Stable magnetically sensitive $CoFe_2O_4$/PVA nanocomposite magnetic hydrogels: synthesis and characterization

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Abstract

Magnetic nano sized particles of cobalt ferrite have been synthesized in an aqueous solution by cost effective and reliable co-precipitation method. After that via crosslinking $CoFe_2O_4$-PVA nanocomposite magnetic hydrogel were prepared. Three samples were prepared at different pH concentration at 8, 9, 10 and average particles size could be varied between 7-13 nm. As the pH increased, the average particle size decreases. Characterization of nanoparticles can be done by Powder XRD, Transmission Elecrtron Microscopy (TEM). $CoFe_2O_4$ and PVA are used for the study because of its specific properties which is suitable for various technological fields mainly in pharmaceutical, medicine and biomedical applications.

Keywords: Cobalt- Ferrite, PVA, Nano magnetic particles, Co-precipitation, XRD, TEM, Crosslinking

1. INTRODUCTION

$CoFe_2O_4$ (cobalt ferrite) having inverse spinal structure due to which it is a subject of interest in lately many years. $CoFe_2O_4$ showing many promising technological advantages especially in the field of biomedical **[4]**. Due to having some specific properties mainly its high magnetocrystalline anisotropy $CoFe_2O_4$ is founded as suitable material for various medical applications like hyperthermia, magnetofection, MRI, medical diagnostics, biosensing and magnetic drug delivery. Also from the different type of ferrites, spinal ferrite is investigated widely because of their electrical, magnetic and physical properties remarkably and having wide practical application in the field of biomedical, information storage system, ferrofluidic technology and many more technological applications. Spinel ferrite unit cell consisting two sub lattices i.e. Tetrahedral [A] and Octahedral [B] sites. Spinel ferrites are classified into three categories viz Normal (Zinc ferrite, Cadmium ferrite), Inverse (Cobalt ferrite, nickel ferrite) and Random spinel (Magnesium, copper ferrite). $CoFe_2O_4$ having certain properties like higher coercivity (at room temperature is 4.3 KOe), saturation magnetization is moderate (80 emu/g) and its higher cubic magnetocrystalline anisotropy which is originated from the crystal lattice's spin-orbit coupling. Basically cobalt ferrite comes under the categories of hard magnetic material with high Curie temperature about 520°C **[2-4]**. In a number of pharmaceutical, medicine and biomedical applications Poly (vinyl alcohol) polymer plays important role because of their desirable characteristics. PVA shows a simple chemical structure with pendant hydroxyl group. PVA is produced by the polymerization of vinyl acetate to poly(vinyl acetate) preceded by the hydrolysis of poly(vinyl acetate) to poly(vinyl alcohol). For the synthesis of PVA, raw material used is vinyl acetate monomer because of the reason that the stable form of vinyl alcohol does not exist. Physical properties like swelling and mucoadhesive, chemical properties, water solubility (very less solubility in ethanol and insoluble in organic solvent) and crystallizability of PVA is affected by the degree of

hydrolysis or the acetate group content in the polymer and following properties make them suitable for drug delivery. PVA can be crosslinked by the help of difunctional crosslinking agents. PVA is generally known as homopolymer, ethanol, vinol, alvyl, coel, alkotex, lemol and PVOH. PVA is granular powder of white colour which is odourless, tasteless, and translucent. PVA shows excellent water imbibing property because it is hydrophilic polymer **[11-12]**. PVA shows hemocompatible nature. PVA is categorised into two parts: Partially hydrolyzed (used in food) and fully hydrolyzed.

Ferrogels or commonly known as magnetic nanocomposite hydrogel are soft polymer matrix containing magnetic particles as a filler that allow the gel to be activated by magnetic field. Ferrogel comes under the low modulus (flexible) smart magnetic material category **[13]**. Basically ferrogel is a physically or chemically cross-linked network swollen by a ferrofluid. Ferrofluids are colloidal suspensions of magnetic nanoparticles which respond to externally applied magnetic field enabling the possibilities of changing the magnetic flux by moving a magnet about it externally **[15]**. In this paper we perform a theoretical study of preparation methods and properties of ferrogels and its application in various fields. Due to its wide application on various fields, ferrogels have fascinated the interest of an Engineers, chemists and physicists now days.

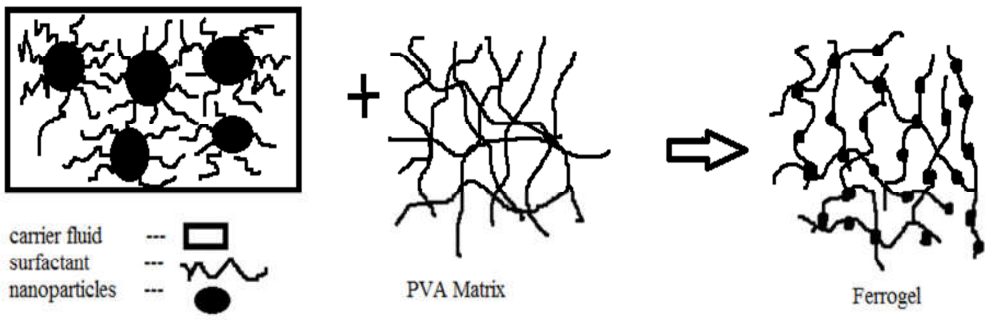

Figure 1. Schematic diagram of the preparation of ferrogel or magnetic nanocomposite hydrogel

Many researchers used various methods for the synthesis of nano magnetic particles varying grain size like Inverse micelles **[5]**, Mechanical milling **[6]**, Melt spinning **[7]**, Chemical vapour deposition **[8]**, Inert gas condensation **[9]**, Pulsed laser ablation **[10]**, Sputtering etc. Nano magnetic particles can also be synthesized by various chemicals methods like Co-precipitation, Sol-gel technique, Oxidation, Reverse micelles etc.

Among various methods available for the preparation of ferrofluids, Chemical co-precipitation technique **[14]** is generally used because of its advantage over other techniques. It is more economical and effective technique, it requires less time as compared to other techniques and there is less chances of contamination. Additionally, the method can be used in an industrial basis, since it can be readily mechanized and automated.

This technique has potential to obtain the controllable particle size and its distribution without affecting the composition, crystallinity and morphology of the particles. The Chemical co-precipitation technique is widely used because it has many advantages over other techniques and also this method is the archetype route used for the preparation of all cubic spinel ferrite. The present work aims to investigate the effect of pH on the size of cobalt ferrite nanoparticles and Powder XRD, TEM and Rheology performance is done in order to characterize their properties. Combination of different characterization process has been done for optimizing the properties.

2. EXPERIMENTAL

For the synthesis of magnetic particles based hydrogel, a two step synthesis method is generally used. Firstly, Cobalt-Ferrite ($CoFe_2O_4$) nanoparticles were synthesized by well known chemical co-precipitation method and then particles are dispersed in water which acts as a carrier fluid. After that a desirable amount of PVA (poly(vinyl alcohol)) is mixed with water and then the solution was constantly stirred at 300 rpm for 15 hours at room temperature.

Firstly, water-based ferrofluid is prepared when a salt solution of ferric chloride ($FeCl_3$) and cobalt chloride ($CoCl_2$) were mixed to maintain Fe^{3+}/Co^{2+} molar ratio proportion 2:1. Thus the precipitate occurred immediately to change the reaction solution into dark brown colour. As primary surfactants oleic acid is used and it is added to the solution at the time of precipitation in order to avoid agglomeration or clumping. As precipitation agent, ammonia solution (25%) is used at temperature 80°C it is added to the solution with constant stirring rate 600 rpm during precipitation **[1]**. Variations in temperature is continuously monitored and maintained about 80±2°C.

Resulted precipitate is washed 8-9 times to remove the ammonia contain and then pH is neutralized **[3]**. The water used here is distilled water. Obtained Cobalt-Ferrite particles were dispersed in sodium oleate aqueous solution, which works as a secondary surfactant in order to get FFW and it enhances the adsorption of PVA in the surface of $CoFe_2O_4$ nanoparticles**[19]**.

After that, three samples of $CoFe_2O_4$-PVA nanocomposite magnetic hydrogel were prepared namely Sample A(at pH 8), Sample B(at pH 9), Sample C(at pH 10) in a PVA solution which is bubble free. Uniformity of the solution is maintained by subjecting it to constant stirring at 120 rpm for 15 hours at environment temperature. Consequently a uniformly distributed magnetic fluid is cross-linked polymer solution was obtained. For the structural characterization X-ray diffraction patterns were measured by Rigaku XRG 2 KW, Powder XRD and at 40kV, 30mA using CuKa (1.546A) radiation diffraction patterns were recorded and TEM measured by High Resolution Transmission Electron Microscope (HRTEM, FEI, Tecnai G2, F30, STWIN) operated at 300 keV accelerating voltage.

3. RESULT AND DISCUSSION

(a) Structural Characterization

Phase information of the material is determined by the diffraction peak positions and order of crystallinity is determined by broadness. Figure (2) shows XRD pattern of the cobalt ferrite nanoparticles synthesized at pH 8, 9, 10 and prepared powder $CoFe_2O_4$ is in cubic crystalline structure confirming all the peaks in the pattern matching well with JCPDS card. Sharp peaks of the XRD diffractogram shows an excellent crystallinity, with peaks corresponds to planes 30.2° (200), 35.4° (311), 43.2° (400), 57.5° (511), 62.3° (440) of $CoFe_2O_4$. Peaks broadening are an indication of the finite size, accordance with the Debye-Scherrer equation $D = \frac{K\lambda}{\beta Cos\theta}$, is used where crystallite size is D, K is Scherrer's constant (0.89), λ is X-ray wavelength (=1.54056 Å, for Cu Kα target), β is Full Width at Half Maxima (FWHM) of the corresponding diffraction peak which is measured in radians and θ is the angel between sample surface and the diffracted beam.

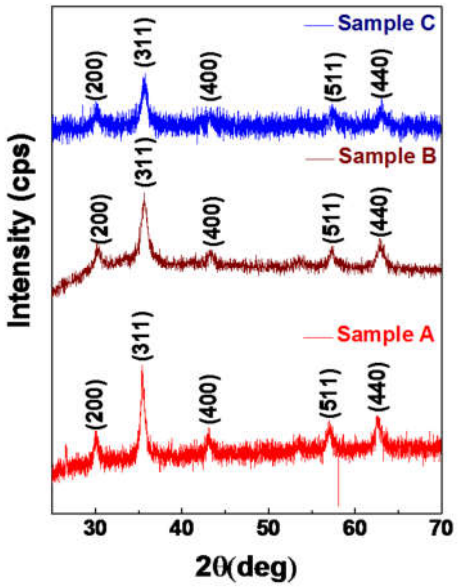

Figure 2. XRD pattern of $CoFe_2O_4$ nanoparticles prepared by Co-precipitation

Figures 3(a) shows the XRD image of $CoFe_2O_4$-PVA gel and corresponds to PVA broad diffraction peaks find out at 19.5°. Figure 3 is the XRD of $CoFe_2O_4$-PVA gel and Figure 4 is the image of XRD of $CoFe_2O_4$-PVA gel after 30 days. Two XRD measurements have been done in the interval of 30 days for the checking of the stability of the ferrogel samples. From the investigation we get the same kind of results as previous which shows the stability of the synthesized ferrogel samples.

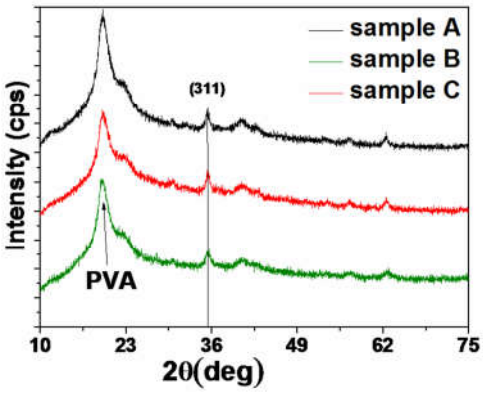

Figure 3(a). XRD of $CoFe_2O_4$-PVA gel

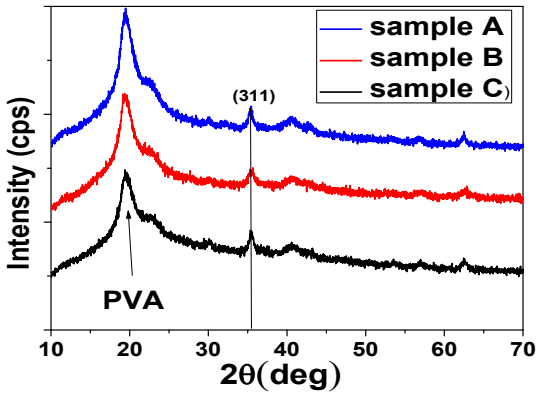

Figure 3(b). XRD of $CoFe_2O_4$-PVA gel (after 30 days)

(b) TEM testing

For the study morphology and microstructure of nanostructured or nanoparticles materials TEM analysis is performed and also it is having high resolution. High Resolution Transmission Electron Microscope (HRTEM) operating at 300 keV accelerating voltage is used for the detailed investigation of the sample A (at pH 8), B (at pH 9), C (at pH 10). It is clear from the figure (4) that the TEM image shows the significant variation in the particles size with increasing pH concentration. Sample A, B, C having average particle size of 12.5 nm, 9.1 nm and 7.5 nm respectively. HRTEM image of the samples shown in fig. which is synthesized at pH 8, 9, 10. For sample A (at pH 8) interplaner spacing is 2.5 Å or 0.25 nm corresponds to [311] atomic plane and particle size is 12.5 nm, sample B (at pH. 9) interplaner spacing is 2 Å or 0.20 nm corresponds to [400] atomic plane and particle size is 9 nm, sample C (at pH 10) interplaner spacing is 2.5 Å or 0.25 nm corresponds to [311] atomic plane and particle size is 8.5 nm.

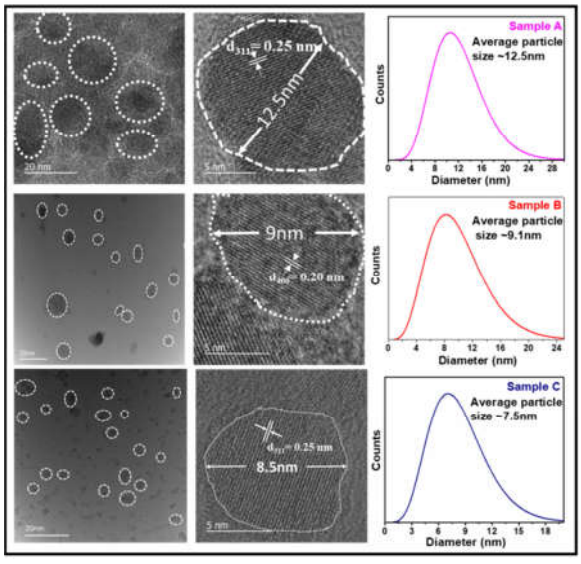

Figure 4. TEM micrographs of $CoFe_2O_4$-PVA gel

4. CONCLUSION

Synthesis of $CoFe_2O_4$-PVA gels have been done in two stages. Three samples were prepared at different pH concentration and it is found that increase in pH causing decreases in particle size. At pH 8, 9, 10 corresponding average particles size we get for sample A, B, C is 12.5nm, 9.1nm, 7.5nm. Characterization process is performed by powder XRD, TEM. Stability of gels can be observed by taking the XRD measurement after 30 days and results founded same as previous.$CoFe_2O_4$-PVA gel is optimized by various tests. Cobalt ferrite nanoparticles are widely used for medical applications because of its good physical and magnetic properties. PVA hydrogel is used because it's showing desirable physical, chemical property which is suitable for drug delivery and other medical applications.

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