SYNTHESIS AND CHARACTERIZATION OF MAGNETITE-POLYANILINE USING CHEMICAL PRECIPITATION METHOD

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Abstract:

Polyaniline/magnetite nanocomposites have been synthesized by chemical precipitation method and its structural characterization were carried using XRD, IR and UV visible spectroscopy. The synthesis is based on the well-known chemical oxidative polymerization of aniline in an acidic medium, with potassium peroxydisulfate as the oxidant. In the present work, polymerization of aniline was carried out in the presence of ferric chloride and ferrous sulphate in alkali medium and then synthesized nanocomposite material annealed at different temperatures. Results confirm the formation of nanocomposite polyaniline magnetite with the crystalline size of 46.42 nm. FT-IR confirms the existence of polyanilne and metal oxide in the composite material. UV-Visible spectroscopy results indicates the molecular level interaction of magnetite nanoparticles in the composite material.

Keywords: Magnetite, polyaniline, Emeraldine base, conducting polymer, crystalline phase.

Introduction:

Metal-polymer nanocomposite has gained considerable attention in various fields like corrosion inhibition coatings, industrial applications, electrical and electronic fields. Magnetic nanocomposite materials have attracted increasing attention because they offer the possibility of a nanostructure materials with diverse applications for immunity assay (Ugelstad J., 1992), separation and purification of biomolecules (Meldrum F., 1992, Tanaka T., 2000) extensive researches have been carried out to develop superparamagnetic organic/inorganic hybrid spheres for biomedical applications as carriers for targeted drug delivery

(Murthy N., 2002), biomagnetic separations, and biosensors (Martin C., 1998, Chan W., 1998, Cao Y., 2002, Wang D., 2004, Mornet S, 2004.) rechargeable batteries, light–emitting diodes, nonlinear optical devices, sensor for medicine and pharmaceutics apparatus, membranes for separation of gas mixture, protection against corrosion, conducting paints and glues and others. Great interest has been focused on polyaniline (PANI) in the field of conducting polymers, due to its important characteristics in excellent chemical stability and obtained in relatively easy, inexpensive and with high yield. The efficient polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation. A variety of inorganic and organic acids of different concentration have been used in the synthesis of PANI; the resulting PANI, protonated with various acids, differs in solubility, conductivity, and stability (Trivedi D., 1997). These composites are conducting polymers have been widely used because of their lower density as well their good environmental stability. The preparation of stable Fe_3O_4 nanoparticles is a challenge as the nanoparticles possess high surface area to volume ratios and tend to aggregate to reduce their surface energy. In addition, the strong magnetic dipole–dipole interaction and Van der Waal's attractive forces among the nanoparticles also cause the particles to aggregate (Gupta A, 2005)

In this paper, we report the synthesis of Magnetite-Polyaniline by chemical precipitation method and its characterization has been studied.

Experiment:

1) **Synthesis of Magnetite-Polyaniline:**

10 ml of aniline was added to the 100ml solution of 2M HCl. The solution was stirred for half an hour to get a clear and homogenous liquid. After that, the glass beaker was placed in an ice-bath so that the addition of potassium peroxydisulfate takes place in cooling condition. The concentration of potassium peroxydisulfate was 0.12M and addition takes place in such a manner that 50ml of the oxidation solution added

in aniline- HCl solution takes 30-40 minutes i.e. oxidation agent added very slowly dropwise in ice-bath condition. After addition of oxidation agent, the solution turns green-blue in colour resulting in the formation of polyanilne in emeraldine form. To this solution 10ml of 0.1M ferric chloride and 10ml of 0.05M ferrous sulphate was added. Both the solution was prepared in HCl (1M) solution. The solution was stirred for half an hour. After addition of 0.1M NaOH solution to the above reaction mixture. Green colour changes to black indicating the formation of the magnetite nanoparticles. The solution was stirred vigorously for 6 hours to obtain a homogenous mixture of the nanocomposite polymer. The solution was filtered, and washed with deionize water and then annealed at 200, 400, 600 and 800^{o}C.

Results and Discussion:

1. X-ray diffraction analysis:

Fig. 1a) show the XRD pattern of pure polyaniline. The pure state of polyaniline shows amorphous nature. X-ray diffraction pattern of amorphous polymer will not show any sharp and highly intense peaks whereas the nanocomposite of amorphous polymer show sharp and highly intense peaks. This is due to the development of crystallinity in the amorphous polymer as shown in Fig.1b. Fig. 1b shows the X-ray diffraction (XRD) patterns of PANI/Fe_3O_4 annealed at 600^{o}C using Cu Kα radiation (λ = 0.154nm). The diffraction peaks at 2θ = 32.948, 35.445 and 53.905 correspond to (221), (311) and (440) crystallographic planes of the spinel phase of Fe_3O_4, respectively with interplanar spacing of d= 2.7165, 2.53123 and 1.69938. The crystalline size of magnetite polyaniline can be calculated using Scherer's formula:

$$D = \frac{0.94\lambda}{\beta \ \mathrm{Cos}\theta}$$

Where 'λ' the wavelength of X-rays (0.154nm), θ is the Bragg's angle, β is the full width at half maximum.

The broad peak of XRD patterns clearly indicates that particle size is of nanometer dimension. The lattice constant and other parameters are calculated using relation.

$$a = d\sqrt{h^2 + k^2 + l^2}$$

where, (a) is lattice constant; d is inter planar spacing; (hkl) are Miller Indices.

The peak at 2θ = 32.948 is chosen to calculate the crystallite size of the composite material and was found to be 46.42nm.

Polymer	2θ (degree)	Interplanar spacing 'd'	hkl	Lattice constant	Relative Intensity
Magnetite Polyaniline	32.948	2.7165	(221)	8.1495	3.82%
	35.445	2.53123	(311)	8.3951	10.54%
	53.905	1.69938	(440)	9.6131	4.93%

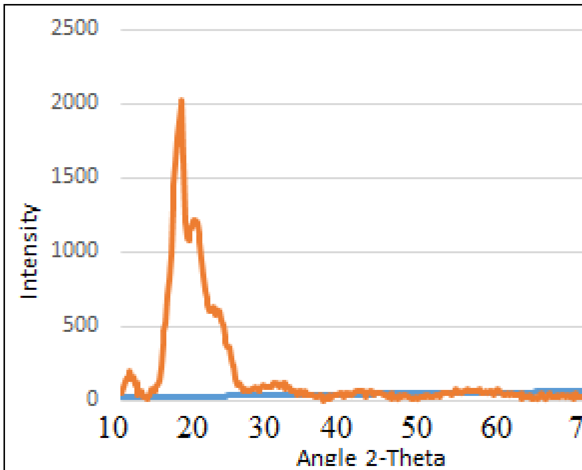

Fig. 1a XRD pattern of pure polyaniline

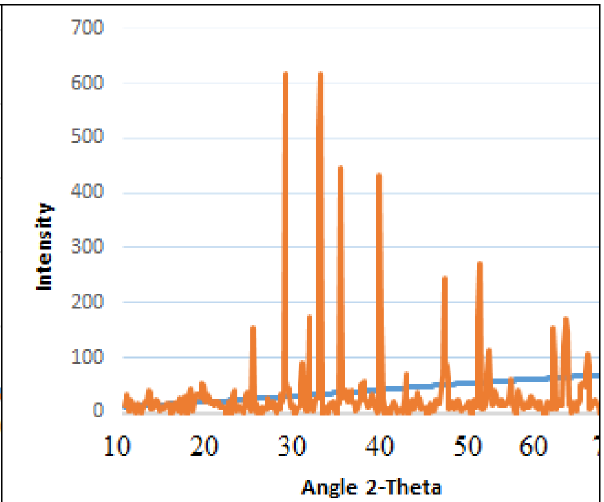

Fig. 1b XRD pattern of Magnetite Polyaniline at 60

2. **Infrared Spectroscopy:**

IR spectrum of polymer nanocomposite shows the presence of both nanomaterial and polymers (depending upon the polymer chain) at various frequencies. Fig. 2. shows the FT-IR spectra of pure Polyaniline and its composites with different annealation temperature. The strong absorption peak of Fig. 2a at 3440 and 2925 cm^{-1} are assigned to the N-

H stretching vibration of amino group of polyaniline. The band at 1445cm^{-1} indicates the stretching frequency of the benzenoid rings. The FT-IR spectra of Fig. 2b,2c,2d corresponds to magnetite –polyaniline composite material. The band at 3435 cm^{-1} and 3465 cm^{-1} are assigned to N-H stretching vibrations of amino group indicate $–NH_2$ group in structural units of PANI rods. The band at 1639 cm^{-1} corresponds to C=C stretching vibration in phenyl ring which indicate formation of Quinone form of polymer. 1456 and 1410 cm^{-1} arise due to benzenoid ring units. The band at 1186 cm^{-1} attributed to N-Quinoid phenyl ring of polyaniline. While 1304 cm^{-1} correspond to the N-H bending mode of benzenoid rings. The band at 850 cm^{-1} is a characteristics peak of C-H vibration out of plane bending of 1, 4-disubstituted benzene ring of polymer. Fig. 2c,2d that have peak at 596cm $^{-1}$ and 594 cm^{-1} are attributed to the intrinsic vibration of Fe-O bond in synthesized magnetite-polyaniline polymer. The above FT-IR data clearly confirms the formation of magnetite-polyaniline and also confirms the presence of Fe-O bond which are bounded to the nitrogen atom of the polyaniline.

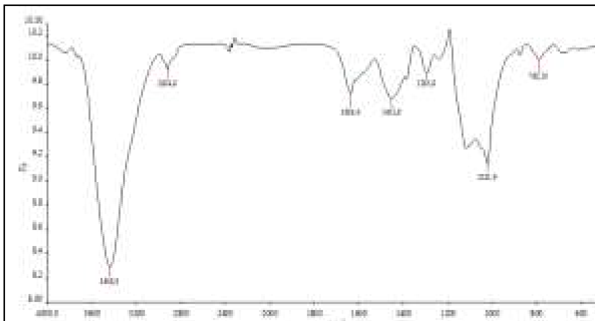

Fig. 2a) FTIR Spectra of Pure Polyaniline

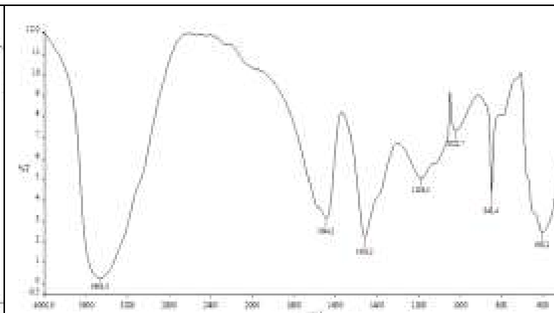

Fig.2b) FTIR Spectra of Magnetite-Polyaniline at 400°C

Fig.2c) FTIR Spectra of Magnetite-Polyaniline at 600°C

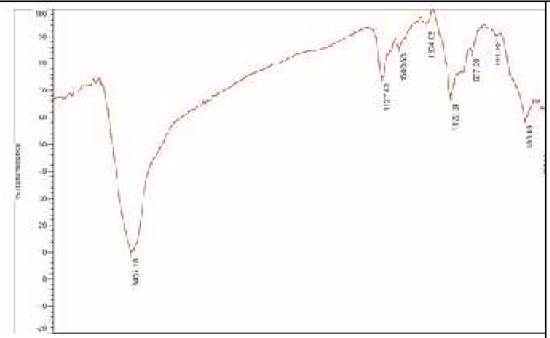

Fig. 2d) FTIR Spectra of Magnetite-Polyaniline at 800°C

3. UV-Visible Spectroscopy:

Fig.3. shows the UV-Vis spectra of PANI-magnetite nanocomposite material annealed at different temperatures as 200°C, 400 °C, 600 °C and 800 °C. It can be seen from the figure that there are two characteristics peaks one at 320 nm and 640 nm.The first peak at 310 nm arises due to π→π* while the second at 640 nm is due to the transition of two benzenoid rings to the Quinoid rings of the PANI chain. UV-Visible data suggested that the loading of iron oxide have an effect on these benzenoid ring of the polymeric material. For the pure PANI, absorption bands occurs at an wavelength of 430 nm-520 nm, indicates blue shift of both the absorption band of the polymer material and also confirms the interaction of the ferric ions with nitrogen atom of the polyaniline.

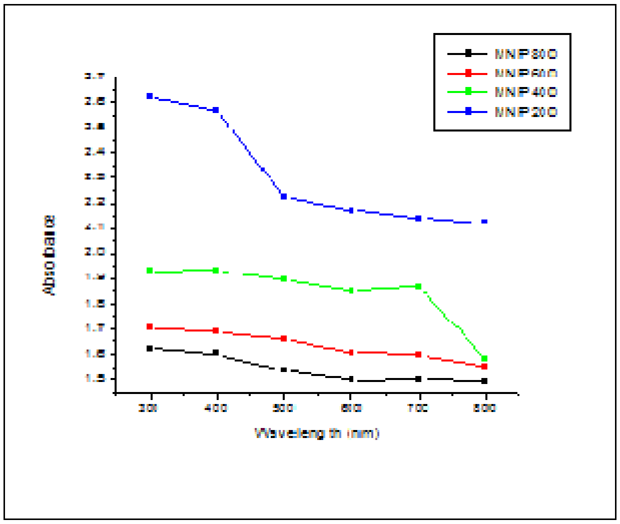

Fig. 3: UV-Visible Spectra for magnetite-polyaniline annealed at different temperature

Conclusion:

We have synthesized polyaniline nanocomposite material by chemical precipitation method. Polymerization of aniline carried out in the presence of potassium peroxydisulfate in acidic medium which was then bind up with ferric ions in alkali medium. The PANI-Fe_3O_4 ferromagnetic nanocomposites have been characterized by FT-IR, UV-Vis and XRD techniques. The FT-IR and UV-visible results demonstrates the formation of Polyaniline in the presence of Fe_3O_4 nanoparticles. XRD results shows the formation of crystalline nanoparticles of nanocomposite material

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