Review Article

Development of Magnetic Nanoparticles and Encapsulation Methods – An Overview

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ABSTRACT

Nanotechnology is a versatile evolving field today. The importance of nanoparticles reaches high in diagnostics, medicine, or pharmaceuticals for drug delivery. Among all the different nanoparticles, Magnetic nanoparticles are novel, easily prepared, and have many biomedical applications. The specific character of Magnetic nanoparticles shows various applications like a diagnosis of diseases, targeted drug delivery, and cancer therapy. An overview of this topic includes all about the history, advantages, disadvantages, preparation methods, and biomedical applications of Magnetic nanoparticles. It also focuses on the overall information of Magnetic nanoparticles and their prospective, challenges faced in the delivery of drugs have also been discussed.

Key words: Applications, Characterization, Magnetic nanoparticles, Nanoparticles, Preparation methods.

INTRODUCTION

Nanoparticles are submicron moieties (between 1 nm and 100 nm as per the standard definition, although there are instances of NPs a few many nanometers in size) made of inorganic or natural (for example polymeric) materials, which could conceivably be biodegradable.[1] Medication conveyance frameworks formed by fusing drugs into biologically degradable polymeric nanoparticles,[2] Solid lipid nanoparticles, liposomes, surfactant-adjusted hydrogels, biologically degradable and bioabsorbable super paramagnetic iron oxide nanoparticles (MNPs).

There are numerous sorts of Nanoparticles with contrasting size, shape, compositions, and functionalities specifically liposomes, polymeric, iron oxides, gold, quantum specks, etc.[3-5]

Magnetic nanoparticles (MNPs) are among the one form of NPs that shows certain reactions when the magnetic field is applied with little molecule size, huge explicit surface region, magnetic response, and superparamagnetism.[6] In such a manner, MNPs have different novel attractive properties like superparamagnetic, low Curie temperature, and huge magnetic susceptibility. MNPs might be amassed and situated beneath a steady magnetic field, and the warmth is spent by the electromagnetic wave in the alternating magnetic field.[7]

The advancement of magnetic nanoparticles (MNPs) is promising for various applications. Magnetic nanoparticles find a unique place in the field of nanotechnology-based materials along with the effect in a study of, biosensing, nanomedicine, and analytical science. The above-mentioned utilization of magnetic nanoparticles and microparticles has helped a long way in discovering and treating microbial infections in the accompanying years.[8]

i). Drug delivery system conjugated with magnetic nanocarriers as like instance drug transporters.

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(ii) Magnetic nanoparticles controlled by using the radio frequency waves gave another way to deal with disease treatment applications[9]

(iii) Magnetic detachment of natural entities added to the improvement of diagnostics for instance magneto acoustic tomography (MAT), computed tomography (CT), near-infrared (NIR) imaging, and magnetic resonance imaging (MRI).

The medications got from a common plant source called herbal medications are generally utilized as a medication due to their less toxicity.[10,11] In late many years the utilization of herbal medications has essentially expanded which is clear from the expanded worldwide market of natural medicines. A magnetic nanoparticle (MNPs) for herbal medicines incorporates focused on drug delivery, which lessens measurement recurrence, builds the solvency and absorption though diminishes disposal. Nanoparticles can be utilized to focus on the herbal medicines[12] to singular organs which improve the focus on targeted drug delivery, adequacy, and wellbeing of the medication, diminish the rehashed administration to beat resistance, yet in addition, help to build the therapeutic worth by decreasing toxicity and expanding the bioavailability.

Preparation of Magnetic Nanoparticles

MNPs, usually magnetite nanoparticles possess much more effective function like a transporter for a wide range of hydrophobic and hydrophilic pharmacological compounds and shows the supplementing properties: (1) biological compatibility (2) Elevated chemical strength (3) held superparamagnetic properties (4) increased colloidal stability (5) reduces the drug wastage (6) decrease unfavorable responses of drug moieties (7) supported conveyance of moieties towards the chosen destinated organ and (8) less expenditure in the production of MNPs identifies them as a most productive delivery system than different novel formulations. MNPs are normally present in the superparamagnetic state and the widely utilized nanomaterial is the iron oxide nanoparticle, including magnetite (γ-Fe_2O_3) and magnetite (Fe_3O_4). Notably, MNPs have a significant part in disease finding, drug conveyance, and treatment. The critical parts of Magnetic nanoparticles[13] are the magnetic core, surface covering, functionalized external covering, and the hydrodynamic layer. Figure 1 shows the components of magnetic nanoparticles. The middle part displays superparamagnetism, which can be worked by an outside magnetic field. This method aids the diagnosing and siting the harmed cells. The particles showing superparamagnetic conduct at room temperature are generally utilized for biomedical applications. Iron,

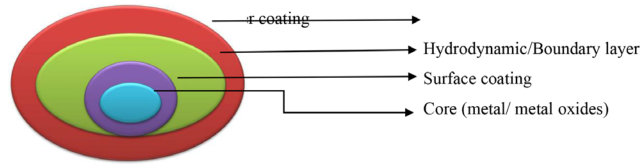

Figure 1: Components of Magnetic nanoparticles.

Cobalt, Nickel is a portion of the attractive material utilized for showing superparamagnetism. Among these nanoparticles with iron oxide is more profitable as it biodegrades effectively, simple to plan, ties to ligands, infiltrates effectively through cells. Because of attractive powers, the conglomeration after some time can be seen if the attractive center isn't covered by a non-attractive grid. Natural materials are regularly utilized for covering. The functionalized shell contains the ligands that empower restricting to the focus available and it goes about as a transporter for the medications expected for the plan, which carries the medication to the site of activity. The hydrodynamic layer over it goes about as a boundary between the functionalized shell and the suspended medium (serum/blood). This is accomplished for water-based suspensions.

Encapsulation Methods of MNPs

Readiness of MNPs with their predefined size and shape (in any event, the size of dissipate particles ought to be $<5 \pm 10\%$ and controllable) are the basic highlights for formulation improvement. The significant highlights for the synthesis of MNP's are predefined shapes and a combination of anisotropic magnetic structures. To decrease, the inter molecule co-operations, the separation of MNPs starting with one then onto the next is finished by immobilization on the surface of the substratum and/or by settling the greater part of the inactive substance. The next significant variable that has to be regulated is the matrix distance between the particles. Their expense adequacy, basic creation, and reproducibility are significant benefits over other nanoparticles. MNPs comprising of an iron oxide center (as a rule magnetite g-Fe_2O_3 or magnetite Fe_3O_4) are assessed for biomedical applications. Covering of the MNPs should be possible utilizing materials, for example, protein, little silane linker, manufactured polymer, lipid, polysaccharide and so on that have great biocompatibility, a total morphology i.e. alluded typically as "center shell" structure. Magnetic nanoparticles Coating gives substance usefulness and also additionally balances out MNPs in the physiologic fluid. Different strategies examined to develop MNPs are co-precipitation, chemical vapor deposition, microemulsion, thermal decomposition, carbon arc, microwave-assisted, solvothermal, laser pyrolysis, combustion synthesis, and sonochemical.[17]

Precipitation from Solution

As per the hypothesis proposed by Lamer, improvement of homogenous nanoparticles are in the increase, and seeding measures are isolated specifically in three particular stages. Stage 1, of the framework, gains its efficiency, and hence the single unit of polymer namely monomer fixation increments occur. When the hyper saturated fixation is accomplished, adequate energy occurs in the framework causing the explosion of the nucleus, which concludes with the formation of uniform scattered colloids possessing restricted area dissemination. The seeds like crystallites present in media that triggers heterogeneous nucleation increase the range of nanoparticle width.

Precipitation

It is a helpful and simple strategy for producing MNPs of ferrites and metal oxides using solid solutions. The addition of alkali takes place in a passive atmosphere at indoor temperature or at higher. The chemical reaction takes place in an aqueous media. Under non-oxidizing conditions, pH levels for total precipitation should be in the midst of 8 and 14, with a stoichiometric proportion of (Fe^{3+}/M^{2+}) 2:1. The mean area of the MNPs can be restrained to a substantial dimension from 15 to 2 nm by controlling the ionic strength and pH of the media in which precipitation occurs. Fe_3O_4 nanoparticles size decrease as pH and ionic strength increase. pH and ionic strength can affect the electrostatic surface charge of particles. Under the aforementioned conditions, the collection of the essential particles brings about magnetite particles that are delivered inside $Fe(OH)_2$ gel. This set up affidavit shapes the globular glasslike particles. To obtain more modest particles, polyvinyl liquor (PVA) is added to iron salts. The parts, size, and shape of the formulated MNPs rely upon various sorts of salts used such as chlorides, nitrates, and sulfates. The arrangement of Fe_3O_4 nanoparticles is made by the hydrolysis in fluid arrangements, for example, ferrous and ferric salt at various percentages used along with the alkali 1, 6-hexane diamine. The molar proportion ratio change between ferrous to ferric particles can result in the production of controlled attractive characteristics of Fe_3O_4 nanoparticles. In this arrangement, soluble base substance, a measure of emulsifier, and response temperature are the basic factors that predominantly affected the eventual outcome. In this technique, the significant deterrent for the arrangement of MNPs is particle agglomeration because of its nano-size range which prompts improve surface energy and enormous explicit surface territory.[14]

Microemulsion

The microemulsion is a thermodynamically steady combination. The water in oil emulsion is the most commonly used microemulsion identified in the formulation of homogenous MNPs. W/O emulsion is the Emulsion frameworks are made of three constituents: water, oil, and a surfactant, which is an amphiphilic molecule that diminishes the interfacial tension. Reagents containing water nanodroplets, fill in, go through quick combination and the blend for precipitation response measure utilized for MNPs production. Surfactants such as nanodroplet dividers encircle the circular outline of the water pool. This nanodroplet divider gives the confines to particle development which brings about the decrease in the particle mean size throughout the gathering and interaction of impacting. In this way, the water pool size is a boundary to control the size of the round nanoparticles (water to surfactant molar proportion, W_0 esteem). For the most part, the bigger the molecule size, the higher the worth of W_0. At the point when two comparative w/o microemulsions are blended, comprising of the favored reactant, will bring about a consistent crash between microdroplets which mix and then break, and eventually structure the aggregation of molecules in colloidal solution and get accelerated. The basic principle behind this technique being the estimation of surfactant, that relies upon various Physico-chemical qualities related to the framework including the antagonistic impact on properties of particles because of outstanding measure of surfactants.[15]

Thermal Decomposition

The presence of iron precursors deterioration and hot natural surfactants results in an improved model with slender mass appropriation, great mass control, unrivaled crystallinity of dispersible and single magnetic NPs. The existence of premium semiconductor nanocrystals and oxides in fluid-less environments enables the production of nanoparticles via thermal degradation. Thermal decomposition of raised bubbling natural solvents of an organometallic compound with settling surfactant can produce a monodisperse magnetic nanocrystal. In warm deterioration, the metal is zero valent precursors of the organometallic compound with the arrangement Iron Pentacarbonyl which prompts the planning of metal nanoparticles yet there is oxidation which may prompt the taking to the soaring value. The ratio of underlying materials such as surfactants, solvents, and organometallic compounds will play a significant boundary in determining the size and morphology of the MNPs.[16]

Solvothermal Routes

Aqueous, otherwise known by the term hydrothermal approach, is the technique employed in the production of MNPs as ultrafine powder. The above process was carried out using the fluid media in reactors or autoclaves, under the pressure increased up to 2000 psi and temperature increased up to 200°C. Crystals of many unusual substances are delivered by the interaction with water. This technique is found to be additionally utilized in shaping dislodging free specific crystal particles, and the molecules created using this strategy may possess a higher degree of structural order contrasted with different strategies. Wang *et al*. used aqueous strategies to make Fe_3O_4 powder. They arranged the nanosized Fe_3O_4 powder (40 nm) at a temperature of 140°C maintained for 6h making a scattering charge of energy 85.8 emu g^{-1}.

Gas-Phase Synthesis

Spray pyrolysis, laser pyrolysis, arc discharge and sonochemical are the demonstrated methods that are identified as promising methodologies for the continuous and direct synthesis of distinct MNPs while keeping all experimental variables under exhaustive control.

Spray Pyrolysis

Spray pyrolysis technique, involves the sprinkling of a homogeneous mixture of solute and solvent passes into the solid in the reactor sequence, solvent evaporation occurs through reactants series, solute condensation as droplets, preceded by chemical decomposition using heat, followed finally by drying up of the particles that precipitate at higher temperatures. By and large pyrolysis-related cycles are utilized in the creation of the attractive nanoparticles which initiates in the presence of Fe^{3+} ions followed by the portion of the natural segments which go about as reducing agents. Ferric salt is partially decreased by the natural compound in this process, for example, a combination of the Fe^{+3} and Fe^{+2}, in this way the advancement of the magnetite, which finally oxidized to the maghemite. Without the diminishing agents, hematite is created as an option of the maghemite. Nature of iron antecedent salts in liquor solutions, uniform Fe_3O_4 components can be accomplished with the molecule sizes ranging from 5 to 60 nm and morphology. Subunits are principally made of denser components of the round shape, with a normal distance between 6 and 60 nm, which have been generated using ferric nitrate and ferric chloride solutions, individually.[17]

Laser Pyrolysis

When compared to gas heating in a furnace, this method provides for extremely limited warming and rapid cooling. Laser light warms iron precursor in the vaporous blend and the combination of gas streams and makes the small, non-totaled, and slight estimated nanoparticles. The pyrolysis is maintained at optimum experimental conditions, and the size of crystal magnetite nanoparticles changes with tight size circulation ranges of 2-7 nm. This strategy incorporates the progression of gases, which warmed with the normal influx of CO_2 laser, to support the substance response. Using Fe_2O_3 NPs, a biocompatible magnetic scattering was produced by conventional laser pyrolysis of $Fe(CO)^5$ fumes. This strategy utilized a beat CO_2 laser, thusly limiting the time allows the creation of yet more modest particles.

Sonochemical Method

Sonochemical strategy is an option cutthroat technique to extra tedious manufacture strategies and makes new materials for certain momentous properties. The acoustic cavitation brings about the ultrasonic physicochemical impacts, which prompts the readiness of huge and implosive imploding of the fluid air pockets. These give the nearby area of interest a stunning wave or adiabatic pressure in deep of the gas portion of folding eddy. Rules are being portrayed tentatively in remembrance of the above areas of interest, keeping the pace of reducing the temperature past 1010 Ks^{-1}, transitory temperatures of 5000 K, and a pressing factor of 1800 atmosphere. These limit conditions were useful in the development of the new stage and seem to possess a cluster shearing force impingement considerable in the development of the large monodispersive nanoparticles.[18]

Arc Discharge

A large number of carbon-covered MNPs are found to be delivered through the circular segment release strategy, in which precursors of the metal are regularly filled inside a cave drill into the graphite anode followed by the curve vaporization. This method can be used to coat magnetic metal carbides. The arc discharge approach is intended to envelop metal nanoparticles using boron nitride. The nanophase nickel in graphite outer covering was effectually Dravid *et al.* effectually developed by Dravid and his co. The item is by and large made out of the mixes of divergent carbon; including carbon exemplified metal particles, pieces of graphite, and carbon nanotubes. During aggregation, the metal particles have expansive size circulation.

Solid Phase Synthesis

Carbon typified Magnetic Nanoparticles are created by using strong stage strategies. Occasions mainly depend upon raised temperature strengthening of substances like Cobalt nanoparticles, Fe_2O_3, polymers, Fe, and carbon powders. Though the size of the formed nanoparticles and the properties related to the magnetic strength of a definitive detailing can't be managed, and even the superparamagnetic particles cannot be accomplished since the basic molecule dimensions were normally greater than 10 nm.

Combustion Synthesis

An ignition reaction is found to be much useful for the manufacture of carbon-exemplified MNPs. Martirosyan *et al.* shaped, $CoFe_2O_4$, cobalt ferrite, translucent nanoparticles (50-100 nm) through the carbon ignition. In their ignition creation technique, the exothermic oxidation of carbon delivers a warm response wave to multiply all through the strong reactant combination of Cobalt Oxide and Fe_2O_3 converting it into the cobalt ferrite. With growing burning temperatures, the normal molecule dimensions of the magnetic nanoparticles were found to be expanded.

Hydrogels

A colloidal gel is usually a gel that will grow incredibly inside the watery arrangement. The gels are normally made out of a hydropic natural elastomer segment which is interlinked through either non-covalent or covalent bonds. A two-step emulsifier-free emulsion polymerization was used to produce colloidal gels merged with attractive nanoparticles. For example, the thermal delicate magnetic immune spheres were formed by covalently joining bovine serum albumin (BSA), which are of immense value in the immune propensity cleaning against BSA antibodies from antiserum.

Evaluation of MNPs

Characterization Methods

For the characterization of the formulated magnetic nanoparticles, it is critical to understand the morphology that includes shape and size and stage an adjunct to the actual properties of the organized magnetic nanoparticles. The complete scheme for the above-mentioned reason is discussed below. For the characterization of the Morphology and stage of the formulated magnetic nanoparticles, the ultimate noted technology for capturing and determining the size and shape of the particles in the transmission electron microscopy (TEM). The main principle in the above-mentioned technique being, the illumination of light emission electrons, in which the electrons are transmitted via the target focal point and later envisioned onto a survey screen like that of a layer of electron fluorescent material to bring about an image. In TEM, the particles are usually seen as small as a couple of angstroms that is comparatively proximate to nuclear levels.[19,20]

Fourier Transfer Infrared Spectra

The above technique of Fourier transfer infrared spectra of the formulated magnetic nanoparticles was recorded by employing a Thermo Nicolet spectrometer (AVATAR 360 FT; Nicolet Instruments, Warwick, UK) between the limits of 400–4000 cm^{-1} at room temperature applying the potassium bromide pellet procedure. The scanning speed for the above technique was kept at 20 cm^{-1} with the spectral resolution of 4.0 cm^{-1} and the procedure was carried out at room temperature.

Size and zeta potential of MNPs

The average hydrokinetic size of the formulated MNPs is determined by using the Quasi-elastic light scattering popularly known as dynamic laser scattering. The measurements for the above determination were carried out at an angle deflection of 90° at a temperature of 25°C by diluting the formulated nanodispersion to an admissible volume using demineralized water. The Zeta potential analyzer named zeta plus was used for measuring the electrokinetic potential of the drug-loaded MNPs. The formulated nanodispersions of MNPs were diluted with demineralized water and measurement was made at a voltage of 4.00 Vs in an automated method.

Scanning Electron Microscopy

The outer or near outer morphology of the bulk nanodispersions formulated can be analyzed by using the Scanning electron microscopy popularly known as SEM which is quite similar to that of transmission electron microscopy TEM that provides information regarding the surface structure, both using a beam of electrons focused at the formulated nanodispersions, the common components of both the instruments being condenser lens, vacuum system, an electron gun. The dimensional resolution of TEM is in the sub-nanometer range which is much superior compared to SEM which has about 15 nm.

Field-emission SEM (FESEM)

The FESEM provides an intensified dimensional resolution and also decreased sample impairment and charging, by employing a field emission cathode placed in an electron gun of SEM to make lean probing beans that operate at high and low electron energy. This method uses a high resolution of 1.5 nm and provides the vision which is a little electrostatically biased and is found to be

Table 1: Biomedical applications of different types of MNPs.

S.No	Biomedical Application	Type of Magnetic Nanoparticles	Advantages
1	Magnetic Resonance Imaging	Maghemite, Magnetite	The highly strong amplifier of transverse proton relaxation, Very good soft-tissue contrast, High Sensitivity[24]
2	Cell and Bacteria Magnetic separation	Super magnetic Iron Oxide Nanoparticles, Conjugation with biotin carboxyl carrier protein, Coated with carboxymethyl dextran.	Facile separation of the cells or bacteria that are targeted from the culture media, blood samples, tissue grinds, bone marrows, etc., Fewer interferences, Low damage and stress to the cells separated, Appropriate method to obtain many living cells and bacteria at a time[25,26]
3	Protein Magnetic Separation	Separation of Bovine Serum albumin amino silane-modified iron silica magnetic spheres[27]	Easy method, Protein under study is not damaged, Less energy-consuming.
4	Nucleic Acids Magnetic Separation	Glucosaminic acid modified, Streptavidin coupled superparamagnetic beads,[28] Paramagnetic particles magnetite clusters modified with polyethyleneimine and poly hexamethylene biguanide[29]	Quick Processing possible, high effectiveness, appropriate method, not damaging the bioentities.
5	Magnetic hyperthermia	Iron oxide nanoparticles, N-propionyl – cysteaminylphenol modulated magnetite nanoparticles[30,31]	Destroying the cancer cells by necrosis improves the effectiveness of chemotherapy.
6	Targeted Drug Delivery	Bacterial magnetosomes containing doxorubicin,[32] Gum Arabic coated Magnetic nanoparticles[33]	The effective concentration of the drug in the site of action like cancer, Fewer side effects by reducing the accumulation of the drug in the noncancerous cells, accessibility to the brain by increasing the permeability of blood-brain barrier.

more firm in nature. The most often used method for determining particle structure, phases, and an average size is X-ray diffraction (XRD). The structure and lattice parameters are calculated by connecting the X-ray patterns by using the structure profile procedures for a neutron and by the use of many software programs, like FULLPROF.[21]

X-ray Absorption Spectra

The principle behind the formation of X-ray absorption spectra is the absorption of X-ray light passing through the nanodispersion of MNPs. The light excited electron is formed by the stimulation of the core electron of the atom which is absorbing a quantity of energy from the X-ray quantum after passing through the steady-state. Thereby the absorption limit is created by the denoting rise in absorption. The four parts of the X-ray absorption spectrum include rising edge, pre-edge, extended x-ray absorption fine structure, and near-edge X-ray absorption fine structure.

Magnetization Characterization

The magnetic nanoparticles formulated in the dimensions less than some tens of nanometers are assigned as one magnetic sphere which differs ineluctably in properties compared with the bulk. The most appealing characteristic of the magnetic nanoparticles is the mitigation practice while contacting heat and cleaving of the local minima for various system symmetry states due to the existence of the energy hurdles. So, the magnetic performance of the nanoscale molecule is found based on the relaxation period.

Other Methods for Characterizing Magnetic Nanoparticles the Mossbauer spectroscopy[22] method is identified as a much important means for exploring the characteristics of magnetic particles. The limitation of which is applicable only for those composed of elements that are considered Mossbauer-active and the presence of prominent nuclide of ferrous 57. In the Mossbauer spectra of magnetic nanoparticles, the magnetic hyperfine field splitting commences just below the blocking temperature TB, where the particle relaxation rate has reduced enough for the reversal energy to outweigh the thermal energy.

Biomedical Applications

The biomedical applications and advantages of different types MNPs are mentioned in Table 1.[23]

CONCLUSION

Magnetic nanoparticles have been developed for modern oncological treatments, in which diagnosis of cancer, recognition, and treatment are tailored to every individual's carcinoma molecular report as well as prognostic oncology, in which genetic and/or molecular indications are utilized to prognosticate the disease growth, development, and medical outcome. When the issues of toxicity, localization, and cost are addressed, magnetic nanoparticles promise to be a prudent strategy for overcoming drug-delivery-related concerns.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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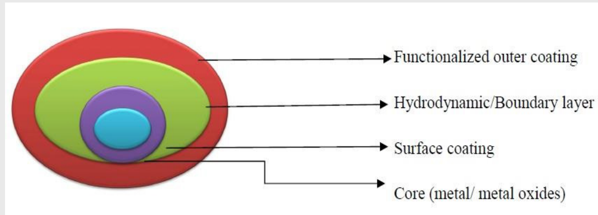
PICTORIAL ABSTRACT



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