

Surface Modification of Magnetite Nanoparticles Lift up the Thermal Stability and Furnishes Superparamagnetism for Poly Meta-Amiphenol Magnetite Nanocomposites

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Abstract

Modification of magnetite nanoparticle with m-aminophenol would results in the formation of a new nanocomposites, poly m-aminophenol magnetite (Pmap/Fe₃O₄) nanocomposites, synthesized by in-situ oxidative polymerization of meta-aminophenol using aqueous HCl and ammonium persulphate used as an oxidizing agent. The Pmap/Fe₃O₄ nanocomposites were characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction Analysis (XRD), Ultraviolet -Visible Spectroscopy (UV-VIS), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA). Magnetic properties of the Fe₃O₄ nanoparticles and Pmap/Fe₃O₄ nanocomposites were studied by using Vibrating Sample Magnetometer (VSM). The FTIR and UV-VIS investigation provided direct and clear evidence for the presence of Pmap shell on the surface of Fe₃O₄ nanoparticles. The XRD patterns indicated the crystalline nature for Pmap/Fe₃O₄ nanocomposites and amorphous peaks for Pmap. The thermal and magnetic properties of the nanocomposites were significantly varied from individual polymer; nanocomposites exhibited excellent thermal stability as compared to pure Pmap. The saturation magnetization value of Pmap/Fe₃O₄ nanocomposites is lower compared with the Fe₃O₄ nanoparticles, which showed the formation of single domain particles and exhibited superparamagnetism. These results confirmed that Pmap were successfully adsorbed/modified the surface of Fe₃O₄ nanoparticles.

Keywords: m-aminophenol; Pmap/Fe₃O₄ nanocomposites; Fe₃O₄ nanoparticles; in-situ polymerization; superparamagnetic

Introduction

Nanocomposites are very promising alternative that can be easily adapted to the requirements of materials with special chemical, electrical, and magnetic properties [1-3]. Research in the field of polymers mainly focused on the modification of existing polymers, so that their visibility and industrial applications could be further improved. One of the successful approaches has been made by preparing the composite polymer network containing different metal oxide nanoparticles such as Fe₃O₄, ZnO, NiO, MnO₂, TiO₂, and fly ash composites [4-6]. Important developments have been reported in drug targeting delivery systems, in which particles of metal oxides are embedded in biocompatible and biodegradable polymeric matrices that build

up in a new class of materials for various medical applications [7-9]. Magnetite (Fe₃O₄) based polymer nanocomposites have made considerable attention in the field of polymer chemistry and physics because of their various applications such as magnetic recording media, photonic crystallites, sensors, and actuators etc. It has been commonly recognized that the dispersion of nanoparticles into a polymer matrix depends on the size, shape, and polarity of nanofillers [10]. Magnetite is categorically the most commonly used material for biomedical applications due to its low toxicity, relative ease of synthesis, and high saturation magnetization [11]. The derivatives of PANI such as poly(o-toluidine), poly(o-anisidine), poly(aniline-co-o-nitroaniline) and poly(m-aminophenol) have attracted scientific interest as their conducting properties and solubility are superior over PANI [12]. Like polyaniline; polyaminophenols are interesting materials and have two groups -NH₂ and -OH both are oxidizing groups and as a result, they can show electrochemical behavior resembling anilines and phenols.

In this work, we proposed a new approach to modify or synthesize the Pmap/Fe₃O₄ nanocomposites, by simple in-situ method. In-situ polymerization was focused on the electrochemical interaction between metal oxide ions and polymers followed by oxidation reduction reactions to obtain homogeneous material, and retain its; control of the nanoscale structure, size and shape of nanocomposites [13-15]. Poly m-aminophenol (Pmap) synthesized from acidic medium is insoluble in water and most of the organic solvents even after dedoping. Based on spectral evidences, a ladder type structure was accepted. In polymerization of aminophenol, the relative position of amino and hydroxyl groups are more important, the amino groups on the surface of magnetite nanocomposites could be easily activated by different electrostatic interaction with various ligands suitable for biological applications [16].

Experimental

Materials

M-aminophenol (Merck, India), Ammonium hydroxide 25% (Merck, India), Hydrochloric acid (S.D. Fine Chem, India),

Ammonium persulphate, A.R (Spectrochem, India), Iron (II) sulphate heptahydrate (Merck, India), Iron (III) chloride hexahydrate (Merck, India). All chemicals used were of analytical grade.

Preparation of Magnetite (Fe₃O₄) Nanoparticles

Magnetite nanoparticles were prepared by chemical co-precipitation method. The stoichiometric ratio of Ferric/Ferrous salts (Fe³⁺/Fe²⁺) is taken in 2:1. 18 g of Iron (III) chloride hexahydrate (FeCl₃·6H₂O) and 9.2 g of Iron (II) sulphate heptahydrate (FeSO₄·7H₂O) are taken in 100 ml distilled water and stirred well for 15 minutes for complete dissolution. Then added 25% NH₄OH solution at regular intervals of time with constant stirring at room temperature until the pH between 8 and 14 for complete co-precipitation [17]. Heat the obtained precipitate at 80°C for 30 minutes in an R.B flask, a black precipitate was obtained exhibiting strong magnetic property. The precipitates were separated by a strong magnet at the bottom and washed with hot distilled water. Dried in an oven at 70°C for two days and it is finely grinded and sieved.

The chemical reaction of formation may be shown in equation (Eq. 1)



Synthesis of Poly m-aminophenol (Pmap)

Pmap was synthesized by taking 0.5M HCl by keeping map: APS (mol/mol) ratio 1.0/1.5 at room temperature (30°C). About 1.635g of m-aminophenol (map) was dissolved in 100 ml of 0.5M HCl. The oxidant Ammonium Persulphate (APS) 5.13 g was dissolved separately in minimum volume of water (25 ml) at room temperature. This APS water solution was added drop wise from a dropping funnel with 45 min and the reaction mixture was stirred constantly for 10–12 hour at room temperature. The solid polymer precipitate was filtered and it was washed with 0.2 M HCl with 2-3 times to remove the unreacted monomers and oligomers. Then the precipitate is washed several times with distilled water until the filtrate become colorless from light brown. Finally the brown colored polymer is dried at 65-70°C in an oven for about 5 hours [18].

Synthesis of Poly M-Aminophenol Magnetite (Pmap/Fe₃O₄) Nanocomposites

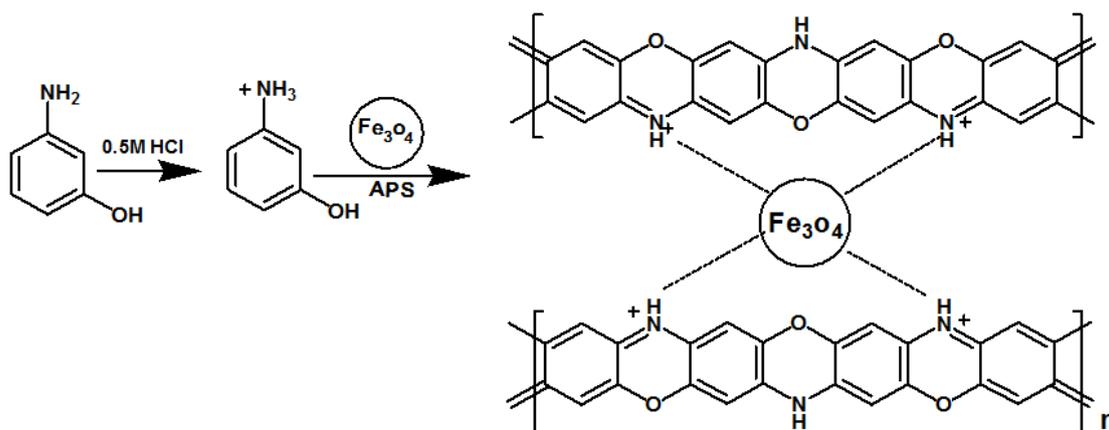
The same procedure was performed for the synthesis of Pmap/Fe₃O₄ nanocomposite by insitu oxidative chemical polymerization using m-aminophenol and Ammonium persulphate. About 5 g of magnetite is added to m-aminophenol in 0.5 M HCl solution. The APS solution was added drop wise to the reaction mixture with 45 minutes and stirred constantly for 4 hour at room temperature. While comparing with Pmap the reaction time was minimized for the nanocomposites otherwise over coating of polymer might took place and lost its magnetic properties. The precipitates were collected by magnetic separation and washed with dilute HCl and deionized water for several times. Dried under vacuum at 65-70°C for 5 hour.

Characterizations

Characterizations were done by JASCO FT-IR 5300 spectrometer using KBr pellet method, at room temperature the absorption bands were recorded in the region 500-4000 cm⁻¹. The average crystalline size was determined from the Debye-Scherrer equation, using XRD analysis. SEM images were performed using the JEOL Model JSM-6390LV scanning electron microscope. TGA was performed on Perkin Elmer Pyris Diamond 6 Thermo gravimetric analyzer and conducted at a heating rate of 10 °C per minute. Magnetic properties of the samples M Vs H @ Room Temperature were measured using a Lakeshore, USA, Model 7407 vibrating sample magnetometer.

Result and Discussion

Pmap/Fe₃O₄ nanocomposites were synthesized in acidic medium, the monomer map was stirred with oxidant, half the time was used as compared to the polymerization of pure Pmap; owing to the formation of multilayer of polymer Pmap on the surface of Fe₃O₄ nanoparticles and lost its magnetic property. The proposed polymerization mechanism was shown in scheme1. In 0.5 M HCl concentration only -NH₂ groups were protonated to -NH³⁺ groups which contains sufficient number of molecule to protonate all the -NH centers of the synthesized polymer and so -NH₂ groups of all the monomers was protonated in the medium. The two groups -OH and -NH³⁺ have comparable oxidation potential in lower HCl concentration causes oxidization of both the groups [19] and the ladder polymer was obtained in dilute acid medium. The m-aminophenol is adsorbed on the surface of Fe₃O₄ via hydrogen bonding between the amino and hydroxide groups of m-aminophenol and Fe-O[16].



Scheme: 1 proposed mechanism of synthesis of Pmap/Fe₃O₄ nanocomposites.

FTIR Analysis

In Figure 1, the FTIR spectra of pure Pmap, a broad peak appears in the region 3600–3300 cm⁻¹ correspond to -NH stretching vibration modes. A peak at 2930 cm⁻¹ is assigned to C-H aromatic stretching in phenyl ring. The peaks at 1625 cm⁻¹ and 1505 cm⁻¹ are assigned to the C-N stretching of the quinoid rings and the C=C stretching of the benzenoid rings, respectively. The peak at 1336 cm⁻¹ was assigned to the C-N stretching vibrations of the second aromatic amine in the polymer [20]. The peak at 1121 cm⁻¹ was ascribed to the stretching of the C-O bond and all peaks supports the formation of Pmap from m-aminophenol [18]. In Fe₃O₄ nanoparticles the broad peak in the region 3600-3100 cm⁻¹ was attributed to the stretching vibrations of -OH, (water molecules) absorbed by the nanoparticles and a peak at 592 cm⁻¹ indicated the Fe-O bond vibration of Fe₃O₄ nanoparticles. For Pmap/Fe₃O₄ nanocomposites, the peaks in between 3500–3300 cm⁻¹ correspond to -NH stretching and other absorption bands are identical to that of pure Pmap. In addition to these bands a band at 589 cm⁻¹ was characteristic of Fe-O bond. All these resulting strong interfacial electrostatic interaction between the nanoparticle and the polymer chain.

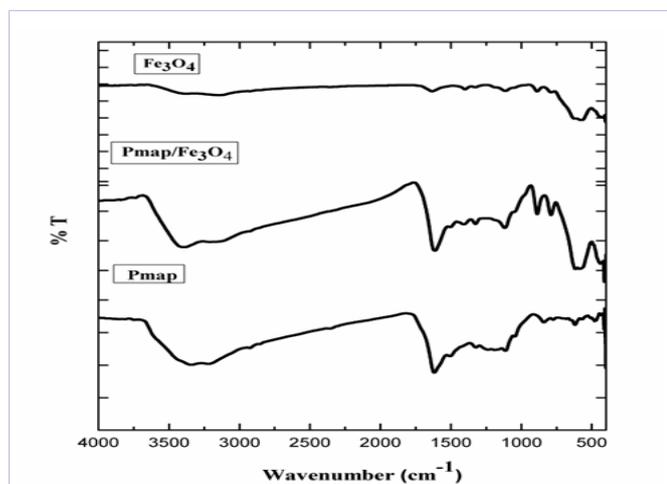


Figure 1: FTIR Spectra of Pmap, Pmap/Fe₃O₄ nanocomposites and Fe₃O₄ nanoparticles.

XRD Analysis

Figure 2 typical X-ray diffraction lines for Fe₃O₄ nanoparticles (2θ =30.100, 35.70, 43.70, 53.480, 56.80and 63.170) are observed in the 10–700 2θ range. Diffraction lines are indexed to (220), (311), (400), (422), (511), and (440) planes are of the Face-Centered Cubic (fcc) of Fe₃O₄ nanoparticles nanoparticles (JCPDS file, No.00-011-0614) [21]. Similar peaks were observed in the XRD of synthesized Pmap/Fe₃O₄ nanocomposites which retained its crystalline nature [22] and magnetite stable phase, which unchanged during the synthetic methodology. The average crystalline size D, was calculated using the Debye-Scherrer formula $D = k\lambda / (\beta \cos\theta)$. The average crystalline size values Fe₃O₄ nanoparticles and Pmap/Fe₃O₄ nanocomposites were 7 nm and 18 nm, an increase in size was found, that the nanoparticles are embedded in the polymer matrix. The XRD pattern of pure Pmap exhibited broad amorphous diffraction peaks indicating the amorphous nature of Pmap.

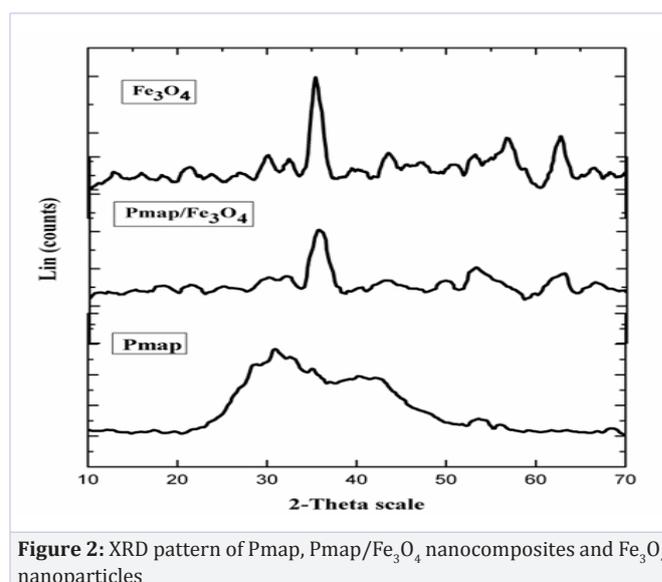


Figure 2: XRD pattern of Pmap, Pmap/Fe₃O₄ nanocomposites and Fe₃O₄ nanoparticles

SEM Morphology

Figure 3 the SEM images, Fe_3O_4 nanoparticles were well dispersed with spherical surface and are observed to be relatively loosely packed. The surface morphology of Pmap, looked like

overlapped spherical structures like bunch of grapes [23]. In Pmap/ Fe_3O_4 nanocomposites, the particles are aggregated, nearly-spherical morphology and distributed non-uniformly resulting in the encapsulation of magnetite nanoparticles by Pmap.

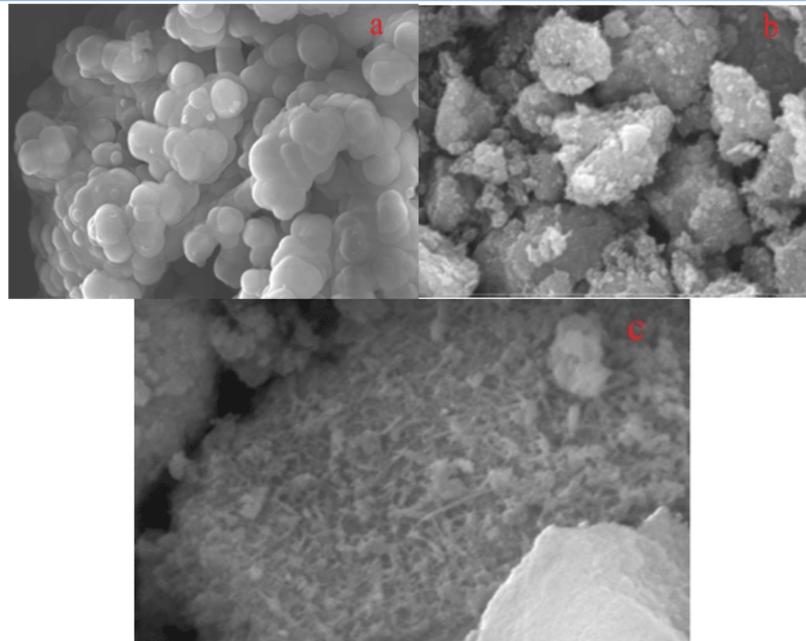


Figure 3: SEM images of (a) P Map, (b) P Map/ Fe_3O_4 nanocomposites and (c) Fe_3O_4 nanoparticles

UV-VIS Analysis

Figure 4 UV-VIS spectra of Pmap/ Fe_3O_4 nanocomposites, absorption maximum at ~ 311 nm might be due to π - π^* transitions of conjugated C=C in the aromatic rings [24]. After polymerization the structure would be ladder type, the C=O groups were absent thus only π - π^* transition was seen. The disappearance of n- π^* transition reveals the absence of keto group and a ring structure in the nanocomposites at its synthesis in lower HCl concentrations [25].

TGA Analysis

TGA curves of the Fe_3O_4 nanoparticles, Pmap/ Fe_3O_4 nanocomposites and pure Pmap are shown in Figure 5 the initial weight loss up to 120°C is due to the removal of water. The second weight loss which occurs in the range 150°C to 190°C corresponds to the sublimation and removal of low molecular weight polymer/oligomer from the polymer matrix. Distinctive thermal stability was shown by Fe_3O_4 nanoparticles and a steady state was observed. The decomposition of Pmap starts nearly 340°C ,

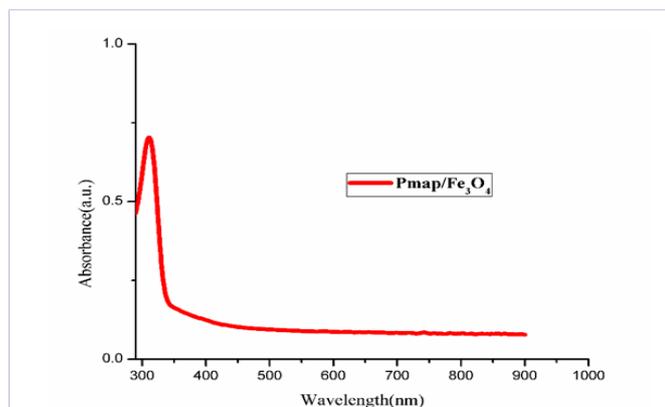


Figure 4: VSM of Pmap/ Fe_3O_4 nanocomposites and Fe_3O_4 nanoparticles.

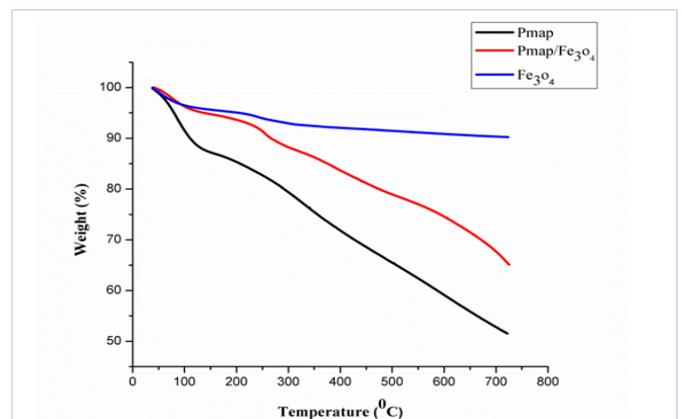


Figure 5: TGA of Pmap, Pmap/ Fe_3O_4 nanocomposites and Fe_3O_4 nanoparticles

while comparing with Pmap/Fe₃O₄ nanocomposites temperature between 390°C - 463°C corresponds to the decomposition of the skeletal polymer chain in the structure after the elimination of the dopants. Enhanced thermal stability was observed for the Pmap/Fe₃O₄ nanocomposites and its complete decomposition starts at 590°C might be due to the strong binding interaction between Pmap and Fe₃O₄ nanoparticles, which restricts the thermal motion of Pmap chain in the nanocomposites.

VSM Analysis

Figure 6 the magnetic properties of the nanoparticles and the nanocomposites were studied by using a vibrating sample magnetometer (VSM) as a function of applied magnetic field at room temperature (300K). Saturation magnetization (Ms) and retentivity (Mr) values of Fe₃O₄ nanoparticles and Pmap/Fe₃O₄ nanocomposites were 37.53, 30.04 emug⁻¹ and 0.1428, 0.3996 emug⁻¹ respectively as shown in Table 1. The saturation magnetization value of Pmap/Fe₃O₄ nanocomposites was lowered as compared with Fe₃O₄ nanoparticles caused by the decrease of Fe₃O₄ content in the nanocomposites by surface modification. The nanocomposites did not exhibit hysteresis loop and

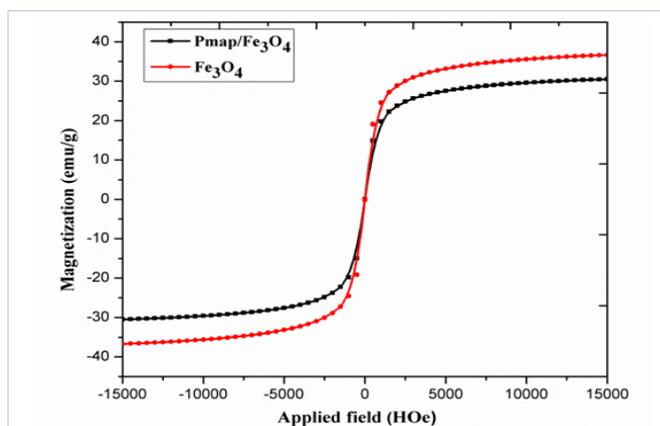


Figure 6: VSM of Pmap/Fe₃O₄ nanocomposites and Fe₃O₄ nanoparticles

coercivity; the lack of hysteresis loops and coercivity features of superparamagnetic particles with single-domain [26]. The magnetic responsiveness of Pmap/Fe₃O₄ nanocomposites was still strong enough to be efficiently separated from a solution using strong magnets [27] (Table 2).

Table 1: Comparison of present work results with published articles

Samples	IR band of Fe-O bond(cm ⁻¹)	Crystalline size (nm)	π-π* transitions(nm)	Ms (emug ⁻¹)	References
(a) Fe ₃ O ₄ nanoparticles	592 cm ⁻¹	7 nm		37.53 emug ⁻¹	Present work
(b) Pmap/Fe ₃ O ₄ nanocomposites	589 cm ⁻¹	18 nm	311 nm	30.04 emug ⁻¹	Present work
(c) PANA/Fe ₃ O ₄ nanocomposites	586 cm ⁻¹		275-283 nm	0.00027-0.0054 emug ⁻¹	P. Jayakrishnan, M. T. Ramesan (2016)
(d) Magnetite/ poly(aniline-co-8-amino-2-naphthalenesulfonic acid	580 cm ⁻¹	5.6 nm	350 an 440 nm	44.57 emug ⁻¹	Kakarla Raghava Reddy, Kwang-Pill Lee, Anantha Iyengar Gopalan and Ali Md Showkat (2006)
(e) PMMA/Fe ₃ O ₄ nanocomposites	580 cm ⁻¹	-	-	0.67-5.12 emug ⁻¹	Maneesh Kumar Poddar, Mohammed arjmand, Uttandaraman Sundarraj, Vijayanand S, Moholkar (2018)
(f) Fe ₃ O ₄ @PANI nanocomposites	600 cm ⁻¹	-	-	3.75 emug ⁻¹	Sanjeev Kumar and Sapna Jain (2014)
(g) PANNA/ Fe ₃ O ₄ nanocomposites	-	19.04-23.32 nm	-	19.01-23.09 emug ⁻¹	M.Sh.Zoromba, Mohamedi.M.Ismail, M.Bassyouni, M.H.Abdel-Aziz, Numan Salah, Ahmed Alshahrie, Adnan Memic (2017)

(h) PANI/Fe ₃ O ₄ nanocomposites	550 cm ⁻¹	13.4 nm	-	22.9 emug ⁻¹	Hongbo Gu, Yudong Huang, Xi Zhang, Qiang Wang, Jiahua Zhu, Lu Shao, Neel Haldolaarachchige, David P. Young, Suying Wei, Zhanhu Guo (2011)
(i) BISA-APTSCMNPs	573 cm ⁻¹	35-50 nm	210-285 nm	18 emug ⁻¹	Alireza Banaei, Hossein Vojoudi, a Soheyla Karimi, a Shahriyar Bahar, a Eslam Pourbasheera (2015)
(j) Fe ₃ O ₄ @PANI@P(MAc-co-AA)	577 cm ⁻¹	35.6 nm	275 nm	29.77 emug ⁻¹	Fatemeh Khodadadi, Peyman Najafi Moghadam, Mohammad Mahmoodi Hashemi (2016)
(k) PANI-Fe ₃ O ₄ nanocomposite	620 cm ⁻¹	11.2-25.3 nm	-	74.3 emug ⁻¹	A.C.V. de Araújo, R.J. de Oliveira, S. Alves Júnior, A.R. Rodrigues, F.L.A. Machado, F.A.O. Cabral, W.M. de Azevedo (2010)

Table 2: Magnetic properties Ms and Mr values of (a) Fe₃O₄ nanoparticles, (b) Pmap/Fe₃O₄ nanocomposites

Samples	Ms (emug ⁻¹)	Mr (emug ⁻¹)
(a) Fe ₃ O ₄	37.53	0.1428
(b) Pmap/Fe ₃ O ₄ nanocomposites	30.04	0.3996

Conclusions

The Pmap/Fe₃O₄ nanocomposites were successfully prepared by simple in situ oxidative chemical polymerization methods. The polymer was adsorbed on the surface of Fe₃O₄ via hydrogen bonding and electrostatic interaction between the amino and hydroxy groups of m-aminophenol and Fe-O. The characteristic Fe-O band in the FTIR spectra directly gives the metal co-ordination in the nanocomposites. UV studies revealed the formation of conjugated double bonds in the rings and intermolecular interaction between Fe₃O₄ nanoparticles and Pmap polymer. The morphological observations indicated that the nanoparticles were uniformly distributed within the macromolecular chain are spherical in shape. From XRD analysis the nanocomposites were crystalline in nature and size increase was observed as compared with Fe₃O₄ nanoparticles while Pmap was amorphous in nature. Rise in thermal stability was observed for the nanocomposites at 590°C as compared to Pmap might be due to the interaction between Pmap and Fe₃O₄ nanoparticles. VSM gives superparamagnetic nature and lowering of saturation magnetization value which indicated the overlay of polymer on nanoparticles. The prepared nanocomposites were able to use in different applications due to its higher thermal and magnetic properties.

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