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SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED MAGNETITE CORE-SHELL NANO-COMPOSITES

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ABSTRACT

Magnetic polymer nano-composites recently received growing attention due to the fact that such composite particles offer potential advantages in wide applications. The present study describes a method for the preparation of three different types of magnetic core-shell nano-composites (diameter is 50-100 nm) of magnetite polyvinylbenzyl chloride, n magnetite polyvinyl aniline and bi-layered polymer magnetite with (-Cl, NH₂ ad -OH) functional groups respectively. The first two types of magnetic core-shell nano-composites have hydrophobic properties, preparation is based on several steps: precipitation of the magnetic iron oxide by a coprecipitation process leading to particles with superparamagnetic properties (diameter is 10–20 nm), coating the magnetite with oleic acid as stabilizing agent and finally the encapsulation of magnetite into the first hydrophobic polymer shell by miniemulsion polymerization. The third type of magnetic core-shell nano-composites with hydrophilic properties is prepared by the costing of magnetite polyvinylbenzyl chloride with a hydrophilic layer of polyethylene glycol (PEG) by condensation polymerization. Vinylbenzyl chloride and vinyl aniline were chosen as hydrophobic monomers because they offer the possibility to anchor additional functional groups for active site attachment and protect magnetite against chemical attack. For the miniemulsion polymerization the influence of the amount of water, the mixing intensity and the surfactant concentration were studied with respect to the formation of particles which can further be used for chemical engineering applications and for binding enzymes on the functionalized surface sites. The resulting magnetic polymer nano-composites were characterized by particle size measurement (Malvern Zeta sizer), chemical stability (acid treatment with hydrochloric acid), iron content (elemental analysis by wet chemistry) and morphology (transmission electron microscopy (TEM), function groups (infrared spectrometer (IR) and proton NMR spectroscopy (H-NMR). Finally Auger electron microscopy (AES) was used to measure elemental profiles across the composite particle diameter.

Keywords

Functionalized Magnetite, core-shell nano-composites, polymerization

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1. Introduction

An interesting magnetic nanoparticle composite system is that which consists of a core/shell structure. The magnetic core is coated with a layer of a nonmagnetic material (polymer). So the obtained structure offers a combination of properties that neither individual material possesses. Magnetic nano-composite particles offer potential advantages in many applications. Because the composite particles have not only polymer functional groups but also magnetic characteristics, which are desired for various targeting and retrieval applications, both medical and environmental applications become possible [1-9].

The common route for synthesizing magnetic polymer particles is monomer polymerization by dispersing magnetite particles directly in the liquid phase of a polymerizable formulation and polymerizing of the monomer in the presence of the magnetite particles to form magnetic polymer particles. Several processes have been developed including emulsion polymerization [10] and miniemulsion polymerization [11].

An economic and simple way for the preparation of the magnetic core particles (Fe_3O_4) is the co-precipitation process, where iron oxides precipitate in the presence of an alkali medium (NH_4OH).

Potential advantages of the miniemulsion process include the ability to control the size of the magnetic nano-composites via formulation, directly dispersing the hydrophobic inorganic particles in the monomer phase, the ability to nucleate all the droplets containing inorganic particles, and faster polymerization [12–15].

Magnetic nano-composites particles are prepared by the miniemulsion process, which is obtained by shearing a mixture of two immiscible liquid phases, one surfactant and one co-surfactant or costabilizer (typical example is hexadecane) is used to stabilize every small monomer droplets. The shearing proceeds usually via ultrasonication of the mixture. Stable droplets are then obtained, which have typically a diameter between 50 and 200 nm.

The monomer, which is insoluble in the continuous phase of water, is miniemulsified in order to form stable and small droplets with a small amount of surfactant. This type of polymerization is classified as radical polymerization of hydrophobic monomers. Potassium peroxydisulfate (KPS) is used as a water soluble initiator.

In this study three different types of magnetic core-shell nano-composites consisting of magnetite polyvinylbenzyl chloride, magnetite polyvinyl aniline and bi-layered polymer magnetite with (-Cl, NH_2 and -OH) functional groups were prepared, respectively. The resulting magnetite core-shell nano-composites were characterized by particle size measurement, iron content, TEM, IR, HNMR, AES and finally acid treatment (hydrochloric acid).

2. Experimental

2.1 Materials

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ammonium hydroxide (26% NH_3 in H_2O), hexane, dichloromethane (DCM), vinylbenzyl chloride (VBC 95%), polyethylene glycol (600 PEG), hexadecane, sodium dodecyl sulfate (SDS), potassium peroxydisulfate (KPS), and oleic acid (90%) were purchased from Fluka AG and used as received.

2.2 Synthesis of magnetic fluid Fe₃O₄ by co-precipitation

The magnetite particles were produced by co-precipitation from an aqueous Fe³⁺/Fe²⁺ solution (molar ratio 3:2) using concentrated ammonium hydroxide in excess. Then an increase of the temperature to 70°C with intensive stirring for 20 min was applied to ensure evaporation of the ammonia excess because ammonium salts could hinder the transfer of the particles into the organic phase. The stabilization step can be performed at room temperature and at higher temperature:

a- Stabilization at room temperature:

The magnetic iron nanoparticles were transferred into the organic phase by the addition of an organic phase (hexane or dichloromethane) and oleic acid into the mixture with stirring at room temperature for 30min. This leads to a complete transfer of the particles to the organic phase [16].

b- Stabilization at higher temperature:

Oleic acid is directly applied during the magnetic iron oxide nanoparticle formation at a temperature of 70°C – 90°C with high stirring speed. The temperature of 70°C- 90°C is applied for the evaporation of the excess of ammonia for 30 min. Iron oxide coated with oleic acid is formed and is separate from the water phase, cooled and washed with water for several times and dried [17, 18].

2.3 Preparation of magnetic polyvinylbenzyl chloride nanoparticles (core shell) by using miniemulsion polymerization [17 18]:

A mixture of 1g iron oxide coated with oleic acid, 3.0g vinylbenzyl chloride (VBC) and 0.15g hexadecane is prepared. After dispersion of the iron oxide in the VBC the surfactant solution made of 0.42g sodium dodecyl sulfate (SDS) and 150ml water is added, then mixed well by an US-sonotrode (ultrasonic homogenizer, Sonopuls HD 200 with sonotrode UW 200, Bandelin, Germany) for 2 min at a power output of 50% and 90% cycle ratio in an ice-cooled bath to form the miniemulsion solution. Start of polymerization was achieved by addition of KPS solution (0.0015g in 5ml water). The time for polymerization was 24hr at 80°C. Colour of solution is changing in the course of the reaction until the final product is a stable dispersion.

2.4 Preparation of magnetic polyvinylaniline nanoparticle (core shell) by using miniemulsion polymerization

The same procedure was used as given in 2.3 with the variation that the monomer now is 3.0 g of vinylaniline. Again the time for polymerization was 24hr at 80°C.

2.5 Synthesis of bi-layered polymer magnetic core/shell composites by condensation polymerization [19]

Coating of magnetic core hydrophobic polymer shell composites with a hydrophilic layer of polyethylene glycol (PEG 600). 0.4 g magnetic polyvinylbenzyl chloride coated nanoparticles were mixed with 44.5 g excess of polyethylene glycol (PEG) by an US-sonotrode (same settings as given earlier). This leads to dispersion of the polyvinylbenzyl chloride coated magnetic iron oxide particles (core) in PEG. Then polycondensation with PEG (shell formation) was started by addition of KOH solution (1.2g in 5ml water). The time for polycondensation was 48hr at 80°C.

2.6 Characterization

Particle size measurements were performed by photon correlation spectroscopy (PCS, Malvern Instruments Nanosizer ZS), the content of magnetite is quantified with a spectrophotometer (Hach Company, DR 4000) using the 1.10 phenanthroline method [20]. The morphology and

diameter were measured by transmission electron microscopy (TEM) on Jeol JEM 2100 Electron Microscope. The binding of iron and oleic acid was investigated by infrared spectroscopy (IR) FT-IR spectrometer from Bruker IFS 66v with Raman module FRA 106, Bruker Optik GmbH. The samples were prepared by mixing with KBr and pressing into a compact pellet. The binding of the oleic acid into the polymer was investigated by H-NMR spectroscopy on Avance 400 nmr spectrometer from BRUKER (Rheinstetten, Germany) with 400 MHz proton frequency. Auger electron spectroscopy (AES) was used for performing surface analysis and to determine elemental composition as a function of depth using a 595 from Physical Electronics and the depth profiling is done by 3.8 keV Ar-ion bombardment. Finally acid treatment was done by concentrated hydrochloric acid.

3. Results and discussion

3.1 Preparation and characterization of magnetite nanoparticles

Ferrofluids or magnetic fluids are stable dispersions of ultrafine magnetite. They were prepared in aqueous carrier medium as water based (hydrophilic character) or in organic carrier medium (hydrophobic character) as organic solvent based liquids. The stabilization of these particles is achieved through a surfactant e.g oleic acid which hinders the particles from flocculation or sedimentation and provides that these particles remain uniformly dispersed in the carrier medium although they are or have been exposed to a magnetic field. In our work hydrophobic magnetite in organic carrier medium were produced by using oleic acid as surfactant.

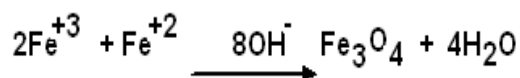
The particle size of magnetite nanoparticles in water phase is bigger than in organic phase, where the type and amount of solvent play an important role in control of morphology and particles size in the preparation of magnetite nanoparticles.

3.1.1 Preparation of magnetite nanoparticles

Supermagnetic Fe₃O₄ nanoparticles (magnetite nanoparticles) with a mean diameter (10–20 nm) were prepared by a co-precipitation process using an aqueous Fe³⁺/Fe²⁺ solution with a base like concentrated ammonium solution (NH₄OH), and coating these particles with an adsorbed layer of oleic acid, which act as surfactant layer on magnetite particles to give hydrophobic character to the particles, decreases aggregation between particles and increases concentration of dispersed magnetite nanoparticles.

Formation step;

Magnetite nanoparticles, black coloured iron oxide, formed immediately by quickly addition of concentrated ammonia solution (26% NH₃ in H₂O) to an aqueous iron salt solution consisting of 2Fe³⁺/Fe²⁺ with intensive mechanical stirring at a temperature of 70°C.



Stabilization step;

After the formation of magnetite nanoparticles, the particles were stabilized by the addition of oleic acid (surfactant, coating magnetic nanoparticles) at room temperature or at elevated temperature to give hydrophobic character to the particles. At room temperature this was done by mixing with hexane containing oleic acid or at elevated temperature (70 °C) by direct addition of oleic acid [16, 17, 18] without any solvent.

A minimum amount of about 0.4 g oleic acid/g magnetite is needed to transfer all the particles into the organic phase. Otherwise an intermediate phase, consisting of none stabilized particles will form, disturbing the transfer procedure of the nanoparticles.

It is also reported that the magnetite nanoparticles prepared by co-precipitation have extensive hydroxyl groups on the surface by contact with the aqueous phase [17]. Since the surface-to-volume ratio is very large, we suppose that the surface hydroxyl groups reacted readily with the carboxylic acid head groups of the oleic acid molecule.

3.1.2 Characterization of magnetite nanoparticles

The magnetite nanoparticles were evaluated by measuring the magnetite content and investigating the stability against concentrated hydrochloric acid.

To evaluate the stability of the magnetite nanoparticles they were treated with concentrated hydrochloric acid. In Table 1 the resistance of magnetic particles against acids like concentrated HCl is tested and found that the rate of dissolving magnetic particles in concentrated HCl is in the time range of a few seconds. The magnetic particles loose their black colour and loose their magnetic properties.

Measurement of Size by PCS photon correlation spectroscopy (Zetasizer) resulted in a diameter of approx. 30 nm, which is bigger than expected. This could be explained by agglomeration of some of the magnetic particles.

The magnetite content of magnetite nanoparticles which were formed at higher temperature was higher than the magnetite content of the samples formed at room temperature. The reason may be that the iron oleate formation is faster at higher temperature.

Transmission electron microscopy (TEM)

The morphology and particle size were measured by TEM. In Figure 1 a TEM image of iron magnetite in hexane indicates that the average particle diameters are between 10 nm to 20 nm. Also we noticed agglomerated particles due to large free surface energy of each nanoparticle.

The agglomeration between nanoparticles in case of the magnetite nanoparticles which were prepared at higher temperature is less than in case of the magnetite nanoparticles which were prepared at room temperature. This can be explained by the better formation of the oleic acid coating, preventing agglomeration.

Infrared spectroscopy (IR)

In Figure 2 the presence of magnetite is characterized by two absorption bands at 632 cm^{-1} and 585 cm^{-1} which correspond to the Fe-O. The bands at 1430 cm^{-1} and 1590 cm^{-1} , which correspond to the symmetric and antisymmetric stretching vibration of oleate ($-\text{COO}$) appeared as well and the band at 1720 cm^{-1} which corresponds to the (C=O) group. This indicates that oleic acid is bonded with iron oxide.

Also we noticed the presence of a strong band of hydroxyl groups (on the surface of magnetite) at 3200 cm^{-1} in the sample prepared at room temperature. This band is stronger in this sample than in the sample prepared at high temperature, since most of the hydroxyl groups were consumed in the formation of the iron-oleic-acid bonding at higher temperature.

3.2 Preparation and properties of magnetic polyvinylbenzyl chloride nanoparticles

A miniemulsion is typically obtained by shearing a system containing monomer, water, surfactant, costabilizer and initiator. The droplet diameter is adjusted by the type and amount of surfactant and costabilizer, the volume fraction of the disperse phase, and the homogenization process. One of the characteristic features of the miniemulsion polymerization technique may be an advantageous encapsulation method. Potential advantages include the ability to control the size via formulation of the miniemulsion, directly dispersing the hydrophobic inorganic particles in the monomer phase, the ability to nucleate all the droplets containing inorganic particles, and a faster polymerization. During the preparation which is described in detail in the experimental chapter the composite formation can be demonstrated in the next Figure 3.

3.2.1 Emulsion stability by effect of water and surfactant (SDS)

The emulsion stability as function of surfactant (SDS) and water ratio was studied for magnetic polyvinylbenzyl chloride nanoparticles. In previous work describing the synthesis of magnetic polymer [17,18] by using the normal preparation (24 g water and .03g SDS) it was found that the amount of water and SDS are not sufficient for make stable emulsions (to make stable droplets of monomer). After 1-2 days it separates water from the emulsion solution as given in Figure 4.

As a result of previous work the monomer/water ratio must be within the range of 75% to 95% for water. The amount of surfactant or inherent surface stabilizing groups required to form polymerizable miniemulsions is rather small, 5% to 25% relative to the monomer phase [21, 22].

In Table 2 the different amounts of water and surfactant (SDS) which were used to investigate the emulsion stability are given. The best amount of water and SDS are 150g and 0.21g respectively with 3.0g of monomer, which was used for further experiments.

3.2.2 Characterization of magnetite polyvinylbenzyl chloride nanoparticles

Transmission electron microscope (TEM)

In Figure 5 (a, b) the morphology of the magnetic polyvinylbenzyl chloride (magnetic core nanoparticles) is depicted. It can be seen that the average particles diameter is 20 nm with less agglomeration. Also the pictures show the encapsulation of magnetic particles in the centre of the polymer spheres where the more dark area is related to magnetic particles and the light area is related to the polymer shell.

To evaluate the stability of the composite particles they were treated with concentrated hydrochloric acid. In Table 2 the rate of resistance to concentrated HCl acid of magnetic polyvinylbenzyl chloride is compiled. The stability is some days, after this time loss of its colour is observed and also loss of magnetic properties. This indicates that magnetite indeed is covered by the polymer, but some “holes” or gaps must be in the coating, allowing slow access of the acid. The samples are more stable in the case of magnetite which was prepared at higher temperature, so it can be concluded that at least some of the oleic acid reacted with vinylbenzyl chloride (VBC) leading to an almost sealed shell.

The magnetic core shell particles (magnetic polyvinylbenzyl chloride) are dispersed in acetone. They can be attracted to a magnetic bar in a few seconds; also they can easily be re-dispersed.

Infrared spectroscopy (IR)

In Figure 6 The presence of magnetite in magnetic polyvinylbenzyl chloride is characterized by two absorption bands at 632 cm^{-1} and 585 cm^{-1} which correspond to the Fe-O and for C-H stretching vibration with absorption bands between 2900 cm^{-1} and 3000 cm^{-1} [23]. The absorption bands at $1500\text{-}1600\text{ cm}^{-1}$ stand for the aromatic ring with di-substitution C=C (ring, two bands). These findings together with the previous measurement indicate that the oleic acid treated iron oxide is encapsulated by the polymer.

Auger electron spectroscopy (AES)

Auger Electron Spectroscopy (AES) [24, 25] is an analytical technique that is used for performing surface analysis and to determine elemental composition as a function of depth of a sample. A primary electron beam is used to probe the surface of a solid material. Secondary electrons that are emitted as a result of the Auger process are analyzed and their kinetic energy is determined. The identity and quantity of the elements are determined from the kinetic energy and intensity of the Auger peaks.

In Figures 7 and 8 the AES shows that the sample has agglomerate particles. AES measurement on the surface layer of the particles show mainly three peaks, related to C at 273 (eV), O at 518 (eV) and Cl at 185(eV). Some material was removed by 3.8 keV Ar-ion bombardment. This allows insight into the deeper layers of the material. After 5 nm ablation Fe was detected.

Besides Fe the elements O, C, S and traces of Si (possibly from the substrate the sample was fixed to) were detected. Some peaks derive from K and Cl, these are residues of the additives used during the preparation. Up to about 20 nm the situation does not change dramatically. Only the carbon proportion is growing a little bit. These findings give evidence that the particles consist of a magnetite core covered by a polymer shell.

3.2.3 The bonding situation of oleic acid in the formation of magnetic polyvinylbenzyl chloride

The bonding situation of oleic acid (co-monomer or mechanical entanglement) was studied. Since many years it is under discussion, if oleic acid forms copolymers with styrene-like monomers [26, 27] Different authors come to different conclusions. Harrison et al., [26] assumed that the saturated and mono-unsaturated esters behave in a neutral fashion, serving as solvents for the monomer and polymer. Small amounts of the ester are included in the polymer Falkenburg et al. [27] assumed that there is no copolymerization between the esters of oleic acid and styrene-like monomers and that homogeneity of some of the reaction products cannot be considered as proof for copolymerization.

Lifen Shen et al [28] mentioned that 10-undecenoic acid, which is comparable to oleic acid, can react as monomer and the bonding is more probable by forming covalent bonds in the polymerization reaction because oleic acid is similar to the example given in the literature.

Infrared spectroscopy (IR)

In Figure 9 the IR spectrum of oleic acid is shown with a band at 1720 cm^{-1} which corresponds to the (C=O) carbonyl group and C-H stretching vibrations with absorption bands between 2900 and 3000 cm^{-1} .

The IR spectrum of vinylbenzyl chloride (VBC) with absorption band at $1500\text{-}1600\text{ cm}^{-1}$ stands for the aromatic ring with di-substitution C=C (ring, two bands) and the absorption bands between 2900 and 3000 cm^{-1} derive from stretching vibration with C-H.

The IR spectrum of a solution, which was gained by extraction of the sample (magnetic polyvinylbenzyl chloride) with acetone is also depicted. This spectrum includes the bands mentioned above to a small extent, also confirming the very small concentration of both of the monomers in the extracted solution. This indicates a strong bonding of oleic acid in the polymer.

Proton NMR spectroscopy (H-NMR)

H-NMR spectrum shows the proton resonances of oleic acid. The only peak that we need for our discussion is the one which is around 5.3 ppm for the two olefinic protons (-CH=CH-). In H-NMR of vinylbenzyl chloride (VBC), the resonances of the signals located around 5.8 ppm belong to one of the vinylic protons (Ar-CH=CH₂).

In the H-NMR spectrum of the extracted solution the above mentioned signals are included only to a small extent, also indicating that the oleic acid and the monomer are strongly bond.

From the last data it can be concluded, that oleic acid can not be extracted from the polymer to a large extent. That means that oleic acid is firmly attached to the polymer, so the bonding of oleic acid to the polymer can be by two ways:

- Chemically as a co-monomer of the polymer, that means covalently
- By mechanical entanglement of the polymer chain of oleic acid with the polymer chain of VBC.

Nevertheless the most important thing is that the oleic acid can not be extracted completely from the polymer, so it can fulfill the protection of the magnetite iron oxide. Both IR and NMR confirm each other, in addition the resistance against acid attack as was tested with HCl indicated that the magnetite particles are well shielded by the polymer.

Our own results reveal that oleic acid is firmly bond in the polymer. By extraction experiments with acetone it could only be removed to a slight extent. Spectroscopic data of the magnetite polymer composites give no clear information to give a final decision, if oleic acid is component of a copolymer or if the firm attachment of the oleic acid is only by entanglement of the polymer chains. Mathematical calculation of the copolymer composition is also not possible since there are no copolymerization parameters published in the literature for oleic acid and VBC. Nevertheless which binding situation is realized in the polymer, chemical treatment with hydrochloric acid does not lead to a chemical dissolution of the most part of the iron oxide. For practical reasons the most important thing is that the iron oxide is well shielded by the oleic acid and the polymer. In Figure 10 the two possible binding situations are depicted.

3.3 Preparation and properties of magnetic polyvinyl aniline nanoparticles:

According to the method given in the experimental chapter a sample with vinyl aniline as monomer was prepared (Figure11).

Transmission electron microscope (TEM)

In Figure 12 the morphology of the magnetic polyvinyl aniline nanoparticles is shown by a TEM picture. The average particles diameter is about 20 nm with some agglomeration.

Infrared spectroscopy (IR)

In Figure 13 the IR spectrum with the strong absorption bands at 1514 cm⁻¹ for the NH₂ scissoring (1°-amines), absorption band at 3350 cm⁻¹ for N-H, absorption band at 1270 cm⁻¹ for C-N and absorption band at 827 cm⁻¹ for NH₂ wagging is given. The presence of magnetite in

the polymer is characterized by two absorption bands at 632 cm^{-1} and 585 cm^{-1} , which give an evidence for the formation of magnetic polyvinyl aniline nanoparticles.

To evaluate the stability of the nano-composite particles they were treated with concentrated hydrochloric acid. In Table 2 resistance against concentrated HCl acid is shown, which indicates that the magnetite is partially covered by the polymer.

3.4 Preparation and properties of bi-layered polymer magnetic core

Bi-layered polymer magnetic core particles were prepared by coating of magnetic core hydrophobic polymer shell composites with a hydrophilic layer of polyethylene glycol (PEG 600), so the final product contains a magnetite core coated (shelled) with two layers. One is the hydrophobic layer and one additional layer is the hydrophilic layer. The formation of this bi-layered composites is reached by treatment of the polyvinylbenzyl chloride coated magnetite with an excess of polyethylene glycol (PEG 600) The same US-sonotrode as given in the previous experiments was used to disperse magnetic polyvinylbenzyl chloride in PEG. Start of the polycondensation was done by addition of KOH as catalyst (Figure 14).

Transmission electron microscopy (TEM)

In Figure 15 the morphology of the Bi-layered polymer magnetic core composite is depicted by a TEM picture. The average particle diameter is from 50 to 100 nm. Also the TEM picture shows the formation of the bi-layered polymer magnetic core with the two layers one with the lighter colour (shell) and the other with darker colour (the magnetic core). This corresponds to the first hydrophobic layer and the second hydrophilic layer surrounding the magnetic core.

To evaluate the stability of the composite particles they were treated with concentrated hydrochloric acid. In Table 2 the resistance to HCl acid is evaluated.

The bi-layered magnetic polymer dispersed readily in water and it can be attracted under the influence of a magnetic bar, also it can easily be re-dispersed, which gives evidence that the formation of the hydrophilic layer on the surface could be prepared successfully.

Infrared spectroscopy (IR)

In Figure 6 the IR spectrum of the bi-layered composite is depicted. The strong absorption bands at 1100 cm^{-1} for the C-O indicates that a coating with PEG on the surface of the polyvinylbenzyl chloride exists. Also the spectra for magnetite and polyvinylbenzyl chloride are given. From all the previous characterization the structure which is given in Figure 16 can be expected.

4. Conclusion

- Stable magnetic nanoparticles were prepared with superparamagnetic properties (<20 nm) by co-precipitation process.
- The magnetite nanoparticles prepared by addition of oleic acid at higher temperature resulted in higher stability and also in higher magnetite content compared to the samples prepared at room temperature.
- Miniemulsion polymerization was successfully used in the preparation of magnetic polymer core shell nanoparticles with a diameter range of 10 to <100 nm.
- Bi-layered magnetic core composites show better resistance to HCl than magnetite, which gives evidence that the magnetic composite has a core/shell-structure where the shell protects the core.

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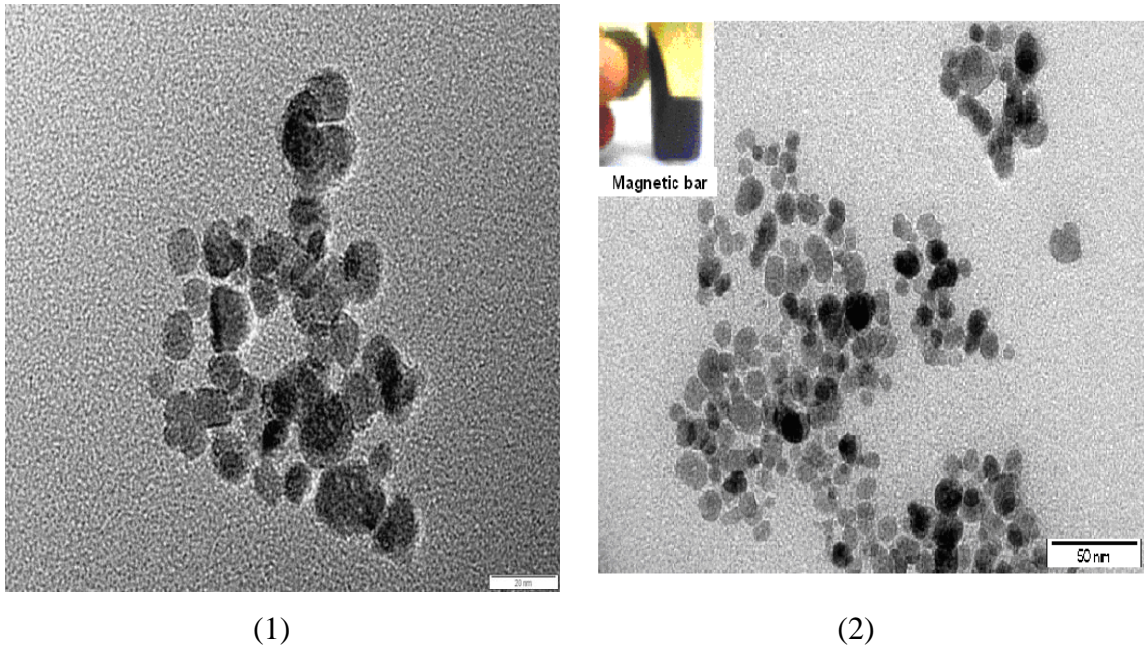


Figure 1: TEM images of magnetic nanoparticles transferred:
 (1) At room temperature into hexane and
 (2) At higher temperature (70°C) without any solvent

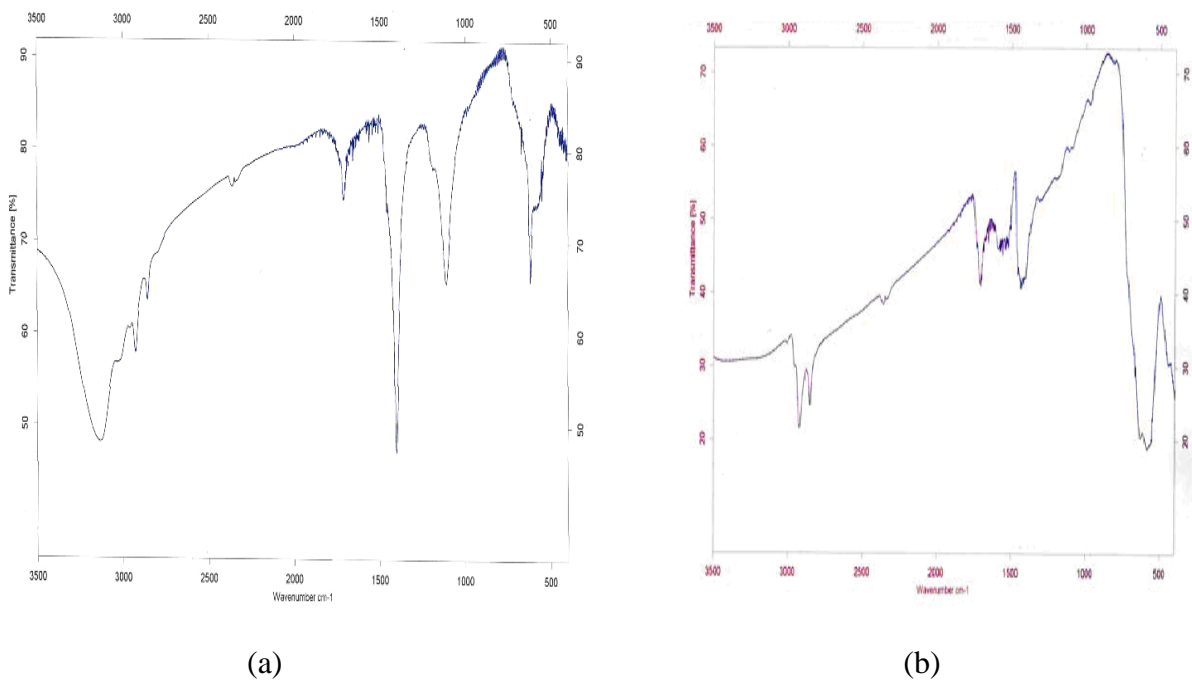


Figure 2: IR spectra of magnetite nanoparticles prepared (a) at room temperature and (b) at higher temperature

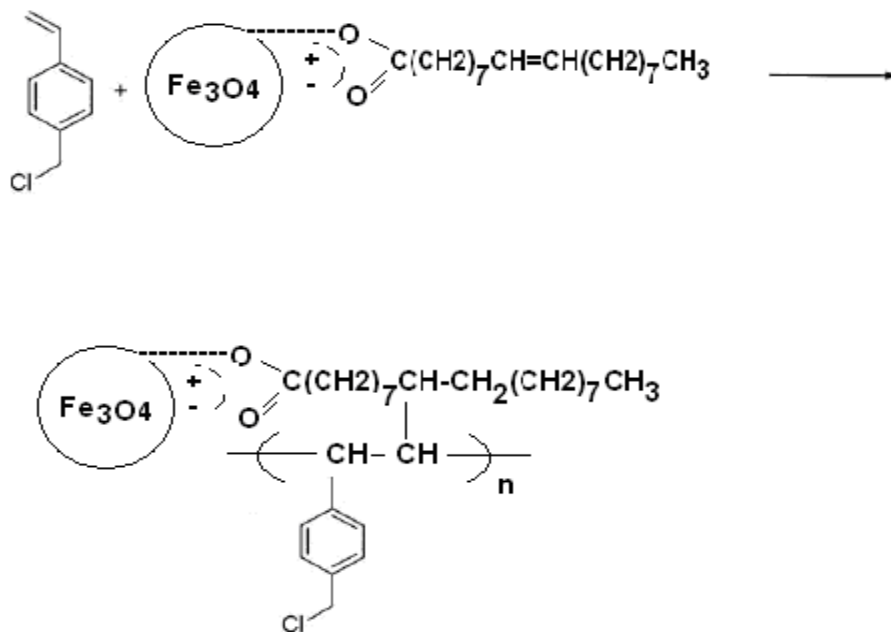


Figure 3: Polymerization of vinylbenzyl chloride in presence of magnetite nanoparticles

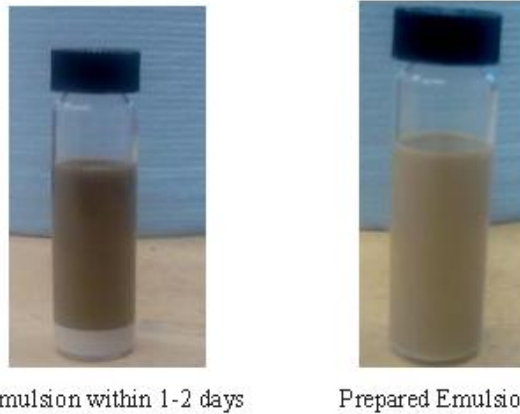


Figure 4: The sedimentation occurred for the emulsion within 1-2 days using the preparation method described in [17, 18]

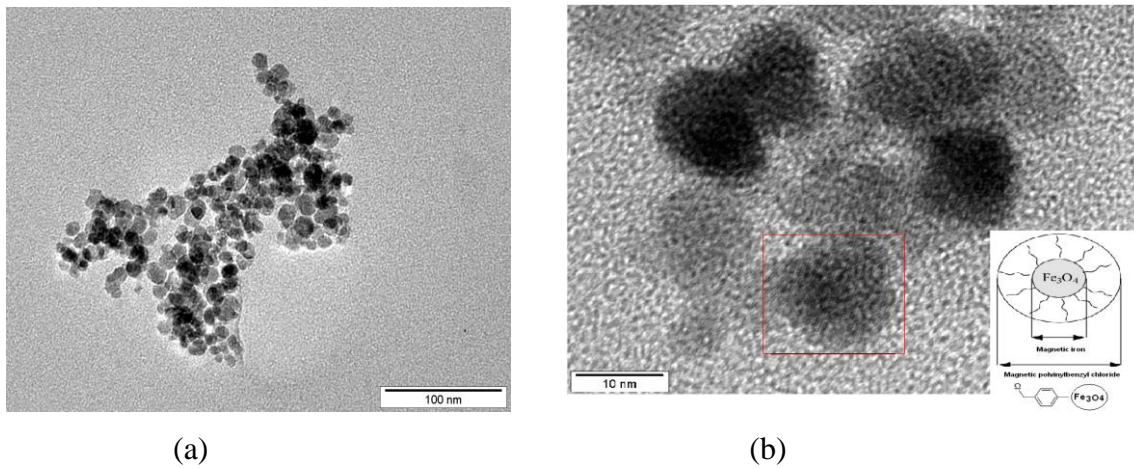


Figure 5 (a, b): TEM Magnetic polyvinylbenzyl chloride (magnetic core nanoparticles)

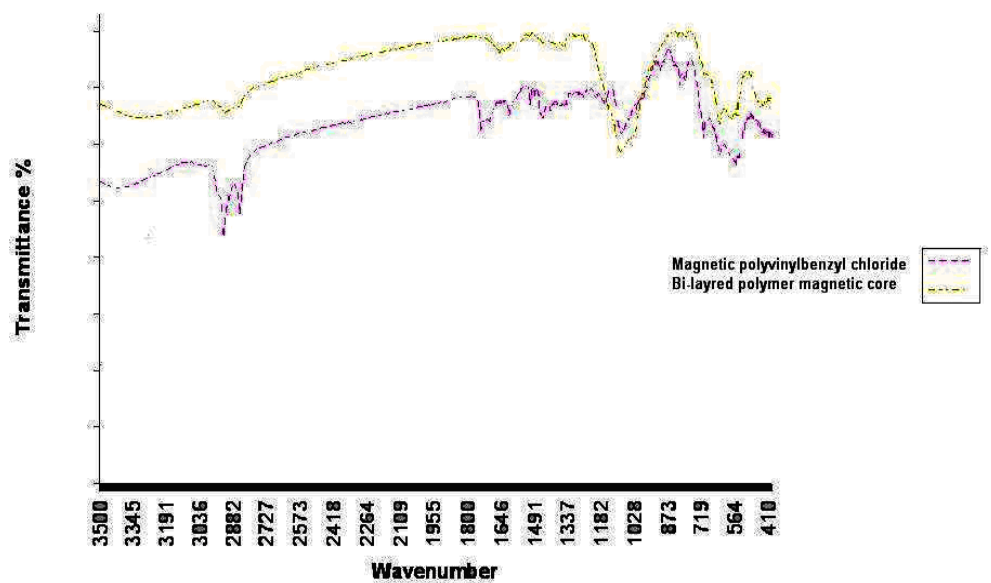


Figure 6: IR spectrum of magnetite polyvinylbenzyl chloride nanoparticles and bi-layered polymer magnetic core

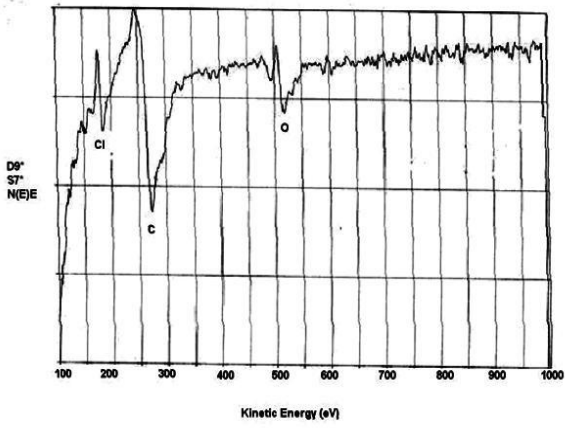


Figure 7: AES Survey for untreated

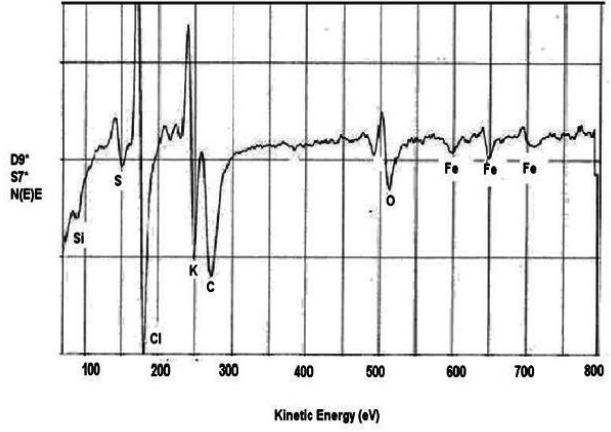


Figure 8: AES Survey after 5 nm sample (surface layer of the particles) depth

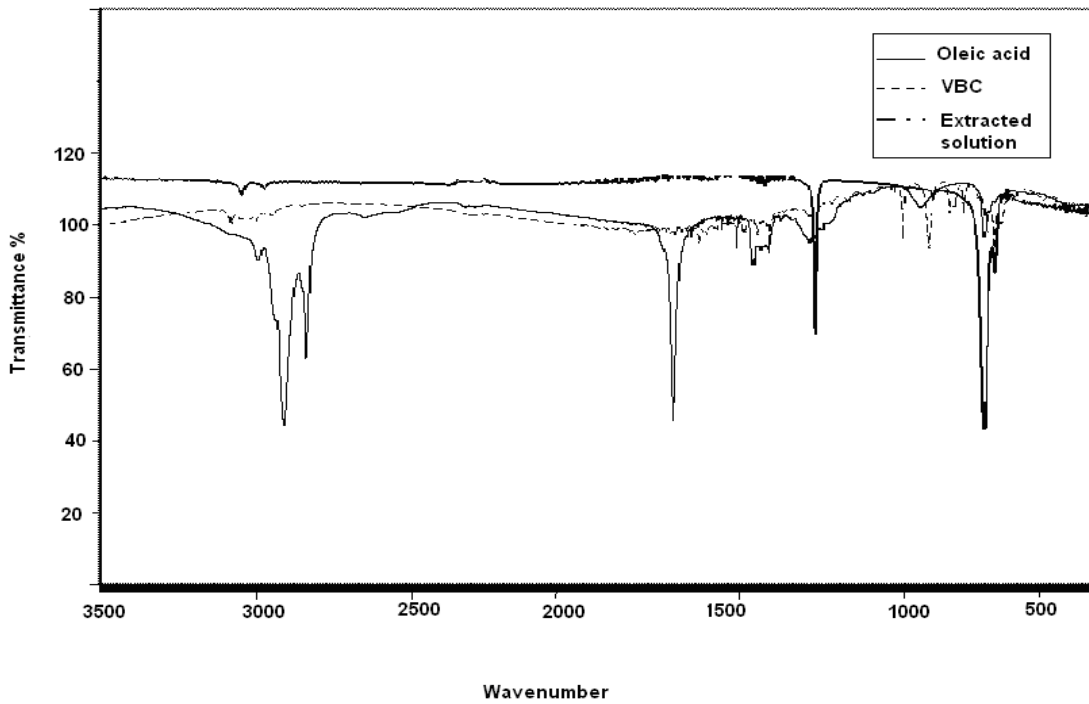


Figure 9: IR spectrum of oleic acid, vinylbenzyl chloride and extracted solution.

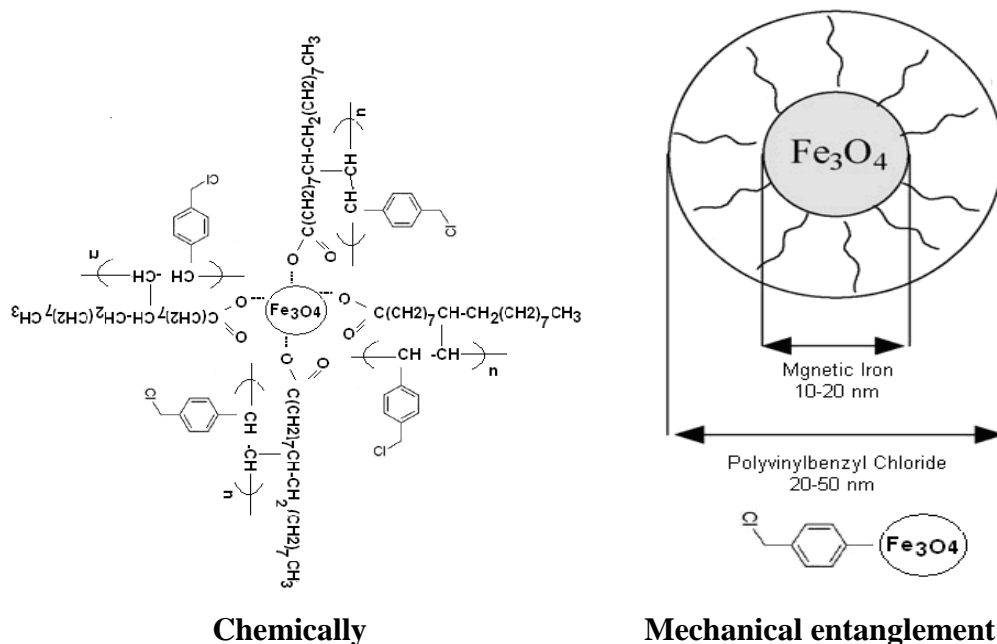
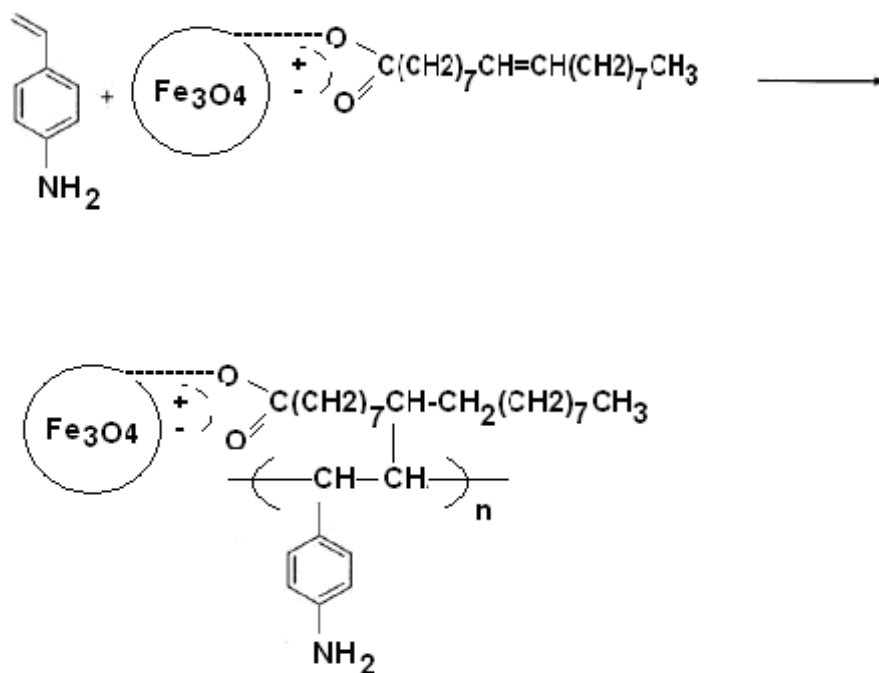


Figure 10: Magnetic polymer composite particles based on the performed characterization



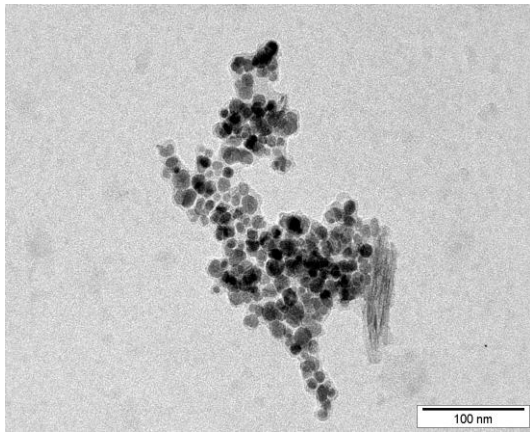


Figure 12: TEM of magnetite polyvinyl aniline nanoparticles

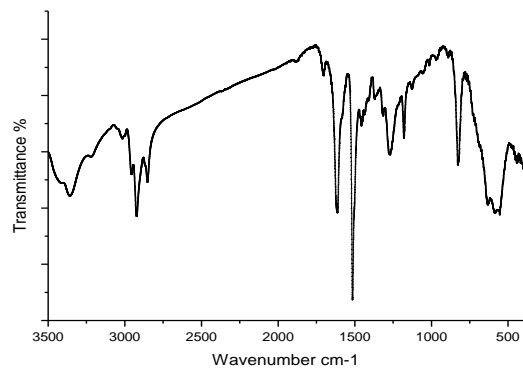


Figure 13: IR spectrum of magnetic polyvinyl aniline nanoparticles

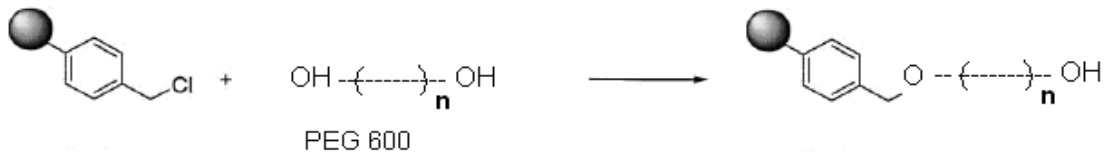


Figure 14: Bi-layered polymer magnetic core

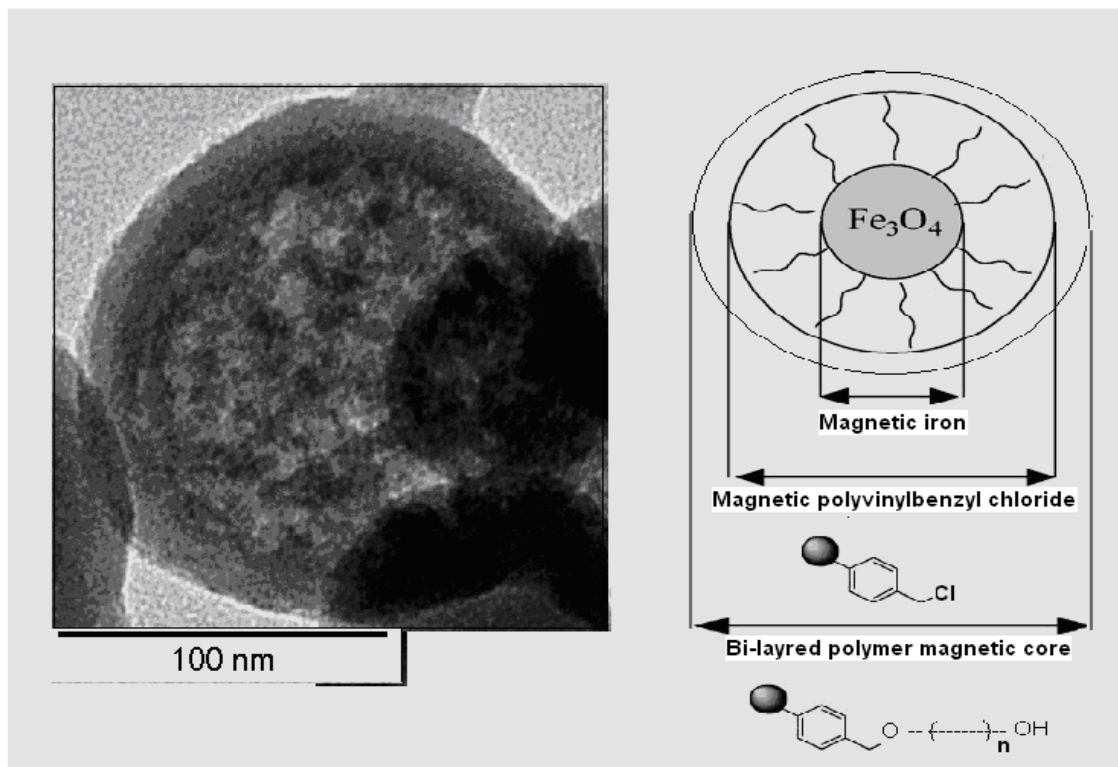


Figure 15: Bi-layered polymer magnetic core composite particles

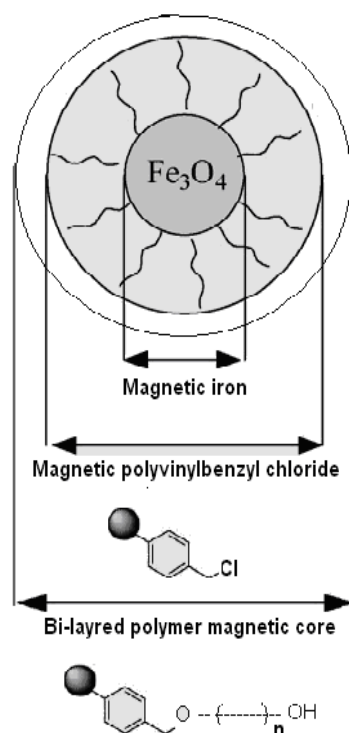


Figure 16: Structure of bi-layered polymer magnetic core composites

Table 1: Effect of water and SDS on emulsion stability.

Sample	Vinylbenzyl chloride	Hexadecane	Water (g)	SDS(g)	Sedimentation
1	3.0g	0.15g	10	0.03	hours
2	3.0g	0.15g	24	0.03	1Day
3	3.0g	0.15g	100	0.07	2Days
4	3.0g	0.15g	150	0.21	month

Table 2: Properties of magnetite and magnetic polymer core shell nanoparticles

Sample	Magnetite content Fe_3O_4 (g/kg)	Average particles size by TEM	Resistance to HCl	Dispersion
Magnetite in Hexane (room temperature)	24.2	~10 nm	–	Hydrophobic properties
Magnetite (higher temperature)	67.3	~10 nm	–	Hydrophobic properties
Magnetic polyvinyl aniline	30.5	~20 nm	+	hydrophobic properties
Magnetic polyvinylbenzyl chloride	28.6	~20 nm	+	Hydrophobic properties
Bi-layered magnetic core	41.8	~50 nm	+	Hydrophilic properties

(–) Poor resistance (+) Good resistance

