MAGNETIC NANOPARTICLE: THE MAGNIFICENT DEVICE TO SUCK OUT THE UNWANTED CULPRITS FROM THE DOMESTIC UNITS

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ABSTRACT

Magnetic nanoparticles are a class of nanoparticle that can be manipulated using magnetic fields. Such particles commonly consist of two components, a magnetic material, often iron, nickel and cobalt, and a chemical component that has functionality. While nanoparticles are smaller than 1 micrometer in diameter (typically 1–100 nanometers), the larger microbeads are 0.5–500 micrometer in diameter. Magnetic nanoparticle clusters that are composed of a number of individual magnetic nanoparticles are known as magnetic nanobeads with a diameter of 50–200 nanometers. Magnetic nanoparticle clusters are a basis for their further magnetic assembly into magnetic nanochains. The magnetic nanoparticles have been the focus of much research recently because they possess attractive properties which could see potential use in catalysis including nanomaterial-based catalysts, biomedicine and tissue specific targeting, magnetically tunable colloidal photonic crystals, microfluidics, magnetic resonance imaging, magnetic particle imaging, data storage, environmental remediation, nanofluids, optical filters, defect sensor, magnetic cooling and cation sensors.

KEYWORDS: Nanobeads, Nanofluids, Nanochains, Magnetic nanoparticle, Sensors, Nanocomposites, Microfluidics, Quantum dots, Ferromagnetism.

INTRODUCTION

A nanoparticle or **ultrafine particle** is usually defined as a particle of matter that is between 1 and 100 nanometers (nm) in diameter. The term is sometimes used for larger particles, up to 500 nm, or fibers and tubes that are less than 100 nm in only two directions.[1-4] At the lowest range, metal particles smaller than 1 nm are usually called atom clusters instead. Nanoparticles are usually distinguished from micro particles (1-1000 μm), "fine particles" (sized between 100 and 2500 nm), and "coarse particles" (ranging from 2500 to 10,000 nm), because their smaller size drives very different physical or chemical properties, like colloidal properties and ultrafast optical effects or electric properties.[5]

Being more subject to the Brownian motion, they usually do not sediment, like colloidal particles that conversely are usually understood to range from 1 to 1000 nm. Being much smaller than the wavelengths of visible light (400-700 nm), nanoparticles cannot be seen with ordinary optical microscopes, requiring the use of electron microscopes or microscopes with LASER.

Figure-1: Steve Papell, the inventor of magnetic nanoparticles [NASA scientist].

For the same reason, dispersions of nanoparticles in transparent media can be transparent, whereas suspensions of larger particles usually scatter some or all visible light incident on them. Nanoparticles also easily pass through common filters, such as common ceramic candles, so that separation from liquids requires special Nano filtration techniques.[6] The properties of nanoparticles often differ markedly from those of larger particles of the same substance. Since the typical diameter of an atom is between 0.15 and 0.6 nm, a large fraction of the nanoparticle's material lies within a few atomic diameters of its surface. Therefore, the properties of that surface layer may dominate over those of the bulk material. This effect is particularly strong for nanoparticles dispersed in a medium of different composition since the interactions between the two materials at their interface also becomes significant.[7]

Synthesis of magnetic nanoparticles
Co-precipitation: Co-precipitation is a facile and convenient way to synthesize iron oxides (either Fe_3O_4 or $\gamma\text{-}Fe_2O_3$) from aqueous Fe^{2+}/Fe^{3+} salt solutions by the addition of a base under inert atmosphere at room temperature or at elevated temperature. The size, shape, and composition of the magnetic nanoparticles very much depends on the type of salts used (e.g. chlorides, sulfates, nitrates), the Fe^{2+}/Fe^{3+} ratio, the reaction temperature, the pH value and ionic strength of the media, and the mixing rate with the base solution used to provoke the precipitation. The co-precipitation approach has been used extensively to produce ferrite nanoparticles of controlled sizes and magnetic properties.[8] A variety of experimental arrangements have been reported to facilitate continuous and large–scale co–precipitation of magnetic particles by rapid mixing. Recently, the growth rate of the magnetic nanoparticles was measured in real-time during the precipitation of magnetite nanoparticles by an integrated AC magnetic susceptometer within the mixing zone of the reactants.[9]

Thermal decomposition: Magnetic Nano crystals with smaller size can essentially be synthesized through the thermal decomposition of alkaline organometallic compounds in high-boiling organic solvents containing stabilizing surfactants.[10]

Micro emulsion: Using the micro emulsion technique, metallic cobalt, cobalt/platinum alloys, and gold-coated cobalt/platinum nanoparticles have been synthesized in reverse micelles of cetyltrimethlyammonium bromide, using 1-butanol as the cosurfactant and octane as the oil phase.

Flame spray synthesis: Using flame spray pyrolysis and varying the reaction conditions, oxides, metal or carbon coated nanoparticles are produced at a rate of > 30 g/h.[11]
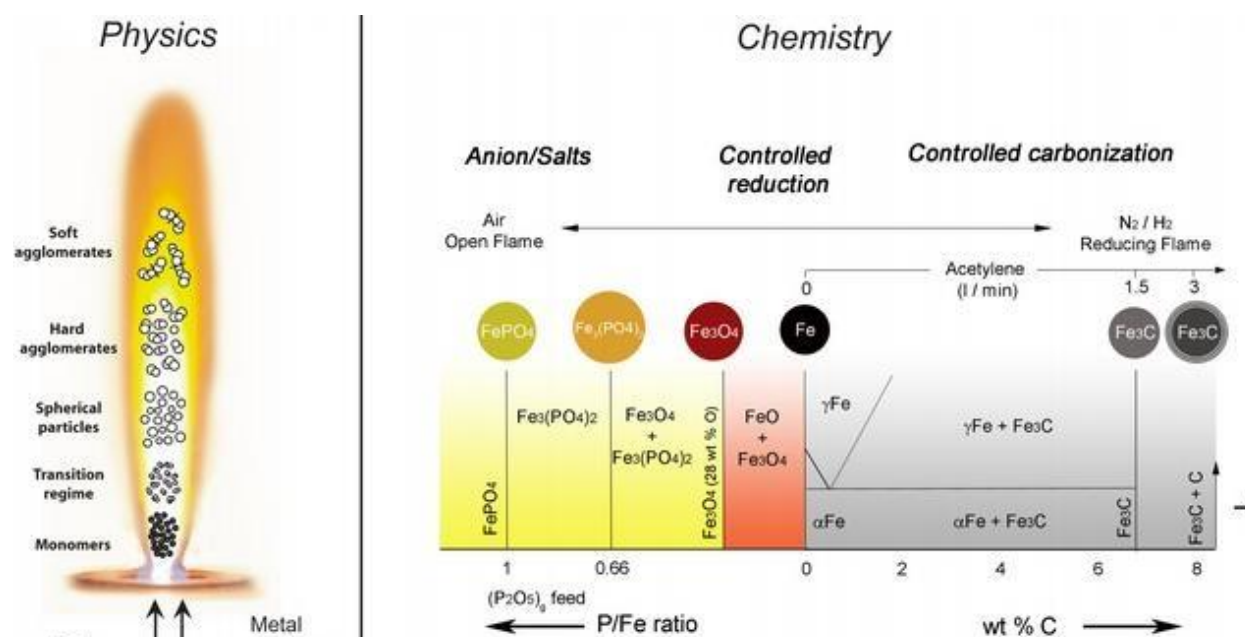

Figure-2: Flame spray synthesis of magnetic nanoparticles.

Idealized model of a crystalline nanoparticle of platinum, about 2 nm in diameter, showing individual atoms.

Nanoparticles occur widely in nature and are objects of study in many sciences such as chemistry, physics, geology and biology. Being at the transition between bulk mater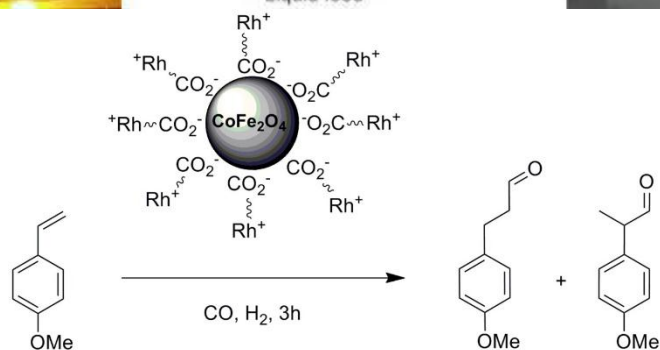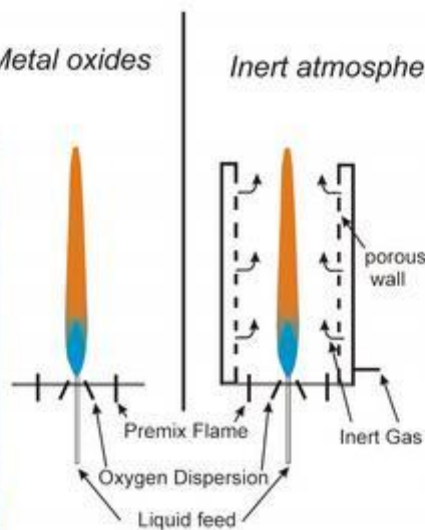ials and atomic or molecular structures, they often exhibit phenomena that are not observed at either scale. They are an important component of atmospheric pollution, and key ingredients in many industrialized products such as paints, plastics, metals, ceramics, and magnetic products. The production of nanoparticles with specific properties is a branch of nanotechnology.[12]
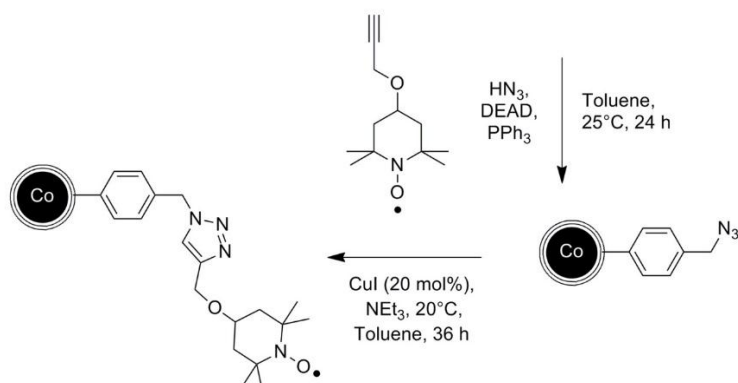
Conventional flame spray synthesis

Ambient atmosphere, Metal oxides

Reducing flame spray synthesis

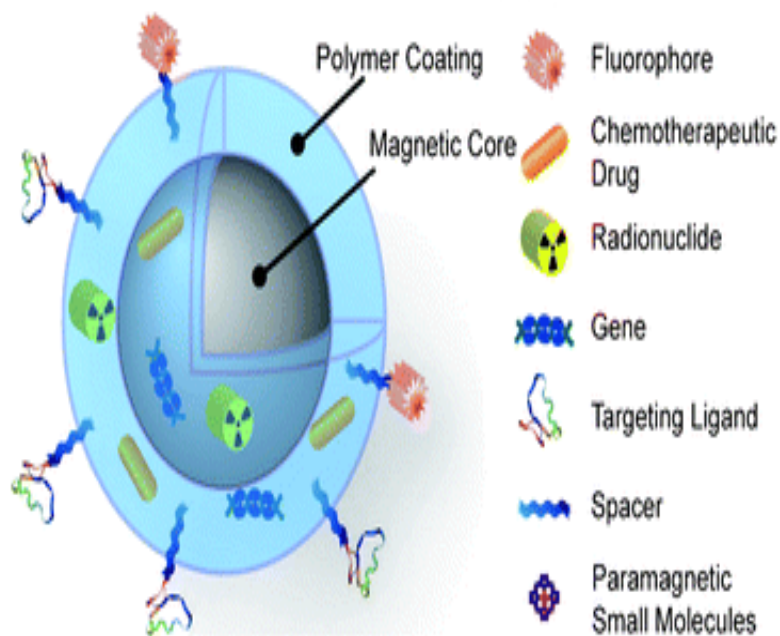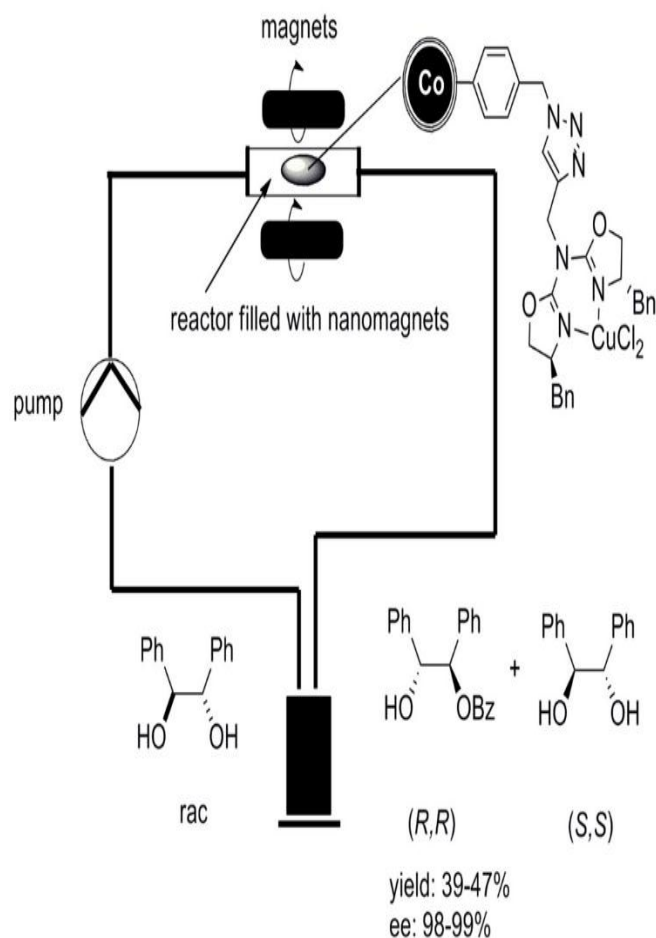Inert atmosphere, Metal nanoparticles

Figure-3: Magnetic nanoparticles synthesis.

Definitions

IUPAC: In its 2012 proposed terminology for biologically related polymers, the IUPAC defined a nanoparticle as "a particle of any shape with dimensions in the 1×10^{-9} and 1×10^{-7} m range". This definition evolved from one given by IUPAC in 1997. In another 2012 publication, the IUPAC extends the term to include tubes and fibers with only two dimensions below 100 nm.[13]
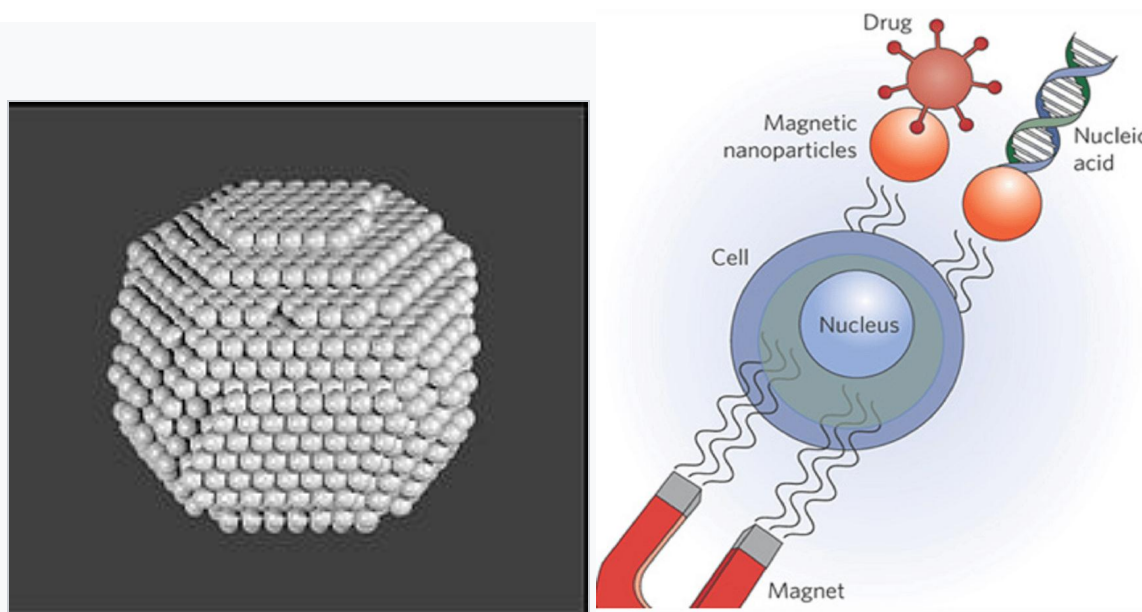
Figure-4: Nanoparticles after magnetic sequencing.

Controlling Properties: The properties of a nanoparticle are heavily influenced by the initial nucleation stages of the synthesis process. Nucleation, for example, is vital to the size of the nanoparticle. A critical radius must be met in initial stages of solid formation, or the particles will redissolve into the liquid phase. The final shape of a nanoparticle is also controlled by nucleation. Possible final morphologies created by nucleation can include spherical, cubic, needle-like, worm-like, and more particles. Nucleation can be controlled predominately by time and temperature as well as the supersaturation of the liquid phase and the environment of the synthesis overall. The properties of a material in nanoparticle form are unusually different from those of the bulk one even when divided into micrometer-size particles. Many of them arise from spatial confinement of sub-atomic particles (i.e. electrons, protons, photons) and electric fields around these particles. The large surface to volume ratio is also significant factor at this scale.[14]

A bulk materials (>100 nm in size) are expected to have constant physical properties (such as thermal and electrical conductivity, stiffness, density, and viscosity) regardless of its size, for nanoparticle, however, this is different: the volume of the surface layer (few atomic diameters-wide) becomes a significant fraction of the particle's volume; whereas that fraction is insignificant for particles with diameter of one micrometer or more. In other words, the surface area/volume ratio impacts certain properties of the nanoparticles more prominently than in bulk particles.[15]

Figure-5: 1 kg of particles of 1 mm^3 has the same surface area as 1 mg of particles of 1 nm^3.

Interfacial layer: For nanoparticles dispersed in a medium of different composition, the interfacial layer — formed by ions and molecules from the medium that are within a few atomic diameters of the surface of each particle — can mask or change it's chemical and physical properties. Indeed, that layer can be considered an integral part of each nanoparticle.[16]

Solvent affinity: Suspensions of nanoparticles are possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences, which otherwise usually result in a material either sinking or floating in a liquid.[17]
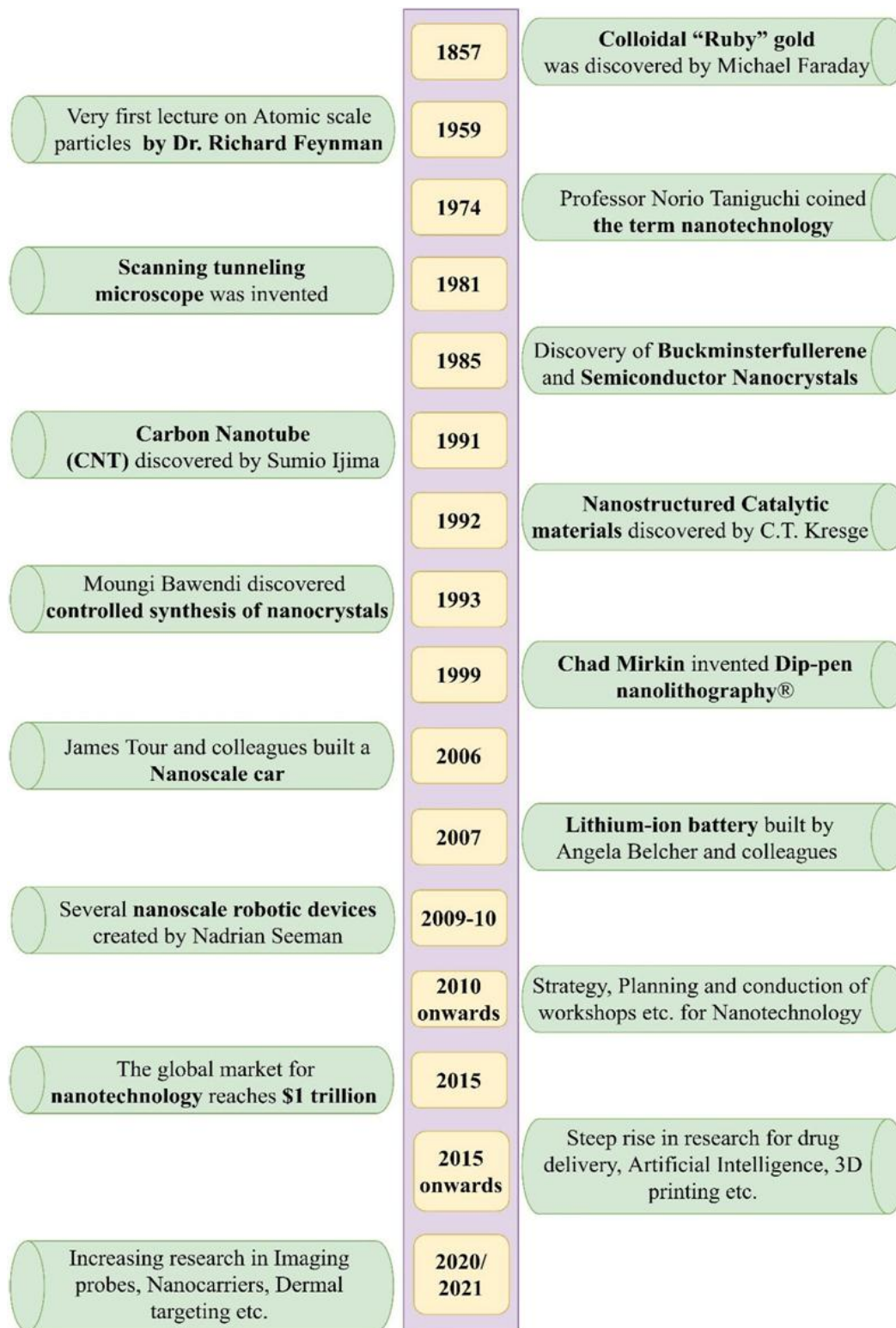
Year	Development
1857	Colloidal "Ruby" gold was discovered by Michael Faraday
1959	Very first lecture on Atomic scale particles by Dr. Richard Feynman
1974	Professor Norio Taniguchi coined the term nanotechnology
1981	Scanning tunneling microscope was invented
1985	Discovery of Buckminsterfullerene and Semiconductor Nanocrystals
1991	Carbon Nanotube (CNT) discovered by Sumio Ijima
1992	Nanostructured Catalytic materials discovered by C.T. Kresge
1993	Moungi Bawendi discovered controlled synthesis of nanocrystals
1999	Chad Mirkin invented Dip-pen nanolithography®
2006	James Tour and colleagues built a Nanoscale car
2007	Lithium-ion battery built by Angela Belcher and colleagues
2009-10	Several nanoscale robotic devices created by Nadrian Seeman
2010 onwards	Strategy, Planning and conduction of workshops etc. for Nanotechnology
2015	The global market for nanotechnology reaches $1 trillion
2015 onwards	Steep rise in research for drug delivery, Artificial Intelligence, 3D printing etc.
2020/2021	Increasing research in Imaging probes, Nanocarriers, Dermal targeting etc.

Figure-6: Chronological developments in the field of nanotechnology.

Coatings: Nanoparticles often develop or receive coatings of other substances, distinct from both the particle's material and of the surrounding medium. Even when only a single molecule thick, these coatings can radically change the particles' properties, such as and chemical reactivity, catalytic activity, and stability in suspension.[18]
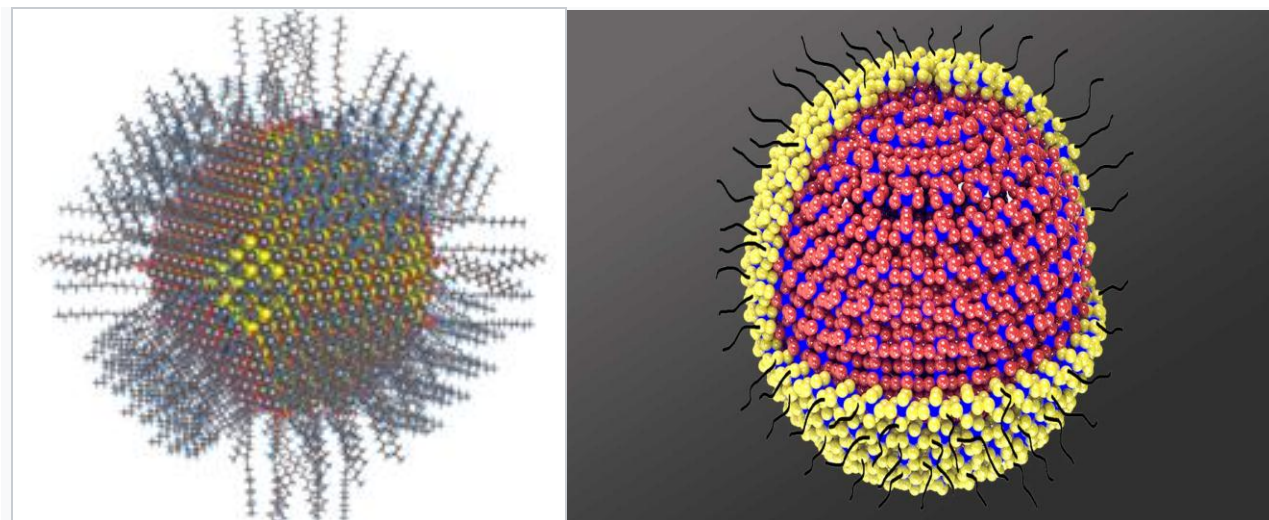
Figure-7: Semiconductor nanoparticle (quantum dot) of lead sulfide with complete passivation by oleic acid, oleyl amine and hydroxyl ligands (size ~5nm).

Diffusion across the surface: The high surface area of a material in nanoparticle form allows heat, molecules, and ions to diffuse into or out of the particles at very large rates. The small particle diameter, on the other hand, allows the whole material to reach homogeneous equilibrium with respect to diffusion in a very short time. Thus many processes that depend on diffusion, such as sintering can take place at lower temperatures and over shorter time scales inducing catalysis.[19]

Ferromagnetic and ferroelectric effects: The small size of nanoparticles affects their magnetic and electric properties. The ferromagnetic materials in the micrometer range is a good example: widely used in magnetic recording media, for the stability of their magnetization state, those particles smaller than 10 nm are unstable and can change their state (flip) as the result of thermal energy at ordinary temperatures, thus making them unsuitable for that application.[20]

Mechanical Properties: The reduced vacancy concentration in Nano crystals can negatively affect the motion of dislocations, since dislocation climb requires vacancy migration. In addition, there exists a very high internal pressure due to the surface stress present in small nanoparticles with high radii of curvature. This causes a lattice strain that is inversely proportional to the size of the particle, also well known to impede dislocation motion, in the same way as it does in the work hardening of materials. For example, gold nanoparticles are significantly harder than the bulk material. Furthermore, the high surface-to-volume ratio in nanoparticles makes dislocations more likely to interact with the particle surface. In particular, this affects the nature of the dislocation source and allows the dislocations to escape the particle before they can multiply, reducing the dislocation density and thus the extent of plastic deformation. There are unique challenges associated with the measurement of mechanical properties on the Nano scale, as conventional means such as the universal testing machine cannot be employed. As a result, new techniques such as Nano indentation have been developed that complement existing electron microscope and scanning probe methods. Atomic force microscopy (AFM) can be used to perform Nano indentation to measure hardness, elastic modules, and adhesion between nanoparticle and substrate. The particle deformation can be measured by the deflection of the cantilever tip over the sample. The resulting force-displacement curves can be used to calculate elastic modules. However, it is unclear whether particle size and indentation depth affect the measured elastic modulus of nanoparticles by AFM.[21]

Magnetic Nanoparticles— Magnetic nanoparticles are a class of nanoparticles that can be manipulated using magnetic fields. Such particles commonly consist of two components, a magnetic material, often iron, nickel and cobalt, and a chemical component that has functionality. While nanoparticles are smaller than 1 micrometer in diameter (typically 1–100 nanometers), the larger micro beads are 0.5–500 micrometer in diameter. Magnetic nanoparticle clusters that are composed of a number of individual magnetic nanoparticles are known as magnetic Nano beads with a diameter of 50–200 nanometers. Magnetic nanoparticle clusters are a basis for their further magnetic assembly into magnetic Nano chains. The magnetic nanoparticles have been the focus of much research recently because they possess attractive properties which could see potential use in catalysis

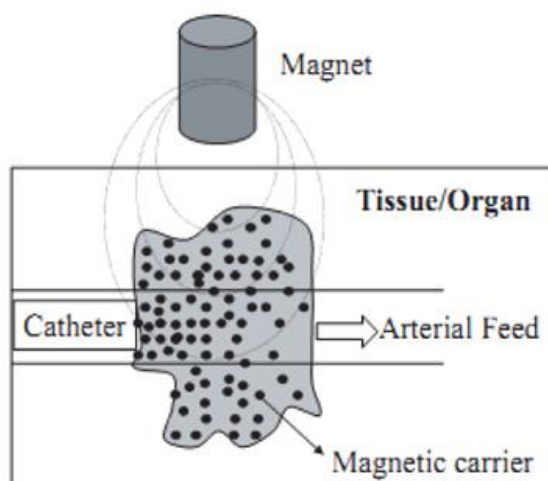including nanomaterial-based catalysis, biomedicine and tissue specific targeting, magnetically tunable colloidal photonic crystals, microfluidics, magnetic resonance imaging, magnetic particle imaging, data storage, environmental remediation, Nano fluids, optical filters, defect sensor, magnetic cooling and cation sensors.[22]
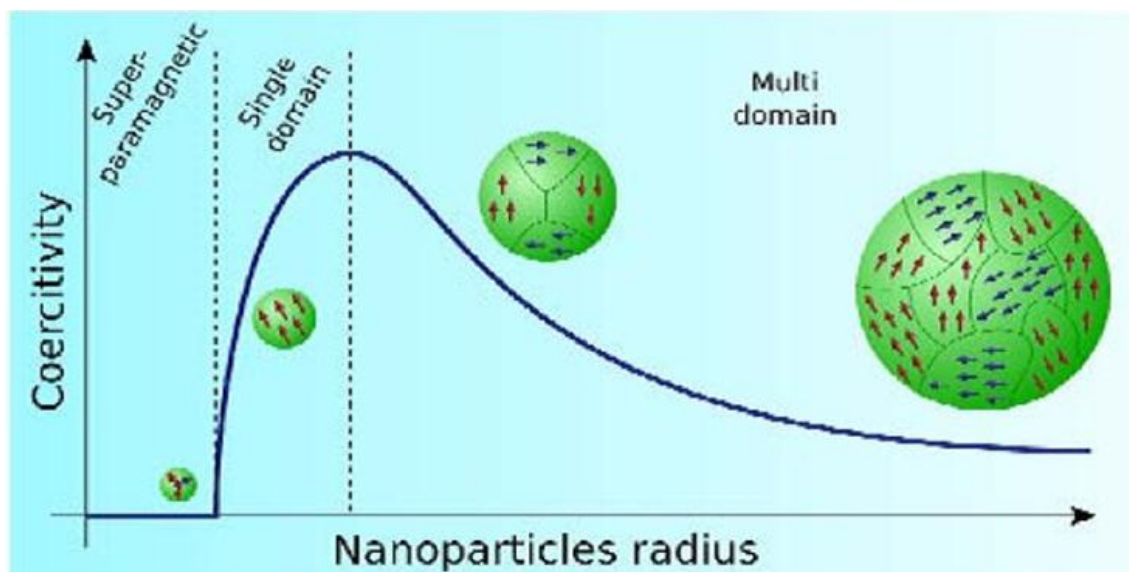
Figure-8: Relationship between coercitivity vs radius of nanoparticles.

Physical properties of magnetic nanoparticles: Magnetic effects are caused by movements of particles that have both mass and electric charges. These particles are electrons, holes, protons, and positive and negative ions. A spinning electric-charged particle creates a magnetic dipole, so-called magnetron. In ferromagnetic materials, magnetrons are associated in groups. A magnetic domain (also called a Weiss domain) refers to a volume of ferromagnetic material in which all magnetrons are aligned in the same direction by the exchange forces. This concept of domains distinguishes ferromagnetism from paramagnetism.[23]

Figure-9: Magnetic field from Nano magnet to tissue.

When the size of single-domain particles further decreases below a critical diameter, the coercively becomes zero, and such particles become super paramagnetic. Superparamagnetism is caused by thermal effects. In super paramagnetic particles, thermal fluctuations are strong enough to spontaneously demagnetize a previously saturated assembly; therefore, these particles have zero coactivity and have no hysteresis. Nanoparticles become magnetic in the presence of an external magnet, but revert to a nonmagnetic state when the external magnet is removed. This avoids an 'active' behavior of the particles when there is no applied field. Introduced in the living systems, particles are 'magnetic' only in the presence of an external field, which gives them unique advantage in working in biological environments. There are a number of crystalline materials that exhibit ferromagnetism, among others Fe, Co, or Ni. Since ferrite oxide-magnetite (Fe_3O_4) is the most magnetic of all the naturally occurring minerals on earth, it is widely used in the form of super paramagnetic nanoparticles for all sorts of biological applications.[24]

Nanomaterials for Water and Wastewater Treatment Zero-Valent Metal Nanoparticles
Silver Nanoparticles: Silver nanoparticles (Ag NPs) are highly toxic to microorganisms and thus have strong antibacterial effects against a wide range of microorganisms, including viruses, bacteria, and fungi. As a good antimicrobial agent, silver nanoparticles have been widely used for the disinfection of water. The mechanism of the antimicrobial effects of Ag NPs is not clearly known and remains under debate. In recent years, several theories have been put forward. Ag NPs have been reported to be able to adhere to the bacterial cell wall and subsequently penetrate it, resulting in structural changes of the cell membrane and thus increasing its permeability. Besides, when Ag NPs are in contact with bacteria, free radicals can be generated.[25]
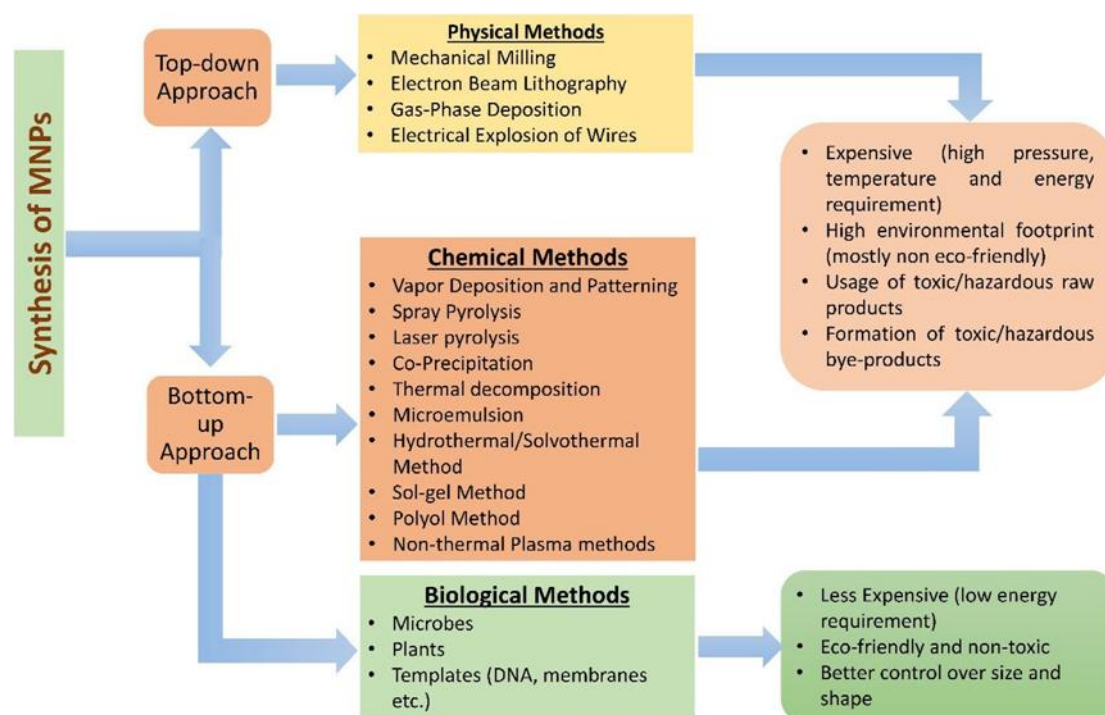
Figure-10: Classification of synthesis methods for MNPs and their key features.

They have the ability to damage the cell membrane and are considered to cause the death of cells. In addition, as DNA contains abundant sulfur and phosphorus elements, Ag NPs can act with it and thus destroy it. This is another explanation for the death of cells caused by Ag NPs. What is more, the dissolution of Ag NPs will release antimicrobial Ag^+ ions, which can interact with the thiol groups of many vital enzymes, inactivate them, and disrupt normal functions in the cell. With the development of nanotechnology, Ag NPs have been successfully applied in water and wastewater disinfection in recent years.[26]
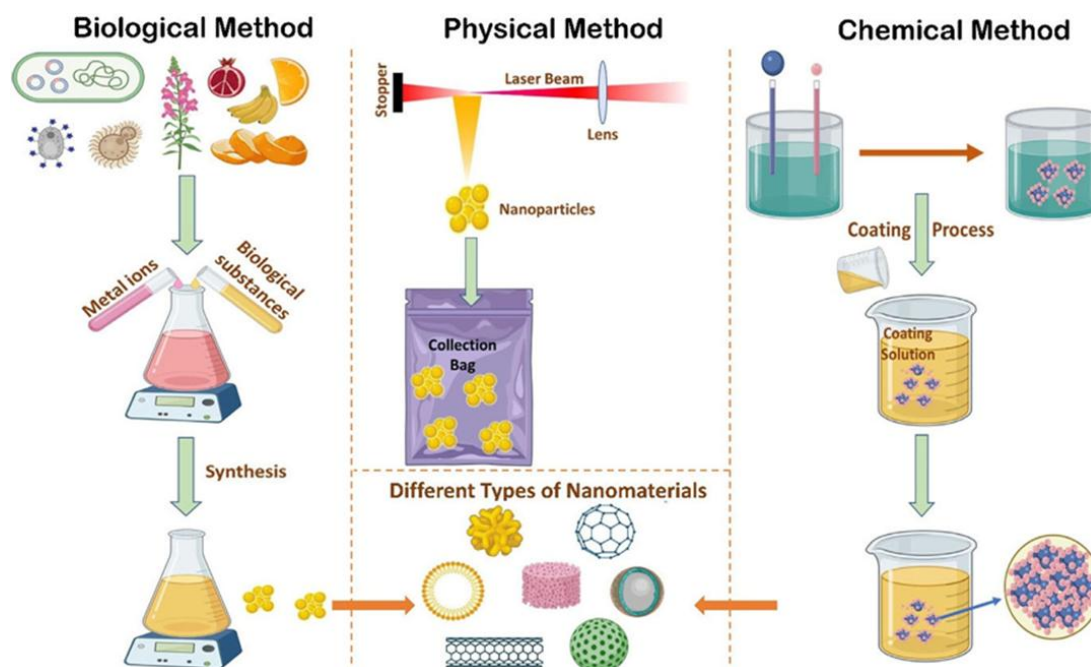

Figure-11: Various methods of magnetic nanoparticles.

Iron Nanoparticles: In recent years, various zero-valent metal nanoparticles, such as Fe, Zn, Al, and Ni, in water pollution treatment have drawn wide research interest. The standard reduction potentials of Fe, Al, Ni, and Zn are listed. Due to the extremely high reductive ability, nano-zero-valent Al is thermodynamically unstable in the presence of water, which favors the formation of oxides/hydroxides on the surface, impeding (completely) the transfer of electrons from the metal surface to the contaminants. Compared with Fe, Ni has a less negative

standard reduction potential, indicating a lower reducing ability. With a moderate standard reduction potential, nano-zero-valent Fe or Zn holds good potential to act as reducing agents relative to many redox-labile contaminants. Despite a weaker reduction ability, Fe possesses many prominent advantages over Zn for

applications in water pollution treatment, including excellent adsorption properties, precipitation and oxidation (in the presence of dissolved oxygen), and low cost. Therefore, zero-valent iron nanoparticles have been the most extensively studied zero-valent metal nanoparticles.[27]
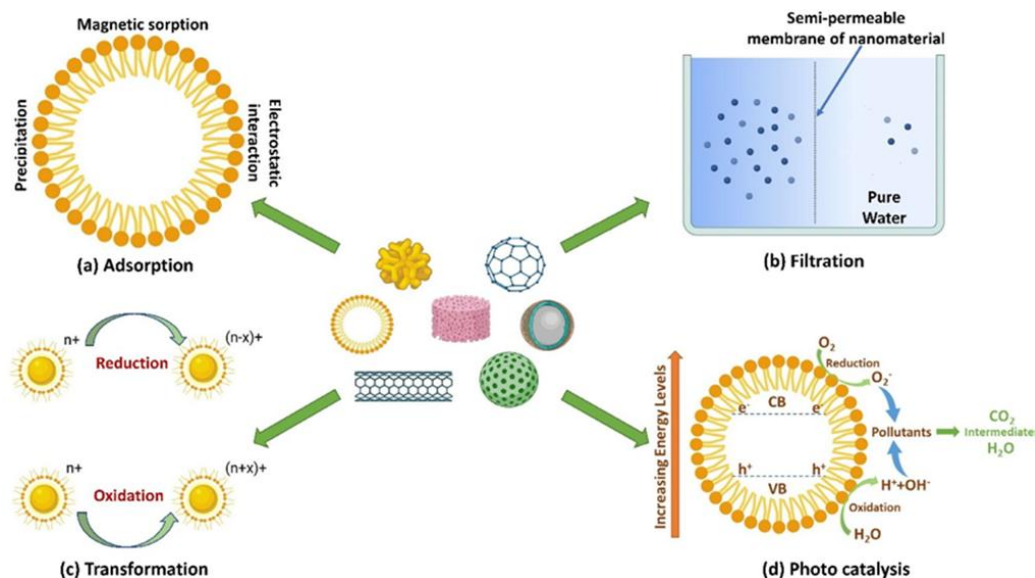
Figure-12: Various mechanisms of contaminant removal using MNPs, (a) Adsorption, (b) Filtration using semi-permeable membranes synthesized through MNPs, (c) Redox reactions for contaminant degradation, (d) Pollutant removal through photo catalysis. CB: Conduction band; VB: Valence band; e: electron, h: hole.

Zinc Nanoparticles: Although most studies on contaminant degradation in water and wastewater treatment by zero-valent metal nanoparticles have been focused on iron, Zn has also been considered as an alternative. With a more negative standard reduction potential. Zn is a stronger reductant compared with Fe. Therefore, the contaminant degradation rate of zinc nanoparticles may be faster than that of nZVI. For the application of nano-zero-valent zinc (nZVZ), most studies have been focused on dehalogenation reaction. Research indicated that the reduction rates of CCl_4 by nZVZ were more significantly affected by solution chemistry than particle size or surface morphology. By comparing the reactivity of various types of nZVI and nZVZ, it was found that nZVZ could degrade CCl_4 more rapidly and completely than nZVI under favorable conditions. Besides, a study has been carried out to examine the degradation of octachlorodibenzo-p-dioxin (OCDD) in water with four different zero-valent metal nanoparticles: zero-valent zinc (nZVZ), zero-valent iron (nZVI), zero-valent aluminum (nZVAL), and zero-valent nickel (nZVN).[28]
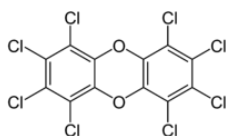
Metal Oxides Nanoparticles: TiO$_2$ Nanoparticles: As an emerging and promising technology, photo catalytic

degradation has attracted great attention since 1972 when Fujishima and Honda observed electrochemical photolysis of water on TiO_2 semiconductor electrode. In recent years, photo catalytic degradation technology has been successfully applied in the contaminant degradation in water and wastewater. At the presence of light and catalyst, contaminants can be gradually oxidized into low molecular weight intermediate products and eventually transformed into CO_2, H_2O, and anions *such as sulfate/chloride and cations such as titanium/zinc etc.* The majority of common photo catalysts are metal oxide or sulfide semiconductors, among which TiO_2 has been most extensively investigated in the past decades. Owing to its high photo catalytic activity, reasonable price, photo stability, and chemical and biological stability. TiO_2 is the most exceptional photo catalyst to date.[29]

ZnO Nanoparticles: In the field of photo catalysis, apart from TiO_2 NPs, ZnO NPs have emerged as another efficient candidate in water and wastewater treatment because of their unique characteristics, such as direct and wide band gap in the near-UV spectral region, strong oxidation ability, and good photo catalytic property. ZnO NPs are environment-friendly as they are compatible with organisms, which makes them suitable for the treatment of water and wastewater. Besides, the photo catalytic capability of ZnO NPs is similar to that of TiO_2 NPs because their band gap energies are almost the same. However, ZnO NPs have the advantage of low cost over TiO_2 NPs. Moreover, ZnO NPs can adsorb a

wider range of solar spectra and more light quanta than several semiconducting metal oxides.[30]

Iron Oxides Nanoparticles: In recent years, there is a growing interest in the use of iron oxides nanoparticles for the removal of heavy metal due to their simplicity and availability. Magnetic magnetite (Fe_3O_4) and magnetic maghemite (γ-Fe_2O_4) and nonmagnetic

hematite (α-Fe_2O_3) are often used as Nano adsorbents. Generally, due to the small size of Nano adsorbent materials, their separation and recovery from contaminated water are great challenges for water treatment. However, magnetic magnetite (Fe_3O_4) and magnetic maghemite (γ-Fe_2O_4) can be easily separated and recovered from the system with the assistance of an external magnetic field.[31]

Table-1: Remediation of various types of organic pollutants from wastewater by MNPs and their removal mechanism.

Sl	Name of MNP	Contaminant removed	Removal mechanism	Duration	Removal Efficiency	MNP reusability
1	Humic acid functionalized Fe_3O_4	Carcinogenic green dye	Adsorption	35min	97%	Up to five cycles for 85% removal
2	Combination of Fe_3O_4 and Fe_2O_3	Bromophenol blue dye	Photocatalytic degradation	60min	98%	Up to three cycles for 95% removal
3	Silica coated ferro-ferric oxide (Fe_3O_4@SiO_2)	Emulsified oil	Transformation	05min	98%	Up to five cycles for 95% removal
4	Magnetic activated carbon-Fe_3O_4 (AC-Fe_3O_4)	Pharmaceutical substance	Adsorption	06min	99.97%	Up to five cycles for 99% removal
5	JC-Fe_3O_4 and CT-Fe_3O_4 NPs	Organic dyes	Adsorption	120min	99%	Not studied
6	Nano porous Co_2O_3/Cu_2O_3: Al_2O_3:SiO_2	*E. faecalis*	Disinfection	05min	100%	Not studied
7	Magnetic Janus nanoparticles (M-Janus NPs)	Cooking oil and crude oil	Phase-separation	15min	96%	Up to five cycles for 90% removal
8	$FeNi_3$@SiO_2@TiO_2	Humic acid	Photo catalytic degradation	30min	100%	Not studied
9	Chitosan-coated magnetic nanoparticles (cMNPs)	Bio-refinery wastewater containing phenol	Adsorption	90min	46%	Up to five cycles for 20% of initial removal efficiency
10	Moringa extract modified MNP	Colour	Coagulation	07min	89%	Up to two cycles for 80% removal
11	Copper-doped ZrO_2 MNPs	Methyl orange dye	Photocatalytic degradation	100min	98%	Up to four cycles for 90% removal
12	MOM-Fe_3O_4	Pharmaceutical substance	Adsorption	720min	94%	Not studied
13	Novel MNP-alum Conjugate	Adsorption cum enhanced coagulation–flocculation	Natural organic matter	30min	99%	Up to five cycles with ~91% removal
14	MCPEI (polyetheleneimine and magnetic nanoparticle)	Black 5 dye	Adsorption	180min	100%	Up to five cycles for 48% removal
15	Magnetic silica-based Nano adsorbents	Pharmaceutical substance	Adsorption	200min	80%	Up to eight cycles for 100% removal
16	Fe_3O_4@Ag@MESNa	Hg(II)	Adsorption	30sec	100%	Up to two

						cycles for 100% removal
17	Magnetic eggshell membrane (MESM)	Lead	Adsorption	48hr	95%	Reusable
18	Fe_3O_4@EPS	PO_4^{-2}	Adsorption	13hr	91%	Not studied
19	Magnetic tubular carbon nanofibers (MTCFs)	Cu(II)	Adsorption	10min	100%	Up to six cycles for 85% removal
20	JC-Fe_3O_4 and CT-Fe_3O_4 NPs	Co^{2+} and Cu^{2+}	Adsorption	120min	513.7 mg/g for Co^{2+} and 463.23 mg/g for Cu^{2+}	Not studied
21	Hyper branched polyglycerol HPG-MNPs	Ni, Cu and Al	Adsorption	130min	94%	Up to nine cycles for 90% removal
22	Maghemite nanoparticles coated *Bacillus subtilis*	Cd^{2+} ions	Adsorption	60min	84%	Reusable
23	Chitosan-coated magnetic nanoparticles (cMNPs)	Bio-refinery wastewater containing heavy metals	Adsorption	90min	Cu (42.2%), Cr (18.7%), and As (2.44%)	Up to five cycles for 20% of initial removal efficiency
24	Super paramagnetic Fe_3O_4@SiO_2@GLYMO(S)-en	Pb^{2+} and Cd^{2+}	Adsorption	55min	Pb^{2+}: 93.5 mg/g, Cd^{2+}: 80.64 mg/g	Up to five cycles for 90% removal
25	Eucalyptus leaf extracts (EL-MNP@zeolite)	PO_4^{2-}	Adsorption	30min	100%	Not studied
26	MNP@SiO_2–PEI-DTPA	NH_4^+, Pb^{2+} and Cd^{2+}	Adsorption	72hr	>90%	Up to five cycles for 80% removal
27	Nano chitosan coated MNPs	Pb(II), Cu(II) and Cd(II)	Adsorption	10-30min	57.6%−95.5%	Up to three cycles for 96% removal
28	Epoxy-Triazinetrione-Functionalized	Malachite green (MG) and Pb(II)	Adsorption	15min	95%	Up to six cycles for 61% removal
29	DES/GO-Fe_3O_4 Nano hybrid	Pb(II)	Adsorption	20min	80%	Not studied
30	Magnetic nanoparticles coated mixed fungal biomass (MNP-FB)	Cr(VI)	Adsorption	60min	99%	Not studied

Carbon Nanotubes: Carbon nanomaterial (CNMs) are a class of fascinating materials due to their unique structures and electronic properties which make them attractive for fundamental studies as well as diverse applications, especially in sorption processes. Their advantages for water and wastewater treatment are due to great capacity to adsorb a wide range of contaminants, fast kinetics, large specific surface area, and selectivity towards aromatics. There are several forms of CNMs, such as carbon nanotubes (CNTs), carbon beads, carbon fibers, and Nano porous carbon. Among them, CNTs have attracted the most attentions and progressed rapidly in recent years. Carbon nanotubes are graphene sheets rolled up in cylinders with diameter as small as 1 nm.

CNTs have attracted great interest as an emerging adsorbent due to their unique properties. With an extremely large specific surface area and abundant porous structures, CNTs possess exceptional adsorption capabilities and high adsorption efficiencies for numerous kinds of contaminants, such as dichlorobenzene, ethyl benzene, Zn^{2+}, Pb^{2+}, Cu^{2+}, and Cd^{2+}, and dyes. According to their (super) structures, CNTs can be classified into two types: multiwalled carbon nanotubes (MWCNTs), which comprised multiple layers of concentric cylinders with a spacing of about 0.34 nm between the adjacent layers, and single-walled carbon nanotubes (SWCNTs), which consist of

single layers of graphene sheets seamlessly rolled into cylindrical tubes.[32]

Nano composites: As mentioned above, every nanomaterial has its own drawbacks. For example, nZVI has the disadvantages of aggregation, oxidation, and separation difficulty from the degraded systems. The light adsorption of TiO_2 NPs and ZnO NPs is limited in the ultraviolet light region due to their big band gap energies. Nano filtration membranes are troubled by the problem of membrane fouling. Carbon nanotubes are mainly limited by their low volume of production and high cost as well as the need for supporting medium or matrix.[33]

Mechanisms of contaminant removal using MNPs: Rapid industrialization and increasing population is the major reason behind the release of various contaminants in wastewater including both organic and inorganic pollutants such as dyes, pesticides, personal care products, heavy metals etc. The biggest challenge comes from the partial or un-treated wastewater directly getting discharged into the surface water bodies causing severe environmental risk, endangering aquatic species, affecting the food chain and subsequently affect human health through bioaccumulation and bio magnification. For efficient remediation and removal of these contaminants, eco-friendly nanomaterials have been developed over years and the research is continually expanding.[34] Various types of MNPs have been synthesized and used for remediation purposes, with varying sizes, chemical properties, and morphologies. These MNPs act through four major removal/degradation mechanisms viz., (a) adsorption, (b) filtration, (c) transformation, and (d) catalysis. Adsorption is a surface phenomenon that involves the binding of pollutants on the surface of the adsorbent mediated through physical or chemical interactions. Broadly, the adsorption process for contaminant removal/wastewater treatment occurs in three steps, (i) movement of the contaminant to the surface of the adsorbent, (ii) binding at the adsorbent surface, and (iii) movement within the adsorbent. In general, the MNPs have higher specific surface areas, hence, they can be easily functionalized towards a target contaminant. Moreover, the nano-sized pores present on the surface of MNPs help in the adsorption of contaminants. Furthermore, the magnetic properties of nanomaterials enhance their ability to be separated from the contaminant and regenerated to improve reusability.[35]

Recent applications of MNPs in wastewater treatment: The presence of various organic contaminants such as dyes, pesticides, personal care products, phenols etc. in wastewater has become a major source of pollution. These pollutants adversely affect aquatic life and human health as well. These organic pollutants are extremely difficult to remove using conventional wastewater treatment technologies. Their degradation is achieved mostly through methods such as

acidic decomposition, heating, or employing biological treatment methods. Hence, the identification of a suitable method becomes important for wastewater treatment. Many studies have made use of nanomaterials for wastewater treatment through Nano sorption, photo catalytic degradation mechanisms, and membrane filtration.[36]

CONCLUSION

Several studies have been published concerning the utilization of MNPs for wastewater treatment and contaminant removal/degradation. The literature present in this review paper demonstrated that various types of organic and inorganic pollutants can be successfully removed from wastewater using MNPs. These methods have been proven to be cost-effective, highly efficient and provide rapid results, as studies have reported that >95% removal efficiency can be achieved within 5 min. However, it is worth noting that the removal efficiencies increased in case of magnetic Nano composites as compared to other types of MNPs. Moreover, photo catalytic degradation, adsorption and transformation through redox reactions have been the most successful mechanisms for the contaminant removal and offers better sustainability. It has been found that various MNPs have very high magnetic saturation which reaches up to 70 emu/g. MNPs have been proven to be more stable, shown capabilities to target specific contaminants, offer easy separation, and have a high degree of reusability and regeneration capacity. Results also suggested that removal efficiency is not affected even up to recycling for 5 cycles retaining >95% removal efficiency. It can also be concluded that the use of MNPs, especially for biosynthesized MNPs, is more cost-efficient as compared to most of the traditionally used methods such as activated carbon, activated sludge process, membrane filtration etc in case of wastewater treatment. However, more studies on economics and toxicity of using magnetic nanomaterials for wastewater treatment must be conducted.

REFERENCES

1. Abou Hammad, A.B., El Nahwary, A.M., et al. Nanoceramics and novel functionalized silicate-based magnetic nanocomposites as substitutional disinfectants for water and wastewater purification. Environ. Sci. Pollut. Res., 2020; 2721(27): 26668–26680.
2. Arabkhani, P., Asfaram, A. Development of a novel three-dimensional magnetic polymer aerogel as an efficient adsorbent for malachite green removal. J. Hazard. Mater, 2020; 384: 121394.
3. Bharath, G., Alhseinat, E., et al. Development of adsorption and electrosorption techniques for removal of organic and inorganic pollutants from wastewater using novel magnetite/porous graphene-

based nanocomposites. Sep. Purif. Technol, 2017; 188: 206–218.

4. Boretti, A., Rosa, L. Reassessing the projections of the world water development report. npj Clean Water 2, 1–6. http://dx.doi.org/10.1038/ s41545-019-0039-9, 2019.

5. Dron Modi, Rahul Desai, Hardik Gosawami, Hitendra Vaghela, Vaibhav Shah, Sunita Chaudhary, Dhrubo Jyoti Sen; Dissocubes: A novelty in the preparation of nanosuspension to enhance solubility of poorly water soluble drugs: a review: Internationale Pharmaceutica Sciencia, 2013; 3(4): 55-64.

6. Chen, F., Xie, S., et al.. Ionothermal synthesis of Fe3O4 magnetic nanoparticles as efficient heterogeneous Fenton-like catalysts for degradation of organic pollutants with H2O2. J. Hazard. Mater, 2017; 322: 152–162.

7. Prof. Dr. Dhubo Jyoti Sen; Bio-friendly magnetic water is ecofriendly: World Journal of Pharmaceutical Sciences, 2015; 3(10): 1949-1956.

8. Darwesh, O.M., Matter, I.A., Eida, M.F. Development of peroxidase enzyme immobilized magnetic nanoparticles for bioremediation of textile wastewater dye. J. Environ. Chem. Eng, 2019; 7: 102805.

9. Das, S., Chakraborty, J., et al. Prospects of biosynthesized nanomaterials for the remediation of organic and inorganic environmental contaminants. Environ. Sci. Nano, 2018; 5: 2784–2808.

10. Majid Sharifi Rad, Javad Sharifi Rad, Gholam Ali Heshmati and Dhrubo Jyoti Sen; Biological synthesis of gold and silver nanoparticles by Nitraria schoberi fruits: American Journal of Advanced Drug Delivery, 2013; 1(2): 174-179.

11. Govarthanan, M., Jeon, C.H., et al. Non-toxic nano approach for wastewater treatment using Chlorella vulgaris exopolysaccharides immobilized in iron-magnetic nanoparticles. Int. J. Biol. Macromol, 2020; 162: 1241–1249.

12. Dron P. Modi, Sunita Chaudhary, Ragin Shah and Dhrubo Jyoti Sen; Gold nano shells: the advancing nanotechnology to fight against cancer: British Biomedical Bulletin, 2013; 1(1): 023-034.

13. He, X., Liu, Q., Xu, Z. Treatment of oily wastewaters using magnetic Janus nanoparticles of asymmetric surface wettability. J. Colloid Interface Sci., 2020; 568: 207–220.

14. Javad Sharifi Rad, Seyedeh Mahsan Hoseini Alfatemi, Mehdi Sharifi Rad, Majid Sharifi Rad, Dhrubo Jyoti Sen and Sasan Mohsenzadeh; In-vivo titanium dioxide (TiO2) nanoparticles effects on chromosomal abnormalities and lactate dehydrogenase activity: American Journal of Advanced Drug Delivery, 2013; 1(3): 232-237.

15. Kaul, S., Gulati, N., et al. Role of nanotechnology in cosmeceuticals: A review of recent advances. J. Pharm, 2018; 1–19.

16. Khan, F.S.A., Mubarak, N.M., et al. Magnetic nanoadsorbents' potential route for heavy metals removal—a review. Environ. Sci. Pollut. Res., 2020a; 27: 24342–24356.

17. Dr. Sampa Dhabal, Dr. Dhrubo Jyoti Sen & Dr. Dhananjoy Saha; Inner eye of nanoscience focusses the outreach of milestone: World Journal of Pharmaceutical Research, 2020; 9(14): 531-564.

18. Lakshmanan, R., Sanchez-Dominguez, M., et al. Removal of total organic carbon from sewage wastewater using poly(ethylenimine)- functionalized magnetic nanoparticles. Langmuir, 2014; 30: 1036–1044.

19. Lerner, M.I., Glazkova, E.A., et al. Synthesis of Al nanoparticles and Al/AlN composite nanoparticles by electrical explosion of aluminum wires in argon and nitrogen. Powder Technol, 2016; 295: 307–314.

20. Niraj V Patel, Sunil J Patel, Yatin M Chaudhary, Ankit M Patel, Vahan J Prajapati and Dr. Dhrubo Jyoti Sen; Correlation between sp2 hybridization and bloom strength of carbon nano tubes: International Journal of Advance Pharmaceutical and Biological Sciences, 2012; 2(1): 49-55.

21. Natarajan, S., Harini, K., et al. Multifunctional magnetic iron oxide nanoparticles: diverse synthetic approaches, surface modifications, cytotoxicity towards biomedical and industrial applications. BMC Mater, 2019; 11(1): 1–22.

22. Prajapati P M., Sen D J.; Nanotechnology: A new technique in water purification: International Journal of Innovative Ideas & Research And Development, 2013; 1(1): 28-32.

23. Österle, W., Orts-Gil, G., et al. Impact of high energy ball milling on the nanostructure of magnetite-graphite and magnetite-graphite-molybdenum disulphide blends. Mater. Charact, 2013; 86: 28–38.

24. Dhrubo Jyoti Sen, Avani H. Sheth and Naman B. Doshi; *Carbon nano tubes and Its application in pharmacy*: International Journal of Pharmaceutical Sciences, 2009; 1(1): 71-82.

25. Rajput, S., Singh, L.P., et al. Lead (Pb2+) and copper (Cu2+) remediation from water using superparamagnetic maghemite (γ -Fe2O3) nanoparticles synthesized by Flame Spray Pyrolysis (FSP). J. Colloid Interface Sci., 2017; 492: 176–190.

26. Sahu, U.K., Sahu, S., et al. Synthesis and characterization of magnetic bio-adsorbent developed from Aegle marmelos leaves for removal of As(V) from aqueous solutions. Environ. Sci. Pollut. Res., 2018; 26: 946–958.

27. Parimal M Prajapati, Yatri Shah and D J Sen; Gold nanoparticles: A new approach for cancer detection: Journal of Chemical and Pharmaceutical Research, 2010; 2(1): 30-37.

28. Vicente-Martínez, Y., Caravaca, M., Soto-Meca, A. Total removal of Hg (II) from wastewater using magnetic nanoparticles coated with nanometric Ag and functionalized with sodium 2-mercaptoethane sulfonate. Environ. Chem. Lett., 2020; 18: 975–981.

29. Dr. Dhrubo Jyoti Sen*, Dr. Dhananjoy Saha, Arpita Biswas, Supradip Mandal, Kushal Nandi, Arunava

Chandra Chandra, Amrita Chakraborty and Dr. Sampa Dhabal; Interface of extramural research in nano level complies with advanced pharmaceutical science and basic science in the umbrella of nanoscience: World Journal of Pharmaceutical and Medical Research, 2021; 7(4): 393-409.

30. Wang, W., Chen, D., et al. Monte Carlo study of magnetic and thermodynamic properties of a ferrimagnetic ising nanoparticle with hexagonal core–shell structure. J. Phys. Chem. Solids, 2017a; 108: 39–51.

31. Xu, J., Luu, L., Tang, Y. Phosphate removal using aluminum-doped magnetic nanoparticles. Desalin. Water Treat., 2017; 58: 239–248.

32. Dr. Sampa Dhabal, Dr. Dhananjoy Saha and Dr. Dhrubo Jyoti Sen; Annealing stability of cristobalite nano crystal in Bravais crystal lattice and biochemical health hazards of silica: European Journal of Pharmaceutical and Medical Research, 2020; 7(10): 742-748.

33. Yang, H., Zhang, J., et al. Rapid removal of anionic dye from water by poly(ionic liquid)-modified magnetic nanoparticles. J. Mol. Liq, 2019; 284: 383–392.

34. Dr. Sampa Dhabal, Dr. Dhrubo Jyoti Sen & Dr. Dhananjoy Saha: Inner eye of nanoscience focusses the outreach of milestone: Lambert Academic Publishing GmbH & Co. KG, Germany, 2021; 1-77.

35. Zhu, N., Zhang, B., Yu, Q. Genetic engineering-facilitated coassembly of synthetic bacterial cells and magnetic nanoparticles for efficient heavy metal removal. ACS Appl. Mater. Interfaces, 2020; 12: 22948–22957.

36. Prof Dr Dhrubo Jyoti Sen, Maulik K. Prajapati and Parimal M. Prajapati; *Footsteps of nanotechnology by quantum dots with cornell dots in biological tagging, imaging and optical computing*: International Journal of Drug Development and Research, 2010; 2(1): 164-170.