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Chapter 6

Application of Magnetic Surfactants in Nanoparticle Fabrication

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Magnetic nanoparticles (MNPs) are a group of nanoparticles made from a magnetic material such as iron, chromium, manganese, cobalt or nickel and a chemical component that exhibit superparamagnetic properties. They have a wide range of applications in medicine, wastewater treatment and bioremediation, food industries, and molecular biology, among others, due to their size effects, surface-to-volume ratio, interaction, magnetic separation, specificity, and surface chemistry. However, the incorporation of amphiphilic surface active agents called surfactants into MNPs to serve as capping, structure-directing, ion-exchange, oxidation, and reduction agents is known to affect MNPs physicochemical properties including size, shape, dispersability, stability, surface charge, biocompatibility, optical properties, thermal properties, selectivity, cellular uptake, magnetic energy, functionality, and applicability. Thereby increasing their applications in drug delivery, cancer therapy, biosensors, diagnostic testing, bioimaging, water treatment, enhanced oil recovery, catalysis, energy storage, and information storage. This chapter addresses the mechanisms of synthesis of Magnetic Surfactant Nanoparticles (MSNPs), the roles of surfactants in MNPs fabrication, the influence of surfactants on the properties of MNPs, comparative performances and applications of MSNPs, cost analysis and future prospects, and likely challenges.

Introduction

Magnetic nanoparticles (MNPs) are a group of nanomaterials that consist of magnetic materials such as α-Fe_2O_3 (hematite), γ-Fe_2O_3 (maghemite), Fe_3O_4 (magnetite), hexagonal ($MFe_{12}O_{19}$), garnet ($M_3Fe_5O_{12}$) and spinel (MFe_2O_4), where M represents one or more bivalent transition metals (Mn, Fe, Co, Ni, Ba, Sr, Cu, and Zn), or in combination with components such as polylactic

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acid (PLA), doxorubicin hydrophobic (DOX-HCL), paclitaxel (PTX), EPPT-FITC, oleic acid, tannin, 3-Aminopropyltriethoxysilane (APTES), multi-wall carbon nanotubes (CNTs), polyethylenimine (PEI) and polyarabic acid (*1*) that has specific functionality. This group of nanoparticles can be manipulated using magnetic fields. The possibility of clustering forms the basis for their further assemblage as magnetic nanochains (*2*). MNPs have been the focus of several recent studies due to their attractive properties and potential applications in different fields (*3–8*). Some specific applications include magnetic imaging (*9*, *10*), information storage (*11*), pollution remediation (*12*), nanofluids (*13*), optical filters (*14*), defect sensors (*15*), magnetic cooling (*16*, *17*), and cation sensors (*18*). Their functionality greatly depends on the route of synthesis and structure. The materials mostly range from 1 to 100 nm in size and may exhibit superparamagnetic properties (*19*).

Magnetic surfactants (MS) are surfactants with distinct properties and magneto-reactive characteristics. The possibility of self-assemblage using the magnetic field makes them suitable for several environmental applications, such as targeted delivery, catalysis, material separation, oil cleaning, and water purification (*20*). Magnetic surfactants have been applied in the physical, material, and biomedical sciences. By integrating a paramagnetic component in the cationic or anionic structure of surfactant, MS develops a strong magnetic response and improved hydrophobicity (*21*). Brown et al. (*22*) pioneered the methodology of synthesis for a magneto-active metal ion binding with a surfactant's cationic head. Subsequently, a few studies have described further synthesis and procedures for the preparation of magnetic surfactants in different applications (*21*, *23–25*). The early group of these surfactants was made mainly by blending metal trihalides with appropriate cationic surfactants. These surfactants showed a lower surface tension relative to their non-magnetic counterparts in the presence of an applied magnetic field. They gained attention since they can be manipulated by applying a magnetic field, and the aqueous solutions of such surfactants are paramagnetic. Magnetic surfactants are characterized by the regular properties of conventional surfactants coupled with the presence of a magnetic moiety, which could be from a high-spin transition metal or from lanthanide cations (*26*). MS can be anionic, cationic, non-ionic, or zwitterionic in nature. The Gemini magnetic surfactants have also been reported in the literature (*27*). Magnetic surfactants have been reported earlier; however, their magnetic properties remained under-investigated until very recently (*22*, *23*, *28*), with a lower surface tension corresponding to cmc (γcmc) over non-magnetic counters parts. Materials in combination with magnetic surfactants could have a range of applications, such as catalysis, water treatment, biotechnology, drug delivery, and several oilfield applications (*20*).

By careful design, magnetic surfactants could self-assemble to generate various magnetic aggregates, biomaterials, and nanomaterials with different applications. In this work, we reviewed the methods of synthesis of magnetic surfactant nanoparticles, roles of surfactants in magnetic nanoparticles fabrication and, influence of surfactants on the properties of nanoparticles. It also covers the comparative performance and application of magnetic surfactants nanoparticles, cost analysis of this unique class of surfactants in nanoparticles and future prospects.

Methods of Synthesis of Magnetic Surfactant Nanoparticles

The fabrication of MSNPs involves several mechanisms and techniques. However, the desired properties and applications of nanoparticles determine the choice of technique to be used. The various methods used in MSNPs synthesis include co-precipitation, thermal decomposition,

microemulsion, hydrothermal, and sol-gel, among others. Table 1 outlines the mechanisms of MSNPs fabrication, and the surfactants used.

Co-precipitation

This involves the use of materials and approaches with less harmful characteristics. It is the most common mechanism of MNPs production, especially in biomedical applications, and helps to control the size and magnetic properties of nanoparticles. This method is very convenient and facile, and it can produce nanocrystals in large quantities (*29*).

Co-precipitation is achieved by mixing ferric ion and ferrous ion in a molar ratio of 1:2 in a highly basic solution at a high or ambient temperature. The size, morphology, and composition of the iron oxide nanoparticles are influenced by the ferric and ferrous ions ratio, type of salt used (e.g., chlorides, nitrates, perchlorates, or sulfates), pH, reaction temperature, ionic strength of the medium, and other reaction parameters such as stirring rate and basic solution dropping speed (*30*, *31*). Morales et al. (*32*) have described a one-step co-precipitation synthesis of MNPs with a magnetite core, surrounded by a maghemite layer, and a casein surfactant layer on top. The casein surfactant acts as protecting and stabilizing agents for particle size control and colloidal dispersion, respectively.

Thermal Decomposition

This process is usually carried out by the decomposition of organo-metallic precursor compounds and surfactants in organic and water solvents at high boiling points (150 - 300°C). Thermal decomposition can be used to produce monodispersed magnetite nanoparticles without aggregation of the particles (*30*). As a result of the nucleation process, different types of MNPs with controlled size, crystallinity, and well-defined shapes can be synthesized. The stabilizing surfactants used in this method include oleic acid, hexadecylamine, and fatty acids. These surfactants slow down nanoparticle nucleation, which influences the MNPs growth and helps in producing a spherical shape and super-paramagnetic nanoparticles of less than 30nm in size (*29*). This method has been reported in the synthesis of Magnesium Iron-Oxide @ Tetramethyl Ammonium Oxide nanoparticles (MgIONPs@TMAH) by (*33–35*). In general, the thermal decomposition method is known to be the best method of synthesizing MNPs of desirable size and morphological control on a large- scale, as it permits high quality, the control of particle size, strong magnetic properties, and a high yield (*30*, *36*). However, the production of toxic organic soluble solvents has been identified as the risk associated with this method and limits its application, especially in the biomedical field (*37*).

Microemulsion

Microemulsions are thermodynamically stable and isotopic colloidal suspensions in which two immiscible hydrophilic (water) and lipophilic (oil) liquids coexist in a single phase in the presence of surfactants. In this method, oil is mixed with a surfactant, and water is magnetically stirred at ambient temperature. The properties of the nanoparticles formed depend on the type and structure of the surfactant, as this lowers the interfacial tension between water and oil. Zhang et al. (*38*) and Okolie et al. (*39*) have reported the use of microemulsion to prepare MNPs for different applications. The uniqueness of this method is due to its distinctive properties such as thermodynamic stability, large interface area, low interfacial tension, and ability to solubilize different immiscible liquids (*40*),

but MNPS prepared by this method are usually of low quality and dispersed uniformly due to poor magnetic presence and the attendant low magnetic properties (*30*, *41*).

Hydrothermal

This is one of the most common techniques for preparing nanoparticles, and it is a solution-based synthesis during which MNPs are produced through hydrolysis and oxidation reactions under high pressure (0.3–4 MPa) and high temperature (130 – 300°C) in an enclosed system (*42*). This method is also referred to as Solvothermal. However, hydrothermal employs an aqueous solution, while solvothermal is carried out in a non-aqueous solution (*31*). This method synthesizes single-crystal nanoparticles by relying on the solubility of the solution in the traditional crystal-making synthesis. In a report by Hou et al. (*43*), superparamagnetic MNPs were synthesized using this approach in the presence of ethylene glycol, oleic acid, and trioctylphosphine oxide. Similarly, magnetite nanoparticles with high crystallinity and uniform morphology were synthesized via hydrothermal methods at different temperatures of 120°C, 140°C and 160°C, with Polyethylene Glycol (PEG) as stabilizer. A method described as simple, economical and scalable (*44*). Overall, this method is known to produce nanoparticles of desirable size, shape, high crystallinity, and consistent composition. However, these advantages are known to be influenced by the mixing of solvent, time, solubility, pressure and temperature (*29*, *45*).

Sol-Gel Synthesis

This is one of the most explored and commonly used techniques of nanoparticle synthesis. The method involves gel formation at ambient temperatures by hydrolysis and condensation reactions of alkoxides of metals. To form sol, metal salts dissolved in water or any other solvent are homogenously dispersed to give a colloidal solution (*46*). During stirring and the rise in temperature, the molecular interaction and Van der Waals forces between the particles increase. Heating the mixture results in the removal of the solvent, the drying of the solution, and the final formation of gel (*47*). Iron oxide and silica-coated MNPs with controlled size and defined shapes, good crystallinity, and turnability can be produced through this method in large quantities. Sol-gel synthesis is cheaper, as it does not require any equipment and can be carried out at room temperature, but it requires a prolonged reaction time and employs toxic organic solvents (*29*).

Ball or Mechanical Milling

This is a simple, convenient, and organized method of synthesizing MNPs by mechanical grinding of coarse-textured bulk materials into fine-textured particles. It is a top-down method of MNPs synthesis (*29*, *48*). Mechanical milling can be achieved using a shaker mill or a planetary mill. The bulk material is enclosed in a hollow jar with steel balls as a grinding medium. Kinetic energy is applied by the balls to the bulk materials, and continuous collision between them results in the formation of fine-textured, nano-sized powder. The production of MNPs through this method is affected by the ball: powder ratio, milling time, milling speed, and ball size, among others.

Polyol

The polyol method involves the use of propylene glycol, polyethylene glycol, and other polyols as alternatives to surfactants in the synthesis of nanoparticles to control particle growth, maintain high crystallinity, and prevent interparticle accumulation (*49*). This method helps to address changes

in nanoparticle surface charge and shape that usually characterize the use of surfactants in the sol-gel method. In this method, metals are directly obtained as small metallic particles by metallic salt reduction and the subsequent precipitation of the metal. It is an efficient method for synthesizing nanocrystalline alloys and bimetallic clusters (*50*).

There have also been reports of the fabrication of surfactant MNPs using a combination of two methods. For example, microwave-assisted hydrothermal synthesis of iron oxides (*51*) and microwave-assisted polyol synthesis (*52*).

Table 1. Examples of Methods of Magnetic Surfactant Nanoparticles Fabrication

Method of synthesis	*Surfactant*	*Nanoparticle*	*References*
Co-precipitation	Casein, SDS, CTAB, PEG, Tween20	Cobalt ferrite, Magnetite	(*32*, *53*, *54*)
Thermal decomposition	Oleic acid, Sodium oleate, dioctyl ether	Magnetite, maghemite	(*55*, *56*)
Microemulsion	Trito x-100, Igepal CO-520, Brij-97, CTAB, Butanol	Magnetite, maghemite	(*57*, *58*)
Hydrothermal	PEG, CTAB, Triton-x-100, SDS	Hematite, Magnetite	(*44*, *59*)
Sol-Gel	EDTA	Zinc ferrite	(*60*)
Polyol method	Ethylene glycol, oleic acid, oleylamine	Magnetite	(*61*, *62*)
Mechanical/Ball milling	Dextran, Oleic acid, oleyl amine	Magnetite	(*63*, *64*)
Microwave-assisted	PEG, β-cyclodextrin	Magnetite, maghemite	(*65*)

Roles of Surfactants in Magnetic Nanoparticles Fabrications

The role of surfactants in MNPs fabrication is influenced by the mechanism of synthesis and the specific reaction environment under which the synthesis takes place. However, six major categories of roles for surfactants have been identified and associated with the use of surfactants in MNPs fabrication. Figure 1 shows the scheme of the roles of surfactants in the synthesis of MNPs. A summary of the roles of surfactants in magnetic nanoparticle fabrication with examples is given in Table 2.

Dispersing Agents

Surfactants prevent the agglomeration and aggregation of nanoparticles in reaction solutions by dispersing the metal particles. Ionic surfactants bring about dispersion by electrostatic repulsion, while polymeric surfactants create a stearic hindrance effect. The electrostatic repulsion and steric hindrance effects on the surface of nanomaterials, in combination with van der Waals force, infer with the large surface area and high surface energy of nanoparticles cause them to disperse stably (*66*, *67*).

Structure/Shape Directing Agents

At a certain concentration in solution, surfactant molecules assemble into aggregates, and as a result of the existence of both hydrophilic and oleophilic groups in surfactants, the aggregates form

different shapes called micelles in reaction solution. This stimulates the metal atoms in nanoparticles to grow anisotrophically into nanocrystals of defined size and shape, such as nanowires, nanocubes, nanospheres, nanosheets, and nanonets (*68*, *69*).

Figure 1. Scheme of the roles of surfactants in the synthesis of magnetic nanoparticles. Reproduced with permission from reference (*66*)*. Copyright 2021 Royal Society of Chemistry.*

Capping Agents

During the formation of nanoparticles crystal seeds, surfactants in solution assemble on the surface of the crystal seeds through one or more of covalent bonding, electrostatic interaction, adsorption, and van der Waal force. Capping agents act as stabilizers, inhibit the overgrowth of nanoparticles, and prevent their aggregation in colloids (*70*, *71*).

Reducing Agents

Some surfactants have reductive groups, which promote their reductive ability in the reaction system. At a high reduction rate, metal atoms always take the shape that is favored by thermodynamics, but when the reductive capacity is low, the crystal seeds can turn into a variety of dynamically controlled nanostructures (*72*, *73*).

Oxidation Etching Agents

Thermodynamically, concave structures are usually unstable, and their Gibbs free energy is less than that of convex and plane regions. Surfactants as oxidation etching agents are beneficial to concave structure and defects, as the formation of concave structure depends on these agents (*74*, *75*). Oxidation etching pairs are formed when oxygen combines with some additives in the nanoparticles fabrication system, and these can selectively etch metastable and unstable atoms to form precise concave structures (*66*).

Ion-Exchange Agents

During nanopartile synthesis, exchange of dissociated ions from surfactants with metal precursors as ligands to form new complex takes place. The new complex will have a different redox potential, and this affects the reduction kinetics and reduction order of different metal atoms, leading to the transition from the alloy structure to the core-shell structure and finally to the heterostructure (*66*).

Table 2. Summary of Roles of Surfactants in Magnetic Nanoparticles Fabrication

Role	*Surfactant*	*Reference*
Dispersant	Polyvinylpyrrolidone (PVP)	(*75*, *76*)
Structure directing	Hexadecyl dimethyl benzyl ammonium chloride (HBDAC)	(*77*, *78*)
	Docosyl trimethyl ammonium chloride (C_{22}TAC)	(*79*)
	Dodecyl trimethyl ammonium bromide (DTAB)	(*80*, *81*)
	Cetyl trimethyl ammonium chloride (CTAC)	(*82*–*84*)
Capping agent	Polyvinylpyrrolidone (PVP)	(*85*, *86*)
Oxidation etching	Cetyl trimethyl ammonium bromide (CTAB)	(*87*–*89*)
	Cetyl trimethyl ammonium chloride (CTAC)	(*90*–*92*)
Stabilizer	Sodium dodecyl sulfate (SDS)	(*93*)
Reducing agent	Polyvinylpyrrolidone (PVP)	(*94*, *95*)

Influence of Surfactants on the Properties of Magnetic Nanoparticles

Generally, surfactants act as capping agents, structure-directing agents, dispersing agents, weak reducing agents, oxidation-etching agents, and ion exchangers in the fabrication of nanoparticles. As a result of these, they influence the physicochemical properties of MNPs such as particle size, shape, surface area, composition, surface charge, stability, dispersibility, optical properties, thermal properties, magnetic energy, biocompatibility, toxicity, cellular uptake, functionality, and applicability (*66*).

The selectivity of surfactants in the synthesis of magnetic surfaces is vital because it plays a key role in vital properties such as magnetic moment, particle size, and shape and also influences agglomeration, which dictates their respective performance on application (*53*). For instance, Sangsuriyonk et al. (*53*) studied the influence of the cationic surfactant (sodium dodecyl sulfate-SDS), anionic (hexadecyltrimethylammoniumbromide-CTAB) and anionic Tween20, respectively, on the synthesis of $Co_xFe_{1-x}Fe_2O_4$. The report shows SDS as the most efficient surfactant due to its impact on particle size reduction (16±3 nm) and superparamagnetic behavior of 100.41 emu/g, apart from the narrow size distribution, which positively influences the stability of the metal ion. The report is similar to the crystallite size reduction (10.6 to 5.8 nm) studied by Pathak et al. (*96*) due to the influence of oleic acid and sodium oleate surfactants used. This could be through the interactive mechanism of the polar head of SO_4^{2-} with the metal ion during micelle formation, consequently improving its crystallinity (*97*, *98*).

Similarly, Song et al. (*66*) added that the choice of surfactants can control the morphology of nanoparticles. The study justified that surfactants characterized by longer chains considerably increase the ordered orientation in the formation of micelles or reverse micelles, which stabilize the metal ion and impede possible agglomeration of the particles (*99*). Furthermore, Hussain et al. (*100*) investigated the effect of the hydrophobic tails of the surfactant on the heat and interfacial properties. Although the report shows no significant effect concerning the varieties of the hydrophobic tail, all surfactants improve the wettability of the system, resulting in lower surface tension (*101*). Also, Atta et al. (*102*) added that the use of the surfactant enhances effective dispersity apart from reducing the size of the particle to 12.5 nm. Haracz et al. (*103*) observed that the effective surface binding of the surfactant to nanoparticles influences the magnetic properties of Fe_2O_3 and imparts appreciable interparticle spacing and orientation, such as susceptibility, barrier energy, and effectiveness. The studies on these surfactants also indicate their ability to act as a capping agent, which influences the resulting morphology and equally provides the colloidal stability needed to resist the process of agglomeration of particles and undesirable growth (*104*). Although the magnetic and structural properties of Fe_3O_4 were unaltered when cetylpyridinium surfactant was used, the use of the solvent greatly initiated efficient dispersion of the MNPs (*105*). This report also agrees with the efficient dispersion and controlled grain size of 12.5 nm of Fe_3O_4 nanoparticles studied by Atta et al. (*102*).

Klekotka et al. (*106*) pointed out that the influence of surfactant in the synthesis of iron oxide nanoparticles greatly influences the separation process, along with the shape, size, and magnetic properties under an external field. From the study, it was observed that the growth pattern of the nanoparticles is in tandem with the type and class of solvent used. The report indicated that the amine-based surfactant facilitated even flower-like growth in the shape of the particles compared to the fatty acid-based surfactants. In addition, studies show that a high ratio of surfactant to precursor enhances the synthesis of a large number of nanocrystals with an effect of controlled growth as a result of the binding activity of the surfactant to the grain surface (*107*, *108*). Also, a shorter chain positively influences the spontaneous growth of the grain, but it gives bigger particle sizes in contrast with long-chain compounds, which favor small particle sizes but at a slower growth rate (*109*). Cetyl TrimethylAmmonium Bromide (CTAB) surfactant has also been identified with exceptional features of improving the yields of the nanoparticles with attendant milder magnetic features when compared to other classes of solvents studied by Filippousi et al. (*110*) due to more prominent oxidation. Nevertheless, the magnetization and coercivity were found to attenuate at room temperature due to finite-size effects for all iron oxide batches, indicating a superparamagnetic nature of the nanoparticles, a prerequisite in most biomedical applications.

Comparative Performances and Applications of Magnetic Surfactants Nanoparticles

As a result of the value-added properties of magnetic surfactants in nanoparticles, such as reversibility due to the presence of magnetic forces and non-invasive external control, there are improvements in their applications in various areas of human endeavor when compared with ordinary MNPs only.

The effective use of nanoparticles in the treatment of water and wastewater to remove pollutants has been reported to be hindered by poor dispersion and distribution and difficulty in recovering the nanoparticles. However, modification of nanoparticles with magnetic surfactants has been demonstrated to address the challenges. Jafaryan et al. (*111*) reported the application of magnetic surfactant functionalized graphene in the removal of 70% cadmium ion from water at optimum

conditions via adsorption. The pH-dependent electrostatic interactions between graphene and magnetic surfactants allow the reversible separation of the adsorbed metal (desorption) from the magnetic surfactants. Hence, the magnetic surfactant could be reused multiple times as long as its properties remain intact. The recyclability of the surfactant and the metal, as well as their high adsorption potential, have made the use of magnetic surfactant nanoparticles a welcome approach in water treatment and decontamination. Guo et al. (*105*) have demonstrated the removal of antimony from water. This was necessitated by the need for the recovery and reuse of the pollutants, which has led to the use of magnetic nanoparticles (e.g., Fe_3O_4 MNPs) coated with surfactants as a better alternative as it increases the electrostatic attraction and surface bonding of the nanoparticles, resulting in efficient adsorption and removal of the pollutants, easy separation from the nanoparticle absorbent, and their regeneration and reuse.

Magnetic surfactants have also been demonstrated to remove pathogens from water. de la Fuente-Nunez et al. (*112*) demonstrated that a magnetic surfactant, dodecyl trimethylammonium bromotrichloroferrate (DTAF) and its polymeric analog, poly(diallydimethylammoniumtetra-chloroferrate (poly-DADMAF) showed antimicrobial ability and killed plantonic *Pseudomonas aeruginosa* PA14 cultures compared to the non-magnetic parent, even at concentrations as low as 0.5mM and 0.03mM, respectively. Apart from removing bacteria from water and wastewater, the magnetic surfactants are also known to be non-toxic.

Biotechnologically, surfactant magnetic nanoparticles can be used in DNA compaction, during which repulsion between adjacent phosphate groups of DNA molecules is reduced and the DNA chains are compacted. The process takes place due to the sufficient binding of cationic surfactants to the backbone of the DNA molecules. The stronger tendency of magnetic surfactants to interact with non-polar groups compared to non-magnetic surfactants makes this possible (*20*). Brown et al. (*22*) demonstrated that magnetic surfactants synthesized on Ho, Fe, and Gd anions and a dodecyl trimethylammonium cation produced higher DNA compaction and maintained DNA helix structure compared to the non-magnetic surfactants. The magnetic surfactants were shown to control stability and DNA migration by effectively controlling the migration of myoglobin and green fluorescent protein (GFP) by binding.

A dual, light- and magnetic-field-responsive cationic surfactant, 4-ethoxy-4-(trimethylamino-ethoxyl) azobenze trichloromonobromoferate (azoTAFe) synthesized by Xu et al. (*113*), has been reported to capture and release DNA molecules, thereby promoting DNA compaction and transport under the control of a magnetic field and decompaction of DNA under the influence of UV light. The potential application of this in nanomedicine is gene therapy, especially in cancer treatment, for the effective delivery of functional DNA fragments to target cells. The dual responsiveness of the magnetic surfactants can promote drug delivery to a target site by the incorporation into surfactant magnetic nanoparticles at lower concentrations to prevent or lower cytotoxicity (*114*).

In a similar work by Wang et al. (*115*), DNA-based magnetic fullerene (C60@CTAF/DNA complex) prepared by hydrophobic interaction of fullerene with magnetic CTAF for anticancer drug delivery was reported to exhibit dual responsiveness (Glutathione (GSH) and magnetic responsiveness) due to the presence of fullerene, and site-specific drug delivery was enhanced by breakage of the disulfide bond of hyaluronic acid by the release of GSH within the cancer cell due to reduction responsiveness. The nano-vehicle had increased magnetic susceptibility compared to non-surfactant magnetic nanoparticles, and its application for target delivery of Doxorubicin (DOX) in HepG2 cancer cells was successful.

Beyond DNA compaction and drug delivery, modification of magnetic nanoparticles such as Gold nanoparticles with cationic surfactants has also resulted in nanoparticles with enhanced ability to bind with biomacromolecules (DNA and proteins) due to the strong electrostatic forces, leading to effective delivery of genes and proteins (*116–119*).

Surfactants are currently being used in the synthesis of nanoparticles as porogens due to their self-assembly, stable dispersion, and compartmentalization. However, magnetic surfactants as structure-regulatory agents provide external control over the aggregate size, surface tension, and contact angle (*20*, *120*).

A magnetic surfactant, CTAF synthesized from CTAB and $FeCl_3$ by Kim et al. (*121*) was reported to act as a structure-directing agent and source of magnetic responsiveness (magnetism), which was used to design hexagonally ordered magnetic mesoporous materials that show low to high spin transition, especially with the increase in transition temperature that decreases with iron contents. Herman et al. (*122*) have also demonstrated the use of cationic magnetic surfactants, $MnC_{16}DOTA$ (based on 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid), as structure-directing agents for the formation of porous silica nanoparticles with 12-fold rotational symmetry.

The application of $GS^{2+}.2FeCl_4$, MGSFe (Magnetic Gemini surfactant), a paramagnetic catalyst for increased bezoin condensation and synthesis of substituted pyrroles with high turnover time and turnover frequency, especially its reusability without loss of activity in a four-cycle run of pyrrole synthesis, has been demonstrated (*27*).

There are several applications of surfactants in the petroleum industry due to their numerous properties, especially their hydrophobicity and hydrophilicity. Therefore, the introduction of magnetic fields into surfactants has been reported and also proposed to increase their properties and applications (*20*). Surfactant magnetic nanoparticles have found application in the petroleum industry in Enhanced Oil Recovery (EOR) due to their small size and stability for long term under high temperature and high salinity conditions that characterize oil reservoirs. Generally, the major limitations to the application of surfactant magnetic nanoparticles in Enhanced Oil Recovery (EOR) are the high temperature and high salinity that characterize oil reservoirs. Inspite of that, successes have been recorded. Sulfonate surfactants such as internal olefin sulfonate with twin-tailed, higher oil solubilization activity, and higher stability at high temperatures of up to 150°C have been identified. Anionic sulfonate surfactants are better preferred in magnetic nanoparticle fabrication over nonionic surfactants as they have good water solubility and stability at high temperatures. The latter, though generally water-soluble, has a low critical micelle concentration (CMC), high salinity tolerance, and good solubility but cannot tolerate high temperatures. To overcome the challenges of high temperature and high salinity, which often limit the applications of surfactant magnetic nanoparticles in EOR, mixing different surfactants with complementary synergistic properties has been demonstrated by Nourafkan et al. (*123*) in which an iron nanoparticle was synthesized and stabilized by a mixture of anionic surfactant with high temperature tolerance and nonionic surfactant with high salinity resistance that is more suitable for application in EOR due to its combined stability and other rheological properties. Hussain et al. (*100*) have also reported the synthesis and evaluation of high-temperature-tolerant magnetic surfactants for application in oilfields.

Cost Analysis and Future Prospects

Not only has the use of surfactants in magnetic nanoparticle fabrication given birth to new techniques, tools, devices, and applications, It has been reported to have led to the development

of new, highly stable, highly selective, non-toxic products and services using simpler, economical operations with easy applications and low costs (*124*, *125*). However, despite the few successes that have been recorded with the roles of surfactants in magnetic nanoparticle fabrication, it can be said that the future looks brighter, as the exploration of magnetic surfactants is still in its infancy and has been recognized as an emerging research area (*20*).

The potential applications of magnetic surfactants in protein separation from biomolecules have been proposed for further application in the food industry, drug development, and the study of disease mechanisms (*126*). It has also been recognized in the field of microsystems. Qureshi et al. (*127*) and Tufani et al. (*128*) have also anticipated the future application of magnetic surfactants in nanomedicines, nanodiagnostics, and biological imaging towards the development of ultra-sensitive and high-throughput technology for quick diagnostics and sensing. The use of magnetic surfactants could facilitate the attachment of multiple functional groups to quantum dots to confer multiple detection abilities on quantum dots, with improved enrichment of scarce targets, sensitivity, binding affinity, and target delivery. This has also been proposed for possible use in cancer diagnosis and cell labeling through quantum dot conjugation (*129*, *130*).

Conclusion

This chapter focused on application of magnetic surfactants in nanoparticle application with emphasis on the methods of synthesis of MSNPs, the roles of surfactants on the properties of magnetic nanoparticles, the influence of surfactants on the properties, functionality, and applications of magnetic nanoparticles, the comparative performances of magnetic surfactant nanoparticles, cost analysis, and the future prospects of magnetic surfactant nanoparticles. MSNPs contain surfactants and a magnetically active metal moiety. The surfactant may either be cationic, anionic, zwiterionic, or non-ionic, depending on the ionic head group's charge. They can be synthesized through complexation reactions, liquid-liquid ion-exchange reactions, and proton abstraction. Surfactant influences the magnetic movement, particle size, shape agglomeration, and application of nanoparticles. As a result, MSNPs are currently used in water treatment and metal recovery, DNA compaction, drug delivery, catalysis, molecular templates, enhanced oil recovery, and deemulsification of crude oil, among others, with better results compared to parent surfactant or nanoparticle alone.

It is believed that MSNP is an emerging research area that is giving rise to new, economically viable techniques, tools, devices, products, and services that are cost-effective and simpler to operate. Future applications have also been proposed in the food industry, drug development, biological imaging, cancer diagnostics, and quick sensing. However, as further research work is being done into the synthesis and application of MSNPs in various areas of human endeavor, there is a need to assess the likelihood of the toxicity and long-term effects of these materials. This is because environmental exposure to nanomaterials is expected as society adopts nanotechnology as part of our daily lives, and as a result, nanotoxicity research is gaining attention. Safety considerations are crucial when thinking about MNPs fabrications and applications, and so the same should be the case with MSNPs. It was thought that nanoparticles had less impact on living things because of their small size, and adverse consequences were not found until more recent times. It is crucial to create methodologies that are specific to the risk evaluation of magnetic surfactant nanoparticles and consider any potential negative effects of MNPs and MSNPs.

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