinking water treatment including some pesticides metabolites, caffeine and DEET.. However, some pesticides metabolites, pharmaceuticals (such as carbamazepine and triclosan), nicotine, food additives and alkyl phosphate are classified as those that can be easily detected.

**Table 1. Classes and Examples of Emerging Contaminants**

| Class of compound | Examples |
|---|---|
| Pharmaceutical and Personal Care Products (PPCPs) | Antibiotics, anticonvulsants, mood stabilizers and cosmetic products |
| Flame retardants and their impurities | Polybromonated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) |
| Pesticides and biocides | Perfluororoctane sulfonates (PFOS) and perfluoroctanoic acid (PFOA) |
| Steroids and endocrine disrupters | Biogenic and synthetic hormones |
| Disinfection byproducts | Nitrosamines and disinfection byproducts containing iodine |
| Industrial / domestic wastes | PAH, Bisphenol A, toluene |
| Food additives | Sucralose, saccharine etc. |

**(Source: ThermoFisher, 2018)**

Currently, awareness of the impacts of these contaminants on groundwater, rivers, and lakes is developing. This is because just about 1% of water on earth is accessible for human utilization Research findings have reveal several information on the fate of emerging contaminants and none of such findings has guaranteed the health of the present and future environment (Rasheed *et al.,* 2018; Dey *et al.,* 2019). Studies have shown that most of the conventional techniques for water and wastewater treatment are not effective in removing some emerging contaminants from water hence there is need for progressive research and development on advanced water treatment processes (Qu *et al.,* 2012). Ferroudj *et al. (*2013) also stated that some of the current advances in wastewater treatment have shortcomings like high-volatility and cost prerequisite, fragmented contamination expulsion and production of toxic sludge. The natural wastewater treatment is generally applied yet these are typically moderate and constrained because of the availability of non-biodegradable contaminant, which may be toxic to microorganisms (Samer, 2015). Physical processes such as filtration can remove the contaminants by transforming them from one phase to another but may produce a concentrated sludge that may be toxic and difficult to dispose (Rasalingam *et al.,* 2014).

In view of the challenges facing conventional water treatment methods, there is need to chanell current researches on water purification to those methods that can overcome present and future challenges. In as much as there are several water treatment methods that handle the non-emerging contaminants, technological advancement requires research and developments in modifying existing modifying existing method or invention of newer methods. It is expected that the newer methods should be effective, ecofriendly and cost effective in the treatment of industrial, munical and domestic wastes contaminated water that is deplete of emerging contaminants (Adejumoke *et al.,* 2018; Ferroudj *et al.,* 2013). Among all the various methods that have been established, nano materials has been found to present and future hope for the removal of emerging contaminants fro water. Consequently, the aim of this study is to review the various aspect of nano technology that are fundamental in the removal of emerging contaminants from water (Zare *et al.,* 2013; Gupta *et al.,* 2015).

## 2.0 Nanomaterials for wastewater remediation

Nanomaterials are natural or engineered small-scale substances that have structural components whose sizes are less than 100 nm in at least one dimension (Amin *et al.,* 2014). These include nanoparticles (NPs) that have particles whose structures are nanoscale in at least two dimensions. Nano-compounds offer unique advantages, such as large specific surface area, small size effect, quantum effect, photosensitivity, catalytic activity and electrochemical/magnetic properties, selective and abundant adsorption sites, short intraparticle diffusion distance, tunable pore size, and easy recovery, and reusability (Shan *et al.,* 2017). These are promising features that make them suitable for use in treating the ECs in wastewater. So far, a large number of nanomaterials such as carbon nanotubes, carbon based material composites, graphene, nano-metal or metal oxides, polymeric sorbents and bio-nanoadsorbents have been studied for the removal of ECs from aqueous solutions, and the results indicate that these nanomaterials show high removal capacity (Uzaira *et al.,* 2012). Nano materials that have been reported to be useful in decontamination of water from ECs are generally grouped into inorganic, carbon based nano tube, composites nanomaterials, polymer-based matrix, ceramic based matrix and metal-based matrix. They are discussed as follows,

### *2.1 Inorganic nanoparticles*

Metal and metal oxide-based nanoparticles are generally grouped as inorganic nanoparticles. Metal based nanoparticles are synthesized from metals to nano units either by destructive or constructive techniques. Practically all the metals can be reduced into their nanoparticles (Salavati-niasari, 2008). The commonly used metals for nanoparticle synthesis are zinc, iron, aluminum, gold, silver and titanium. The nanoparticles have properties such as; sizes as low as 10 to 100 nm, surface qualities like large surface area to volume ratio, pore size, surface charge and surface charge thickness, crystalline and undefined structures, different shapes and colour as well as sensitivity and reactivity to environmental factors.

Metal oxide-based nanoparticles are synthesized to modify the properties of their respective metal-based nanoparticles. According to Tai *et al.* (2007), increased reactivity and efficiency are the major drivers for metal oxide nanoparticles synthesis. The commonly synthesized metal oxide nanoparticles include aluminum oxide ($Al_2O_3$), magnetite ($Fe_3O_4$), zinc oxide (ZnO), silicon dioxide ($SiO_2$), and titanium oxide ($TiO_2$). These nanoparticles have exceptional properties such as increased reactivity, in comparison to their metal counterparts (Saharan *et al*., 2014). Basheer (2018) has identified metal oxides nanoparticles as among the new generation nano-adsorbents that are capable to remove new emerging pollutants even at low concentration *i.e.* µg/L under varied conditions of pH and temperature. Chauhan *et al*. (2019) reviewed some metal oxides nanoparticles as efficient adsorbents for the removal of pharmaceutical products from waste water. Odiongenyi and Afangide (2019) used nano alumina and alumina to remove dispersed dye from aqueous solution and reported higher removal capacity for the nano alumina than the alumina. According to Mustapha *et al*. (2020), $TiO_2$ and ZnO anchored on clay functioned as a good and promising sequesters and explored for wastewater remediation via nanotechnology. Results obtained indicated excellent efficiency. Huang and Keller (2013) found that magnetite is an excellent adsorbent for the removal of para aromatic hydrocarbons from contaminated water and reported higher adsorption efficiency. Eslami *et al*. (2020) found that nano silicate is a good adsorbent for the removal of acetaminophene, a pharmaceutical from aqueous solution and supported their experimental findings with kinetic models. According to Kurwadkar *et al.* (2019) carbon nanotubes are capable of adsorbing and remediating pharmaceutical and personal care product and endocrine disrupting compounds because they have tubular cylinder of carbon atoms attributed to their large specific surface area and developed pore structure. Measured removal percentage for triclosan, acetaminophen and ibuorifen was upto 95 % in optimum experimental conditions

### *2.2 Carbon based nanoparticles*

Carbon based nanoparticles are totally made of carbon (Bhaviripudi, 2007). They may be categorized into fullerenes, graphene, carbon nanotubes (CNT), carbon nanofibers, carbon black and occasionally activated carbon at nano size. Fullerene ($C_{60}$) is a spherically shaped carbon molecule composed of carbon atoms that are held together by $sp^2$ hybridization. Roughly 28 to 1500 carbon atoms form the spherical structure with distances across up to 8.2 nm for a solitary layer and 4 to 36 nm for multi-layered fullerenes.

Graphene which is an allotrope of carbon is a hexagonal network of honeycomb lattice made up of carbon atoms in a two-dimensional planar surface, it has a thickness of about 1 nm. Carbon Nano Tubes (CNT) is a graphene nano-foil with a honeycomb cross section of carbon atoms that is twisted into empty chambers to frame nanotubes of measurements as low as 0.7 nm for a solitary layered and 100 nm for multi-layered CNT with length differing from a couple of micrometers to a few millimeters. The closures can either be empty or closed by a half fullerene particle. Carbon nanofibers are formed from graphene nano foils, which are wound into a cone or cup shape instead of a regular cylindrical tube. Odiongenyi (2020) used nano graphene oxide to remove Congo red dye from contaminated water and recorded percentage removal of up to 85 % under various pH, temperature, adsorbate dose, period of contact and concentration.

### *2.2 Synthesis and properties of nanoparticles*

Various methods are available for the synthesis of nanoparticles. The general principle of classifying methods for synthesizing nanomaterials involves the breaking or building up of molecules into nano dimensions. Consequently, synesthetic methods for nanomaterials can generally be grouped into top-down and bottom-up methods, which are generally categorized into top-down and bottom-up methods. A flow sheet showing the various ways of achieving the two synthetic routes is shown in Fig. 1.

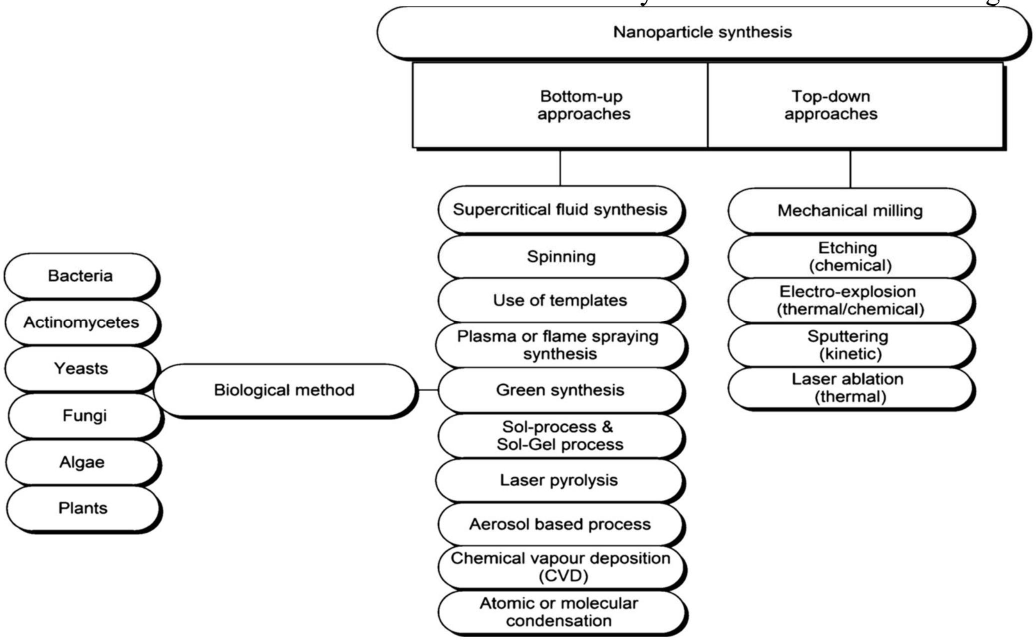

**Fig. 1. Chart showing various methods of nanoparticles synthesis (Source:** Nadaroglu, 2017**)**

Top-down or destructive method is the reduction of a bulk material to nanometric scale particles. Mechanical processing, nanolithography, laser removal, sputtering and thermal disintegration are common examples of top-down methods perhaps the most generally utilized nanoparticle synthesis techniques. Bottom-up or constructive method involves the development of material from atoms to nanoparticles through cluster formation. Precipitation, sol-gel, spinning, chemical vapour deposition (CVD), pyrolysis and biosynthesis are the most are common examples of bottom-up methods.

**Table 2: Type of NMs, their synthesis methods, and examples**

| Nanomaterials | Synthesis methods | Examples |
|---|---|---|
| **Metal nanoparticles (NPs)** | Photochemical<br>Electrochemical<br>Biochemical<br>Thermochemical | Pt, Rh, Pd, Ir, Ag,Au, Cu, Co, Ni, FeNi, $Cu_3Au$, CoNi, CdTe, CdSe, ZnS |
| **Carbon NMs** | Arc-discharge<br>Laser ablation<br>Chemical vapor deposition | Cylindrical nanotube (SWNT, MWNT) fullerenes |

| | | |
|---|---|---|
| **Metal oxide NPs** | Co-precipitation,<br>Hydrothermal<br>Solvothermal<br>Sol-gel<br>Reverse micelles method<br>Electrochemical deposition | ZnO, $Fe_2O_3$, $Fe_3O_4$, MgO, $BaCO_3$, $BaSO_4$, $TiO_2$ |
| **Polymer** | NMs Electrochemical polymerization | Nanowire of polypyrrole, polyaniline, poly (3,4-ethylenedioxythiophane) dendrimers (PAMAM) |
| **Nanocomposite** | Innovative methods | Nanocomposite of polyethylene oxide and polyethyleneimine; CNT<br>epoxy composites include hydrocarbon polymer composites,<br>conjugated polymer composites, CNTs with polycarbonates,<br>fluoropolymers, polyethylene glycol, polyester polyamides, and so forth |

### *2.3 Nanocomposites synthesis methods*

A nanocomposite is a multiphase solid material, where one of the phases has one, two, or three dimensions of less than 100 nm, or structures having nanoscale repeat distances in between the various phases that make up the material (Tyagi and Tyagi, 2014). This definition includes permeable media, colloids, gels, and copolymers, but it is more generally interpreted as meaning the solid mix of a mass framework and nanodimensional phase(s) varying in properties because of dissimilarities in structure and chemistry. Nano composites are typically grouped into three classes namely, metal matrix composites, polymer matrix nanocomposites and ceramic matrix nanocomposites (Liu, *et al.,* 2016). Fabrication techniques for these nanocomposites are shown in Fig. 2 (Lateef and Nazir, 2017).

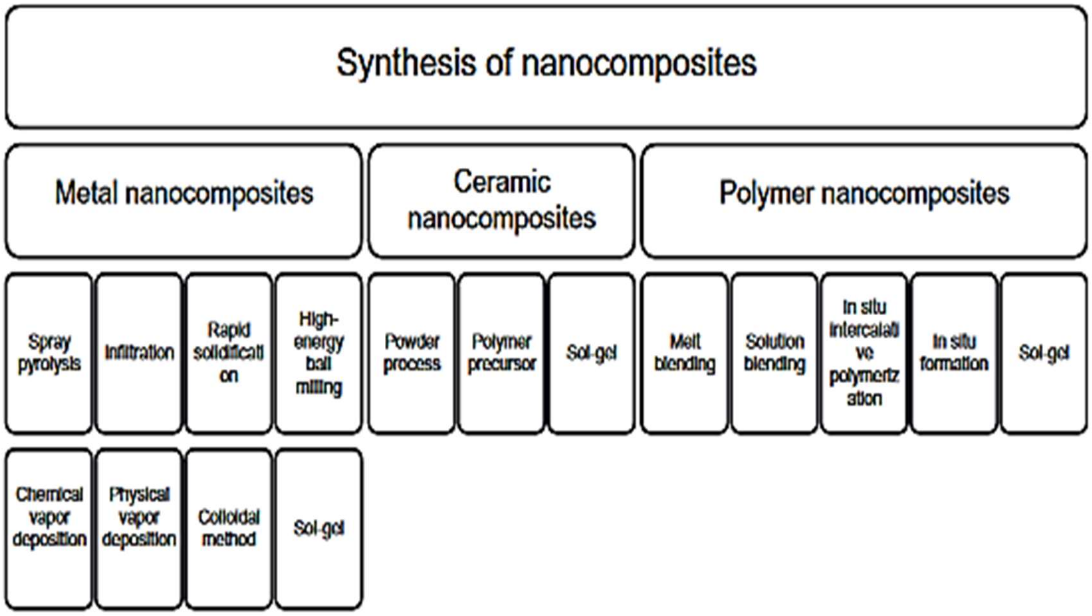

**Fig. 2 Nano-composite fabrication techniques**

### *2.3.1 Polymer matrix nanocomposites*

These are co-polymers that contain polymer as a matrix material with nanoparticles or nanofillers dispersed in the matrix. Although they maybe of different shapes, it is required that at least one dimension must be in the range of 1 to 50 nm. In literature, many processes have been described for the preparation of polymer nanocomposites including layered materials and those that contain carbon nanotubes. The usual ones include: In situ polymerization, intercalation of polymer from solution, direct mixing of polymer and fillers, melt intercalation, Template synthesis; and sol-gel process. The nanocomposites are then fabricated by either compression molding or injection molding.

### *2.3.2 Ceramic matrix nanocomposites*

These are nano composites with at least one phase having nano dimension. They have a wide range of applications in industrial sector. The microstructure of nanoceramic composites results in outstanding electrical and mechanical properties. Various methods abound in literature for the preparation of ceramic matrix nanocomposites, these methods include the conventional powder method, polymer precursor route, spray pyrolysis, and chemical methods such as sol-gel process, colloidal and precipitation approaches and template synthesis (Ray and Okamoto, 2003). Common ceramic matrix nanocomposites include $AL_2O_3/SiO_2$, $SiO_2/Ni$, $Al_2O_3/TiO_2$ and $Al_2O_3/SiC$ $Al_2O_3/CNT$, $MgAl_2O_4/CNT$ and $MgO/CNT$ (Okada *et al.,* 1990).

### *2.3.3 Metal matrix nanocomposites*

Metal matrix nanocomposites are materials supported by nanoparticles consisting of ductile metal or alloy as the matrix and nanoparticle as the reinforcement. They are generally classified as continuous and non-continuous reinforced nano materials (Gupta *et al*., 2016). According to Srivastava (2017), metal matrix nanocomposites have excellent physical and mechanical properties because the filler reinforcement into the metallic matrix improves the stiffness, specific strength, wear, creep and fatigue properties compared to the conventional engineering materials. These composites comprising metal/alloy matrix filled with nanoparticles, show physical, chemical and mechanical properties totally different from the matrix material. The nanoparticles are generally used to improve wear resistance, mechanical properties and damping characteristics. Interest in metal matrix nanocomposites has risen, owing to their superior properties made possible by nanoparticle embedment, they find wide range of applications in structural components (Biswas and Ray, 2001) the nanoparticles act as a barrier in dislocation movement and thereby improve the mechanical properties. The simple preparation techniques of metal matrix nanocomposites are spray pyrolysis, liquid metal infiltration, vapor techniques, rapid solidification, electrode position and chemical methods, which include colloidal and sol-gel methods (Ray and Okamoto, 2003). Examples of metal matrix nanocomposites include $Fe\text{-}Cr/Al_2O_3$, $Ni/Al_2O_3$, $Fe/MgO$, $Al/CNT$ and $Mg/CNT$.

### *2.4 Modification of nanomaterials*

According to Baer (2013), functionalization process is usually applied to nanomaterials during or after synthesis either by a coating technique or chemical modification in order to improve the surface and optical properties, avoid aggregation and eliminate the interaction between the nanomaterials and biological substances. As a result of the small particle size of the nanoparticles, significant drop in pressure maybe ~~is~~ observed due to the introduction of nanoparticles to the fixed matrix. Observed properties of polymer composites depend on the type of nanoparticles that are incorporated, their size and shape, their concentration and their interactions with the polymer matrix. Hybrid nano- composites have been made by coating the fine particles onto solid particles of a larger size to surmount the limitations of NPs. For example, Ling *et al.,* (2019) found that attractiveness of magnetite iron oxide nanoparticles in biosensor, antibacterial activity, targeted drug delivery, cell separation and in magnetic resonance imaging tumor is extremely limited by severe agglomeration, serious oxidation, and irregular size. However, surface modification with inorganic materials, organic molecules, and polymer molecules strongly improved their useful properties. Kango *et* al. (2013) observed that incorporation of inorganic nanoparticles into a polymer matrix for the development of organic-inorganic nano composites can significantly improve thermal, mechanical, rheological, electrical, catalytic, fire retardancy and optical properties. However, their useful properties may be hinder by particle aggregation due to their specific surface area and volume effects. Modification can improve the interfacial interactions between inorganic particles and the polymer matrix. Modification of the surface of a nano material can be achieved through surface adsorption or reaction with small molecules. Surface modification can also be achieved by grafting polymeric molecule through covalent bonding to the hydroxyl group existing in the polymer.

The polymer-based nanocomposite produced, has the innate properties of the nanoparticles; however, the polymer support materials imparts higher stability, processability and improvements owing to the nanoparticle–matrix interaction. Furthermore, the integration of nano-particles (NPs) into polymeric nanocomposites enhances the mechanical, electrical and optical properties.

### *2.5 Characterization of nanoparticles*

Characterization of nanoparticles goes hand in hand with their synthesis. The size and shape of nanoparticle significantly affects its properties therefore accurate measurement of its size and shape is critical to its applications. Currently, several techniques such as UV-visible spectroscopy (UV-vis), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDS), dynamic light scattering (DLS), zeta potential, surface-enhanced Raman spectroscopy (SERS), nuclear magnetic resonance spectroscopy (NMR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF), dual polarization interferometry and many others are available for NPs characterization. Out of these, some techniques (spectroscopy and microscopy) that include UV-vis, DLS, AFM, TEM, SEM, XRD and FTIR, are more frequently used (Fig 5) (Husen and Iqbal, 2019). A summary of the characteristic features of nanoparticles such as particle size, surface area, surface morphology, surface charge, crystallography and concentration and their characterization techniques are displayed in Table 3.

**Table 3. Characterization techniques used during nanoparticles (NPs) synthesis (Husen, and Iqbal, 2019).**

| Type of studies | Characterization techniques and their uses |
|---|---|
| **NPs formation** | ***UV-vis*: Offers information on the size, structure, stabilization and aggregation of NPs |
| **NPs shape and size determination** | ***TEM***: Examines the shape, size ($10^{-10}$ m), morphology and allographic structure of NPs.<br>***HRTEM***: Examines the arrangement of the atoms including their distinct microstructures, viz. lattice fringe, glide plane, lattice vacancies and flaws, screw axes and surface atomic arrangement of crystalline NPs.<br>***SEM***: Examines the morphology by direct visualization<br>***AFM***: Examines the size and form, i.e. length, width and height, and other physical properties, viz. morphology and surface texture.<br>***DLS***: Displays the particle size distribution |
| **Surface charge** | ***FTIR***: Describes NPs to understand their functional groups and determine the emission, absorption, photoconductivity or Raman scattering of a solid, liquid or gas.<br>***XPS***: Examines the mechanism of reaction that takes place on the surface of magnetic NPs and the characteristics of bonding of different elements involved, in addition to confirming the structure and speciation of elements present in the chemical composition of the magnetic NPs.<br>***TGA***: Approves the formation of coatings, viz. surfactants or polymers, to estimate the binding efficiency on the surface of magnetic NPs.<br>***Zeta potential***: Determines the stability and surface charge of colloidal NPs and also the nature of materials encapsulated inside the NPs or coated on their surface. |

| | |
|---|---|
| **Crystallinity** | ***XRD*****:** Identifies and quantifies the various crystalline forms or elemental compositions of NPs. |
| **Magnetic properties** | ***Vibrating sample magnetometry (VSM)*****:** Estimates the magnetization of magnetic NPs.<br>***Superconducting quantum interference device magnetometry(SQIDM)*****:** Examines the magnetic properties of magnetic NPs. |
| **Other techniques** | ***Chromatography and related techniques*****:** Separate NPs based on their affinity towards the mobile phase.<br>***EDX*****:** Identifies the elemental composition of NPs.<br>***Field flow flotation*****:** Separates different NPs based on their magnetic susceptibility.<br>***Filtration and centrifugation technique*****:** Fractionates the preparative size of NPs.<br>***Laser-induced breakdown detection*****:** Examines the concentration and size of colloids.<br>***Mass spectrometry*****:** Examines the fluorescent labelled NPs.<br>***Small angle X-ray scattering*****:** Performs the structural characterization of solid and fluid materials in the nanometre range.<br>***X-ray fluorescence spectroscopy*****:** Recognizes and examines the concentrations of elements present in solid, powdered or liquid samples.<br>***Hyperspectral imaging***: Identifies the type of NPs, studies the fate and conversion of these particles in water samples and characterizes the unique surface chemistry and functional groups added to the NM. |

### *2.7 Biological synthesis of nanoparticles*

The production of nanoparticles by chemical reduction and modification methods and the byproducts generated from the contaminant degradation may lead to absorption of harsh chemicals on the surfaces of nanoparticles raising the toxicity issue (Iravani, 2011). Biosynthesis of metal nanoparticles is an environmentally friendly method that is non-toxic and biodegradable ~~(Nayantara and Pawan, 2018)~~ without making use of hazardous and expensive chemicals (Nayantara and Pawan, 2018). Biosynthesis uses bacteria, plant extracts and fungi along with the precursors to produce nanoparticles instead of conventional chemicals for bio reduction and capping purposes. Also, the biomolecules of plant extract may be ~~will~~ chemically attach to the surface of the nano-structures, stabilize the nanoparticles and impede their aggregation (Ghorbani *et al.*, 2015).

Synthesis of metal nanoparticles exploiting plant extracts (Fig. 4) has been widely established to be economical, and therefore, can be used as a cost effective and important option for the extensive production of metal nanoparticles. The biosynthesized nanoparticles have unique and enhanced properties that find its way in various useful applications, including nano-remediation of environmental matrices (Shah *et al.,* 2015).

There are a number of successful investigations in $Fe_3O_4$-NPs synthesis, using plant extract. For example, leaf extract of *Perilla frutescens* and fruit extract of *Artemisia annua* (Basavegowda, 2014), *Tridax procumbens* (Senthil and Ramesh, 2012), *caricaya papaya* (Latha and Gowri, 2014) peel extract of plantain (Venkateswarlu *et al.,* 2013) as well as seed extract of grape *proanthocyanidin* (Narayanan *et al.,* 2012).

The plant extracts of lemon (*Citrus limon*), black grapes (*Vitis vinifera*) and cucumber (*Cucumis sativus*) were harnessed for the preparation of magnetite nanoparticles according to Stan *et al.,* (2017). The new green adsorbent was characterized and used for the elimination of piperacillin, tazobactam, sulfamethoxazole, tetracycline, trimethoprim, ampicillin and erythromycin from aqueous media. The researchers employed a Box-Behnken design methodology to establish the optimal conditions for removal of the antibiotics. The best fitted adsorption isotherm models were given by Langmuir, Freundlich and Temkin models for the adsorption of the studied antibiotics. Finally, a significant removal of >90 % was noticed for a greater number of the antibiotics.

Yew *et al.,* (2016) also successfully synthesized $Fe_3O_4$-NPs by a simplified and green methodology devoid of any synthetic-reducing agent and stabilizer, by utilizing the seaweed *K. alvarezii* extract. In view of the XRD investigation, crystalline $Fe_3O_4$-NPs of high purity were formed. FT-IR spectroscopy indicated the participating biomolecules present in the *K. alvarezii* extract, which were confirmed in the preparation process of $Fe_3O_4$-NPs. Ramesh *et al.* (2018), reported the synthesis of $Fe_3O_4$ NPs by making use of aqueous leaf extract of *Zanthoxylum armatum DC*. via green route method. He noted that the phytochemical present in aqueous leaf extract of *Zanthoxylum armatum* DC can act as functionalizing agent for the preparation of $Fe_3O_4$ NPs. The spherical morphology was observed for $Fe_3O_4$ NPs with average particle size of 17 nm.

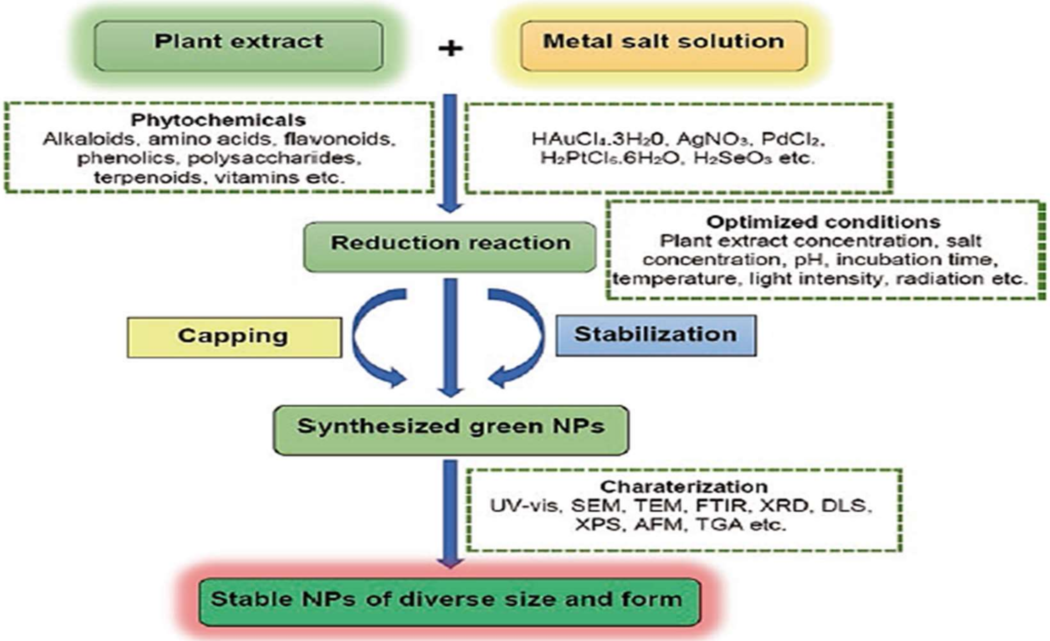

**Fig. 4. A scheme describing the mechanism of in vitro green synthesis of nanoparticles (Husen and Iqbal, 2019)**

Kumar and Prem (2018) showed that iron oxide nanoparticles could be produced by using the aqueous leaf extract of *Phyllanthus Niruri*. Various characterization analyses disclosed that the prepared iron oxide nanoparticles from these two separate methodologies have relatively similar size and morphology.

Many reports abound for green methods of synthesizing ZnO NPs by plant leaves, recent researches include among others. A green novel route for the rapid, eco-friendly and non-toxic synthesis of ZnO NPs using *Calotropis procera* leaf extract was developed by Garadkar, *et al.,* (2017). The FT-IR results showed the possible involvement of polyphenols, terpenoids, amines, alcohols, ketones and carboxylic acids groups in biochemical reactions. The XRD pattern confirmed hexagonal wurtzite structure of ZnO. The preparation of hexagonal wurtzite ZnO nanoparticles from Zn-hyper-accumulator (*Sedum alfredii* (Hance)) plants has been made known as well and according to Qu *et al.* 2011, the prepared nanoparticles formed in aggregates, and single ZnO nanoparticles were pseudo spherical in shape, having a mean size of 53.7 nm.

## 3.0 Application of nanomaterials for the removal of emerging contaminants

The mechanisms through which nanoparticles are applied for water decontamination involves: adsorption, photocatalysis, catalytic ozonation, membrane process and bio-nanoremediation (Qu *et al.,* 2013).

The adsorption of linezolid antibiotic onto MgO nanoparticles and ZnO-MgO nanocomposites has been reported by Fakhri *et al.,* (2015). The parameters investigated were temperature, pH and adsorbent dosage. These were 308 K, pH 10 and 0.5 g $L^{-1}$ of adsorbent. The adsorption capacities obtained were 123.45 and 140.28 mg $g^{-1}$ for MgO nanoparticles and ZnO-MgO nanocomposites respectively. Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich models all gave good fittings to the data; with Langmuir model giving the better fit. The adsorption followed pseudo-second-order model. According to the researchers, the adsorption capacity of ZnO-MgO nanocomposites was greater than that of MgO nanoparticles because of high specific surface area of ZnO-MgO nanocomposites.

Magnetic nanoparticles ($\gamma$-$Fe_2O_3$)-coated zeolite were observed to exhibit more than 95 % removal efficiencies for diclofenac, naproxen, gemfibrozil and ibuprofen from aqueous solution in less than 10 min at an initial concentration of 100 μg $L^{-1}$ and an adsorbent dose of 1 g $L^{-1}$ (Attia *et al.,* 2013). The preparation of magnetic nano-adsorbents gives the possibility for the effortless control and quick separation of nano-adsorbents with the capacity of retaining the vast majority of its surface area when measured with other immobilization techniques, making the methodology of environmental remediation by these nanomaterials more similar to the engineering application. Singh *et al.,* (2011), synthesized a carbon–iron magnetic nanocomposite, which showed an improved ibuprofen removal efficiency compared to its precursor carbon.

Nano adsorbents have also been applied ~~as well~~ for the removal of persistence organic chemicals such as PAHs and pesticides from aqueous media. Kaur *et al.,* (2017) studied the removal of naphthalene from aqueous solution using ZnO nanoparticles (NPs) prepared through microwave approach. Zinc oxide nanoparticles showed a maximum adsorption capacity of 66.80 mg $g^{-1}$. The application of iron oxide NPs, prepared using pomegranate peel extract, for adsorption of pyrene and benzo (α) pyrene was carried out by Hassan *et al*., (2018). Following a pseudo-second-order mechanism of adsorption, the NPs exhibited more than 98% removal efficiency for polycyclic aromatic hydrocarbons (PAH) from contaminated water in a semi-pilot plant. Graphene oxide nano sheet bonded with silica-coated $Fe_3O_4$ microparticles and graphene oxide surface modified with 2-phenylethylamine were reported for the extraction of 10 PAHs from aqueous matrices with a limit of detection (LOD) value of 0.005–0.1 $\mu g \cdot L^{-1}$ (Mahpishanian *et al.,* 2015). Graphene oxide fixed in silica fiber has also been used for the removal of PAHs from river and pond water with an LOD value of 0.005–0.08 $\mu g \cdot L^{-1}$ (Xu, 2012).*Calotropis gigantea* leaf extract was used in combination with $ZnNO_3$ salt to fabricate ZnO NPs of 30–35 nm (Vidya *et al.,* 2013). *Acalypha indica* leaf extract was used in addition to zinc acetate salt to produce NPs of 100–200 nm by Gnanasangeetha and Thambwani (2013). *Parthenium hysterophorus* leaf extract was used in the presence of $ZnNO_3$ salt to fabricate ZnO NPs of 16–108 nm by Sindhura *et al.* (2014). Oudhia *et al.,* (2015) used *Azadirachta indica* leaf extract in the presence of zinc acetate salt to produce NPs of 25 nm, whereas Divyapriya *et al.,* (2014) used leaf extract of *Murraya koenigii* with $ZnNO_3$ salt to fabricate ZnO NPs of 50 nm size. Senthilkumar and Sivakumar (2014) used *Camellia sinensis* leaf extract with zinc acetate salt to fabricate ZnO NPs of 16 nm. Ramesh *et al.,* (2015) used *Solanum nigrum* leaf extract as a capping agent for ZnO NPs' synthesis. Morphologically, they were hexagonal wurtzite and quasi-spherical in shape with their size ranging from 20 to 30 nm. Ali *et al.* (2016) have synthesized ZnO NPs from leaf extract of *Aloe barbadensis*. Particle size ranged from 8 to 18 nm with diverse shapes.

Kuang *et al.* (2013) reported the synthesis of zero-valent iron (α-Fe), maghemite (γ-Fe2O3), magnetite ($Fe_3O_4$) and iron hydroxides using extracts of green tea, oolong tea and black tea. These irregular spherical NPs (with basic size: 20–40 nm and surface area of 5.82m2 $g^{-1}$) mediated Fenton-like oxidation of mono-chlorobenzene (MCB) owing to their high surface and reactivity, complemented by low leaching of $Fe^{2+}$ The link between oxidative degradation efficacy and the associated COD removal was suggestive of the partial mineralization of MCB to carbon dioxide and water. Hassan *et al.* (2018) have also demonstrated the application of iron oxide NPs, prepared using pomegranate peel extract, for adsorption of pyrene and benzo (α) pyrene. Following a pseudo-second-order mechanism of adsorption, the NPs exhibited more than 98 % removal of the polycyclic aromatic hydrocarbons (PAH) from artificially contaminated water in a semi-pilot plant.

Although the widespread occurrence of biomolecules such as polyphenolic, hydroxyl, alkyne, carboxyl, and amide groups of the monoterpenoids, sesquiterpenes, and phytols in the plant kingdom could explain the ability of plant extracts to reduce metal ions, the processes involved in green synthesis is not clearly obvious. In view of the rich biodiversity of plants and microbes, the prospective as biological materials for nanoparticle production is yet to be completely investigated (Pantidos and Horsfall, 2014).

## 4.0 Conclusion

This review focused on the various chemical and phytosynthetic methods of nanomaterials for the remediation of emerging contaminants. General synthesis method involving the top-down and bottom-up approaches have been shown. Literature indicates that several metals, materials and plants have been harnessed for the synthesis of nanomaterials, which have proven overtime to be good materials for removal of ECs. More so, modified nanoparticles and nanocomposites have shown better ECs removal capabilities, based on their enhanced surface properties. The Use of plant materials in the preparation of nanomaterials appear more appealing, because of its environmentally friendly nature and cost effectiveness, when compared to the chemical synthesis. However, there is need for further research in the use of plants as the process is yet to be fully understood.

## 5.0 References

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