Synthesis and Characterization of Grafted Polymeric Nanoparticles

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ABSTRACT

The aim of the present investigation was to design polymer coated iron oxide containing nanoparticles, which are biocompatible super paramagnetic. In order to achieve the proposed objectives Grafted Polymeric Nanoparticles particles were prepared by using Co-precipitation method and characterized by techniques like FTIR , particle size ,zeta potential . The magnetic behavior of nanocomposites and bulk magnetite particles was studied under varying applied magnetic fields . A novel technique was adopted for impregnation of iron oxide nanoparticles into the polymer matrix. By designing of particles with controlled size and super paramagnetic nanoparticles, it is possible to fabricate high performance materials, which could demonstrate fairly good magnetic and biocompatible properties.

Keywords: Gelatin, polymer, nanoparticles, swelling,

1.Introduction:

Magnetic phenomena at the atomic scale were discovered in the early twentiethcentury, whereas the discovery of the first known magnetic material (Fe_3O_4)revolutionized the field of magnetism. The magnetic properties of a material dependon temperature, the applied magnetic field, and pressure.A change in these variableswill result in the existence of two or more forms of magnetism. Ferro- andferrimagnetic materials like Fe_3O_4 and some of their alloys have particles whoseshape is asymmetrical when they are obtained by the grinding of bulk materials,whereas they can possess a spherical shape only when manufactured through plasmaatomization or wet chemistry or when in aerosol and gas phases. Depending on theprocedure used to form particles, they can be crystalline or amorphous spherical inshape. To a large extent, the synthesis process determines the degree of impuritiesin a particle, as well as the presence of structural defects, and, hence, the divisionof these defects inside the particle structure can be used to discover its magneticproperties 1, 2.

Magnetization depends on the number of unpaired valence electrons present inthe atoms of solids and on the relative orientations of the neighboring magneticmoments 3. Two types of motion of electrons in atoms are responsible formagnetism. One is the spin of electrons around the atom’s axis, and the other is themotion of electrons in an orbit around the nucleus. Iron (Fe), nickel (Ni), manganese(Mn), and cobalt (Co) are magnetic materials that have a net magnetic moment.In transition metal atoms, the magnetic moment is due to electron spin 4.

1.1. Classification of Magnetic Materials

In solids, materials may be categorized by their response to an externally appliedmagnetic field. There are five basic types of magnetism, paramagnetism, diamagnetism, ferromagnetism, ferrimagnetism, and antiferromagnetism. The magneticproperties of a material are governed by the electronic structure of the atomswithin the material. They vary from weakly magnetic (diamagnetic) to permanentlymagnetic (ferromagnetic).

The most important property of a magnetic material is the magnetic susceptibility(χ), defined by

$$\chi = \frac{M}{H} \qquad \text{------------------------------ -----(i)}$$

Where*M* is the magnetization and *H* the magnetic field, both of which are measuredin units of A/m. In general, the magnetic susceptibility is different for each material,temperature dependent (except in diamagnetic materials), and of the form

$$\chi = \frac{C}{T \pm \theta} \qquad \text{-----(ii)}$$

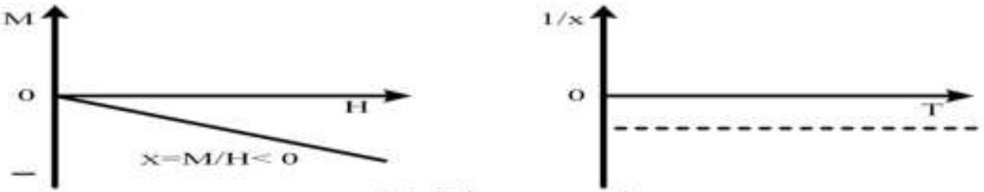
1.1.1 Diamagnetism

Diamagnetism is a basic property of all matter, but it is an extremely weakproperty. The susceptibility (χ) is negative and on the order of approximately10-5. The other characteristic behavior of diamagnetic materials is that theirsusceptibility is independent of temperature. The origin of diamagnetism is dueto the noncooperative behavior of orbiting electrons when exposed to an appliedexternal magnetic field. Diamagnetic materials are composed of atoms having nonet magnetic moments (i.e., all the orbital shells are filled and there are no unpaired electrons). When a small field is applied, a small negative magnetization is generated that is proportional to the applied field strength

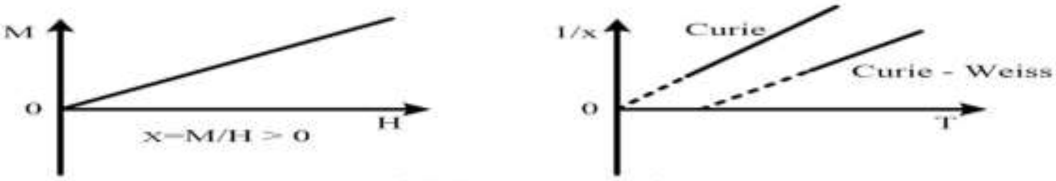
1.1.2 Paramagnetism

Because of the magnetic field generated by unpaired electrons, atoms may behave like magnets under the influence of an external magnetic field. However, whenthe applied magnetic field is removed, the thermal fluctuations would cause themagnetic moment of paramagnetic atoms to move randomly. In the presence of a relatively low magnetic field, this effect can be described by Curie’s law,

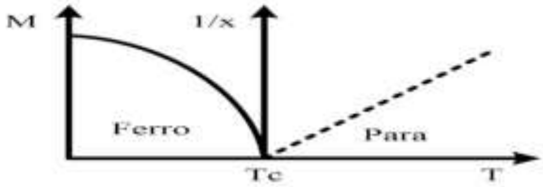
$$\chi_{para} = \frac{M}{H} = \frac{C}{T} \qquad \text{---------(iii)}$$



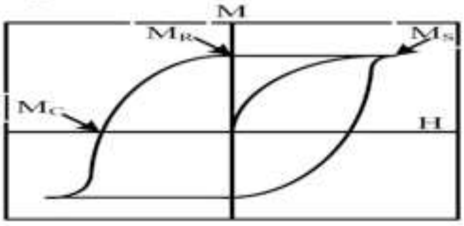
(a) Diamagnetism



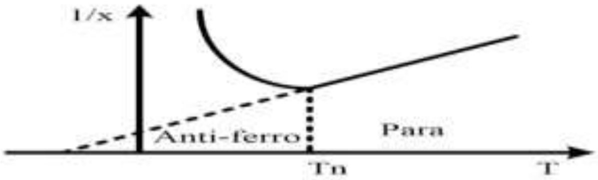
(b) Paramagnetism



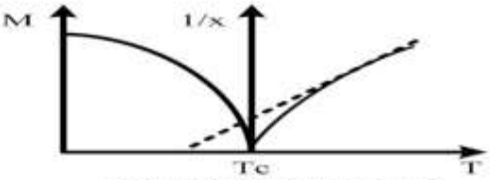
(c) Ferromagnetism



Hysteresis Curve



(d) Antiferromagnetism



(e) Ferrimagnetism

Where *C* is the Curie constant. The expected behaviors of paramagnetic materials with an applied external magnetic field and with temperature are shown in Fig.1.1.2b

In general, the response of a material to a magnetic field, that is, the magnetic susceptibility (χ), is on the order of 10^{-3}–10^{-5}.

1.1.3 Ferromagnetism

Ferromagnetic materials exhibit parallel alignment of magnetic moments to one another, resulting in a large net magnetization, even in zero magnetic fields, knownas spontaneous magnetization. The atomic dipole moments in these materials are characterized by very strong positive interactions produced by electronic exchange forces, which results in a parallel alignment of atomic moments. The two distinct features of ferromagnetic materials are a magnetic ordering temperature and spontaneous magnetization. Ferromagnetism is strongly temperature dependent, and the magnetization of a ferromagnetic material is inversely proportional to temperature by the Curie–Weisslaw:

$$\chi = \frac{C}{T - \theta} \qquad \text{--------------------------(iv)}$$

The Curie temperature is the temperature above which exchange forces ceaseto be present, that is, above that temperature a ferromagnetic material randomize sowing to the thermal energy, as in paramagnetic systems (Fig. 1.1.2c). They have relatively large susceptibilities, and in general, magnetic saturation is achieved through fields lower than for paramagnetic systems by a factor of 104.

1.1.4 Antiferromagnetism

Antiferromagnetic materials are characterized by a weak magnetic susceptibility of the order of paramagnetic materials. In a simple antiferromagnetic material, the atoms can be divided into two Sublattices, where magnetic dipole moments are aligned anti parallel, which causes a small magnetic susceptibility in these materials.The temperature above which antiferromagnetic order ceases to exist is called the Neel (*T*N) temperature (Fig. 1.1.2d). Above *T*N, antiferromagnetic materials have as light positive susceptibility comparable to that of paramagnetic materials. Below *T*N, however, antiferromagnetic materials have a spontaneous magnetization in the absence of an external field that causes the magnetic dipole moments of sub lattices to align antiparallel to each other.

1.1.5Ferri-magnetism

Ferrimagnetic materials, like ferromagnetic materials, have a spontaneous magnetization below a critical temperature called the Curie temperature (*T*C). The magnitude of the magnetic susceptibility (χ) of ferro-/ferrimagnetic materials is identical, while the alignment of magnetic dipole moments is drastically different (Fig. 1.1.2e). The magnetic dipole moments in a ferrimagnetic material are divided into two sub lattices and classified as a subset of antiferromagnetic materials. Each sub lattice can be treated as a ferromagnetic material, and the difference between the magnetic dipole moments for the sublattices results in a net magnetization for ferrimagnetic materials. The major difference between ferrimagnetic and antiferro-magnetic materials is that either the magnitude or the number of moments of sub lattices is different.

The most important crystalline ferrimagnetic substances are double oxides of iron, as in $MO.Fe_2O_3$, where M is a divalent metal. These are based on the Spinel structure; the protypical example is magnetite, Fe_3O_4. As the temperature rises , the alignment of the spins is disturbed by thermal energy and the magnetization decreases. At a certain temperature, called the Curie temperature *T*C, this alignment becomes completely disordered and the magnetization vanishes.

1.1.6 Superparamagnetism

Superparamagnetic materials are a special class of magnetic materials. They are single-domain particles that behave like ordinary ferromagnetic materials below *T*C because they have rather large magnetic susceptibilities, are saturated in moderate magnetic fields, and display coercivity and remanence. Above *T*C, however, super paramagnetic materials behave like ordinary paramagnetic materials in that they display no hysteresis (i.e., no coercivity or remanence).The idea of super paramagnetism was first developed and proposed by Neel 5,6 to describe the possibility of thermal fluctuations in single-domain ferromagnetic clusters. In general, the magnetic anisotropy energy of a particle is proportional to its volume. In a given crystal of volume *V*, the magnetic anisotropy energy is given by

$$E_A = KV\sin^2\theta \qquad \text{-----------------(v)}$$

Where *K* is the anisotropy energy constant and the angle between the magnetization vector and easy axis of nano particles 7. When the volume of a single-domain cluster is small enough, the magnetic anisotropy energy of the cluster approaches its thermal energy, causing the magnetization to flip between easy axes through an anisotropy barrier in the same way as in a classical paramagnetic system 8.but, with a giant magnetic moment, that of a single atom, hence the term *super paramagnetism*.

1.2Structural and Magnetic Properties of Nanomaterials

This section aims to provide an understanding of the structural properties of nanomaterial since their technologically relevant properties depend on their structure at the nanoscale.

1.2.1 Crystal Structures

For iron, there are 16 different forms of oxide. In 13 compounds, iron is in its trivalent form, while in the three remaining compounds, FeO, $Fe(OH)_2$, &Fe_3O_4, it is in divalent form. All oxides, hydroxides, and oxide hydroxides (oroxyhydroxides) of iron have a crystalline structure. Iron oxides are usually arranged in close packed lattices in hexagonal (hcp) or cubic (Ccp) arrangements, where interstitial sites are partially filled by Fe_2C or Fe_3C, mostly in octahedral sites, and in a few cases in a tetrahedral geometry. The iron oxide structures are described here.

1.2.2. Magnetite(Fe_3O_4)

Magnetite occurs in nature as magnetic ore, known as lodestone. Magnetite differs from the majority of other iron oxides in that it contains both trivalent and divalent iron ions. Both magnetite and maghemite have an inverse spinel structure, and differentiating between the two structures in diffraction patterns remains a challenge 9. Magnetite has a face-centered cubic (Fcc) structure on O^{2-} ions arranged in a cubic close-packed arrangement in accordance with 10. in a regular pattern.The lattice parameter of the unit cell is *a* D 0.839 nm. There are eight crystal motifs per unit cell 11. Its chemical formula can be described as $A[AB]O_4$, whereA D Fe_3C, B D Fe_2C, and brackets indicate octahedral sites. In an inverse spinel structure, all the Fe_2C and half of the Fe_3C Cations occupy octahedral sites and the remaining half of the trivalent iron occupy tetrahedral sites 12, 13. The distribution of Fe_3C Cations at the tetrahedral sites suggests the degree of disorder _ in the spinel structure, and , The substituting ions are adjusted by the expansion or contraction of the oxygen frame work to compensate the size difference from Fe_2C 14–18.

1.3.1 Classical Synthesis by Co precipitation

In chemical routes of preparation of nanoparticles with preferred physical properties,the structural and chemical properties of the elements also play an important role. Fine chemical homogeneity can be attained by mixing constituents at the molecular level. Moreover, this makes it possible to control the shape and size distribution during synthesis. Chemical methods of preparation have emerged as an important technique and are used for the synthesis of spinel ferrite nanoparticles 20.

The Coprecipitation process is the most proficient technique used for the synthesisof MNPs. This technique involves mixing ferrous and ferric ions in a molar ratio of 1:2 in a solution at room temperature or higher.

The reaction is controlled by changing the solution PH. The growth of a ferrioxide nucleus is comparatively simple when the pH of the solution is greater than11, while the nucleation of a ferric oxide nucleus is comparatively simple when the solution pH is less than 11 21. Coprecipitation has been examined mostly in the preparation of ferric oxide nanoparticles because of its ease of use in gram-scale fabrication 22. Many researchers have reported the extensive co precipitation synthesis of ferric oxide nanoparticles, where their magnetic properties and morphology at various different temperatures were examined 23. Various modified Coprecipitation processes have been developed. Many researchers have Review the advancements and developments in this field over the last decade 21. By varying the temperature, PH,Fe_2C/Fe_3C ratio, and ionic strength, the shape and size of IONPs can be modified 19.

Moreover, the ionic strength and acidity of the precipitation agent are the main factors on which the mean size of magnetic nanoparticles depends 24. Narrow particle size distribution and small particle size can be attained under elevated ionic strength 25.

Biocompatibility and aggregation are major hindrances in biomedical applicationsof IONPs. In the Coprecipitation process, various biomolecules and surfactants are directly inserted. The Coprecipitation technique is one of the most established and effective techniques used in the synthesis of IONPs with high saturation magnetization, and to overcome the limitations of this technique more attention should be devoted, for instance, to the use of a strong base in reactions and a wide particle size distribution 21.

Coating nanoparticles with a functional polymer and grafting of these coated particles with crosslinker can improve the stability, surface charge, functionality and targeting capability. The nanoparticles thus form less aggregates whilst broadening the end use. Depending on the polymer of choice amino groups, carboxylic acids, phosphates and Sulphates can be bound to the surface of the nanoparticles. The coated nanoparticles will be stable in aqueous solution and can thus be applied to biological applications.

2.1. EXPERIMENTAL

2.1.1. Materials

Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$, 99%), ferric chloride hexahydrate ($FeCl_3.6H_2O$, 99%), polymer, gluteraldehyde were obtained from Loba Chemicals and used as received. Sodium hydroxide (NaOH), sulfuric acid (98%) and methanol were purchased from Merk.

2.2.2 Methodology:

Super paramagnetic particles are synthesized using Co-precipitation method.

The produced particles was filtered & after drying at 150° C for 2 hours the powder will be obtained.

.Coating was done by using polymer

.Grafting was done by gluteraldehyde

.The chemical reaction of Fe_3O_4 formation may be written as:

$Fe^{2+}+ + 2Fe^{3+}+ + 8OH- \rightarrow Fe_3O_4+ 4H_2O$

After the synthesis of grafted nanoparticles, it was characterized using Fourier Transform Infrared spectroscopy (FTIR),Zeta potential Analyser

Fig. 1 Demonstration of magnetic properties of prepared iron oxide nanoparticles dispersed in water

2.2.3 Characterization of prepared magnetic nanoparticles

Malvern Dynamic Scattering(DLS) Nano Zetasizer 90, UK was used to determine an approximate particle size of prepared particles. To study the molecular structure of super paramagnetic particles and coated particles Fourier Transform Infrared Spectroscopy (FTIR, model Impact 400, Nicolet, USA) was used. The FTIR spectra were recorded using KBr pellet technique.

3. Result And Discussion

3.1Particle SizeAnalysis: The Particle Size analysis provided information about size of resulting particles. Obtained micrographs are shown in Fig. 2. The average particle size values of all produced magnetite samples are listed in Table 1. It was observed, that the nanoparticles of noncoated nanoparticles samples have particle sizes below 20 nm.. After coating the size of particles were increased.After grafting particle size decreased.

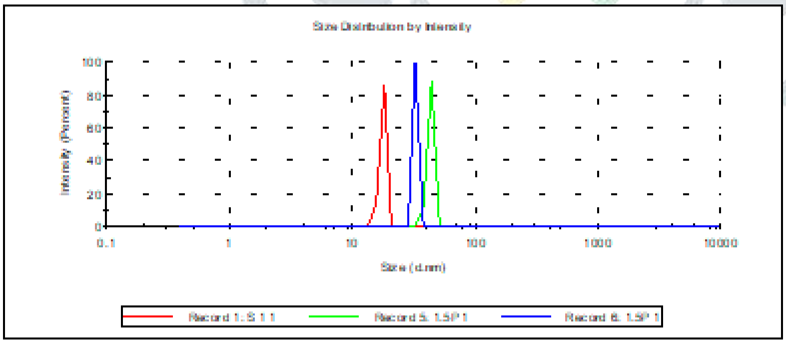


Fig. 2: Particle size of IOINP,Coated and Grafted Nanoparticles

Table : 1 Average particle sizes of magnetic nanoparticles ,coated and grafted particles

Sample	Particle	Sample	Particle Size(nm)
1	IOINP	1	17.82d nm
2	COATED	2PC	43.13d nm
3	GRAFTED	1.5P,1G	32.67d nm

3.2 Zeta Potential Analysis:

Zeta potential Analysis provided information about the surface charge of the particles.Obtained results are shown in fig 3The average zeta potential values of all produced magnetite samples are listed in Table 2.

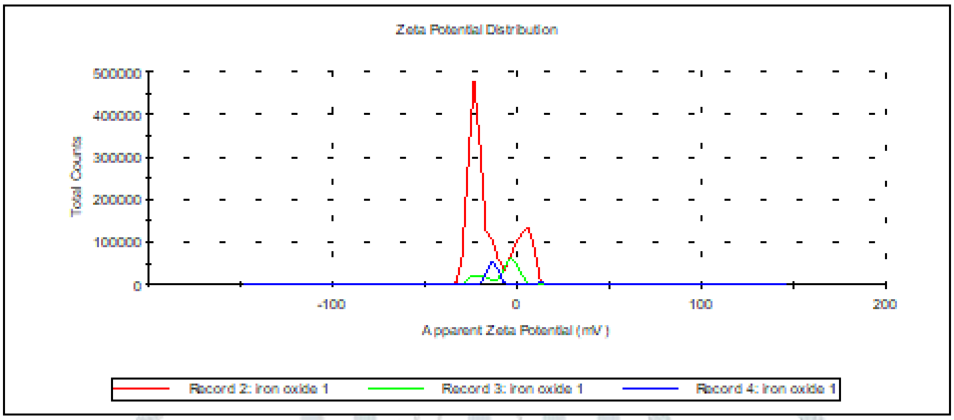


Fig. 3: Zeta Potential of IOINP,coated and grafted particles

Table 2: Average Zeta Potential of magnetic nanoparticles ,coated, and grafted particles

Sample	Particle	Sample	Zeta Potential
1	IOINP	IRON OXIDE	-14.8 mV
2	COATED	PC	-8.25 mV
3	GRAFTED	1.5P G	-13.6 mV

Zeta potential of noncoated particles were obtained -14.8 mV, whereas coated particles were -8.25 mV and grafted particles were -13.6.Result shows that the charge on the surface of the particle is negative in all the cases.

3.3 Ftir Specrtal Analysis:

Fig. 4, 5 & 6 shows vibrational spectra of magnetite particles alone and of those coated with the polymer and crosslinked nanoparticles . IR spectra of the synthesized Fe_3O_4 nanoparticles (Fig.-4) has the distinctive vibration of O–H groups on its surface (3393 cm-1), enabling the possibility of its surface to be coated by the polymer. The presence of magnetic Fe–O bending in 667 – 420 cm-1 region showed the existence of magnetite .Successful coating of Fe_3O_4 by polymer was indicated by the presence of hydroxyl (O–H), carbonyl (C–C), and Fe–O–C bonds vibrations, nevertheless there was an existence of ammonia in the region of ~3711 cm-1, ~2357 cm-1,. IR spectra of the synthesized polymer– Fe_3O_4 showed –OH (3425 cm-1), C–H (2357 cm-1), and C–C stretching (1457 cm-1), confirming the presence of polymer. 1316and 1457 cm–1 are associated with C–H symmetric and asymmetric stretching modes, respectively. The interaction of the surface of $Fe_3O_4$with Polymer and with cross-linked Polymer could be identified bythe presence of Fe–O–C stretching in the region of 1158-1022 cm-1

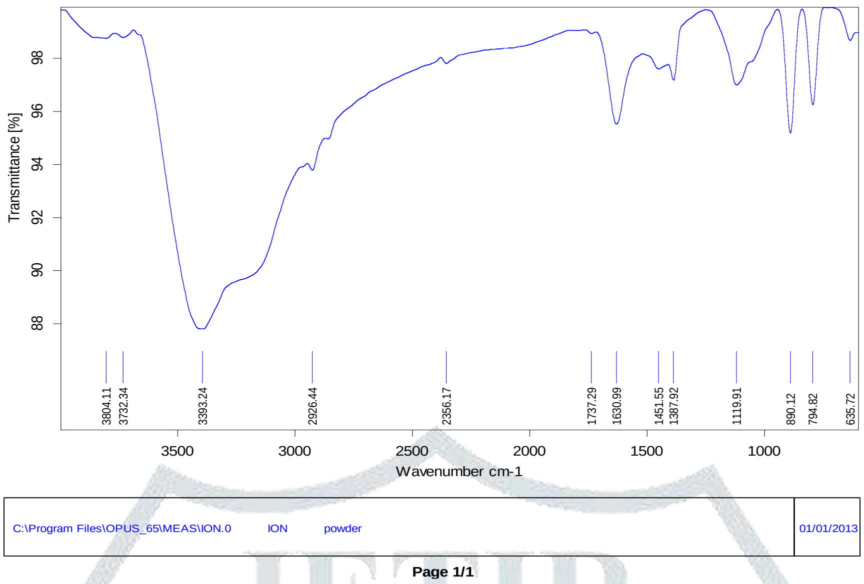


Fig. 4: IR Spectra of non coated IONP

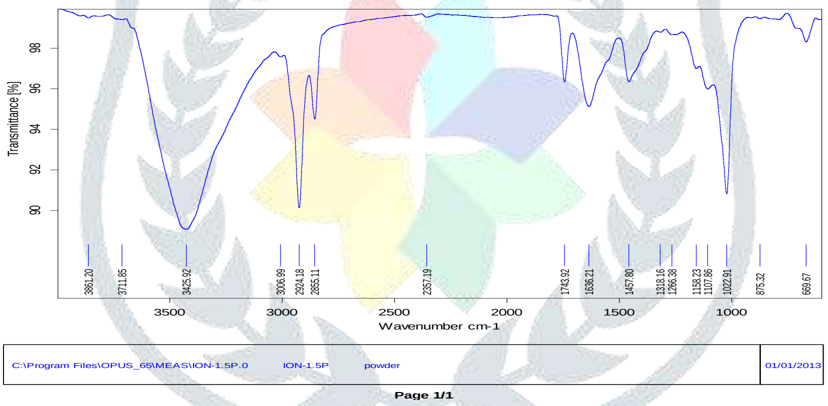


Fig.5:IRSpectraofcoated IONP

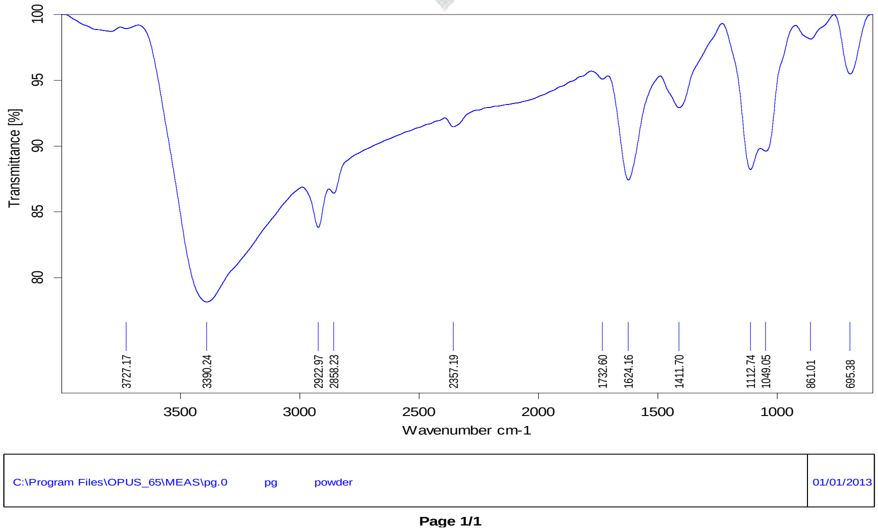


Fig. 6: IR Spectra of grafted particle

4. Conclusion:

It was found that prepared nanoparticles revealed the magnetic properties in water suspension when external magnetic field was applied, that particles were generally spherical in shape and have particle size between 20-50 nm. The presence of the polymer in the nanoparticles was confirmed by means of FTIR spectroscopy.Low concentration of Polymer in thepresence of crosslinker is highly recommended to generate supreme magnetic properties;hence forward possibly applicable as a part of a drug delivery system and water purification.

5. Scope for Future work:

In the coming years, despite all the recent progresses made, it is still a challenge to be faced that synthesis of high-quality functionalized magnetic iron oxide NPs with a tunable sizes and shapes in a controlled manner. Moreover synthesis and surface engineering of iron oxide NPs involves complex chemical, physical, and physic-chemical multiple interactions, it is the another challenge to understand the synthetic mechanisms in detail. However, the magnetic properties and function of uncoated and surface functionalized iron oxide NPs depend upon their physical properties: the size and shape, their microstructure, and the chemical phase in which they are present. Luckily, several physicochemical techniques have been developed to determine these parameters. Therefore, how to improve the stability and availability of functionalized iron oxide NPs in extreme environmental conditions, how to develop an efficient and orderly magnetic micro- or nano-assembly structures, and how to realize large-scale or industrial synthesis, these problems are urgent to be solved for obtaining a ideal functionalized iron oxide materials. For all that, we still believe the surface functionalization and modification of magnetic iron oxide NPs to introduce additional functionality will attract more and more attention. Furthermore, multifunctional magnetic iron oxide composite nanoparticle systems with designed active sites will promise for a various applications, such as catalysts, magnetic recording, bioseparation, biodetection, etc. The future work in this area must be focused on the research of the toxicity and degradability of uncoated and surface functionalized iron oxide NPs, and preparing it via green chemistry for reducing the environmental pollution in the removal of toxic heavy metals from the industrial wastewater as much as possible. Successful development in this area will aid the growth of the various scientific researches or industrial applications as well as improving the quality of life in the population.

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