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Effect of cobalt doping on the magnetic properties of superparamagnetic γ -Fe₂O₃-polystyrene nanocomposites

Swapna. S. Nair^a, Mercy Mathews^{a,1}, P.A. Joy^b, S.D. Kulkarni^b,
M.R. Anantharaman^{a,*}

^aDepartment of Physics, Cochin University of Science and Technology, Cochin-682 022, India

^bPhysical Chemistry Division, National Chemical Laboratory, Pune-411 008, India

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Abstract

Superparamagnetic nanocomposites based on γ -Fe₂O₃ and sulphonated polystyrene have been synthesized by ion exchange process and the preparation conditions were optimized. Samples were subjected to cycling to study the effect of cycling on the magnetic properties of these composites. The structural and magnetization studies have been carried out. Magnetization studies show the dependence of magnetization on the number of ion exchange cycles. Doping of cobalt at the range in to the γ -Fe₂O₃ lattice was effected in situ and the doping was varied in the atomic percentage range 1–10. The exact amount of cobalt dopant as well as the iron content was estimated by Atomic Absorption Spectroscopy. The effect of cobalt in modifying the properties of the composites was then studied and the results indicate that the coercivity can be tuned by the amount of cobalt in the composites. The tuning of both the magnetization and the coercivity can be achieved by a combination of cycling of ion exchange and the incorporation of cobalt.

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*Corresponding author. Department of Physics, CUSAT, Ernakulam District, Kerala, 682 022, India. Tel.: +91-484-257740439; fax: +91-484-2532495.

E-mail address: mra@cusat.ac.in (M.R. Anantharaman).

¹Present address: Systems and Materials for Information Storage Group, University of Twente, P.B. No 217, 7500 AE, Enschede, The Netherlands.

1. Introduction

Magnetic nanocomposites in which magnetic particles, which are in the nano regime, embedded in a nonmagnetic matrix, have gained great interest in recent years as they possess both the magnetic properties of the inorganic component

and the mechanical and physical properties of the nonmagnetic matrix. Particles possessing nanometric dimensions in the range of 1–10 nm show superior properties compared to their bulk counter parts [1,2]. It is possible to observe quantum size effects at finite temperatures in these ultra fine particles. Their quantum size effects include shift in the energy gap and also quantum magnetic tunneling. Their large surface to volume ratio also provides some excellent modification of their physical properties due to the large reduction in linear dimensions [3,4]. These peculiar properties include their single domain and super paramagnetic nature at the nanolevel [5]. Optical properties also change enormously including the band gap due to the small wave function overlapping resulting from their extremely small sizes. These materials find applications in magnetic refrigeration, ferrofluids, colour imaging magnetic recording and sensors [6,7]. If these composites can be made transparent, they can be potential material for magneto-optical storages.

Gamma ferric oxide belongs to the class of inverse spinels and it exhibits a vacancy ordered spinel structure, where the vacancies are exclusively in the octahedral (B) sites [8]. This material has been extensively used for enormous applications in the bulk due to its very high saturation magnetization and remanence. But they exhibit novel behaviour at the nanolevel due to its vacancy ordered structure. This helps to tailor the magnetic and structural properties of γ -Fe₂O₃ since cations having a strong octahedral site preference with the appropriate ionic radius can occupy the B site. This possibility gives maneuverability for modifying the saturation magnetization and coercivity.

The structure of gamma ferric oxide can be written as, Fe³⁺ [Fe_{5/3}³⁺ θ_{1/3}] O₄²⁻ where θ represents vacancies and are exclusively on the octahedral sites. Nanocomposites can be synthesized by different methods like high energy ball milling, sol-gel method and ion exchange method.

It has been reported recently that the magnetization of these nanocomposite samples can be increased by iron cycling up to saturation, which depends on the vacant sites in the polymer matrix [9]. However a systematic study on their coercivity

variation by doping of nanocomposites is seldom seen in the literature.

It is known that coercivity originates from the irreversible motion of domain walls. The coercivity of magnetic particles is one of the important parameters that determine the usefulness of these materials for different applications including magnetic recording. The coercivity should be at least a few hundred Oersteds to be of any importance for useful applications. However in nanoparticles and nanocomposites, the particles are in single domain/superparamagnetic state and hence the coercivity and remanence tends to zero and the hysteresis exhibit almost zero loss [10].

Coercivity of magnetic samples has a striking dependence on their size. As the particle size decreases the coercivity increases and reaches a maximum and then decreases. The increase in magnetization is attributed to its change from the multi-domain nature to the single domain [10].

The size dependence of coercivity is experimentally deduced and is as follows:

$$H_c = a + b/D, \quad (1)$$

where ‘a’ and ‘b’ are constants and ‘D’ is the diameter of the particle if it is assumed to be spherical.

But as the particle size decreases below D_s (which is the critical size for a single domain magnetic particle) the coercivity decreases because of thermal effects. As the particle size decreases, H_c tends to zero below a critical particle size as governed by the equation

$$H_{ci} = g - h/D^{3/2}, \quad (2)$$

where ‘g’ and ‘h’ are constants.

Below a critical diameter, the coercivity tends to zero again because of the thermal agitation which are now strong enough to spontaneously demagnetize the previously magnetized assembly of particles and such systems, which have the coercivity and remanence tending to zero, are termed as superparamagnetic.

So it is difficult to achieve very large coercivities in the nanoregime below a critical diameter. Enhancing coercivities by other means has to be resorted to.

The coercivity also arises from anisotropies present in the crystal. It is known from literature that shape, size and magneto-crystalline anisotropy contribute to this [8].

Shape anisotropy can be expressed as

$$H = h(N_a - N_c)M_s, \quad (3)$$

where N_a and N_c are the demagnetizing coefficients along 'a' and 'c' axes. If $N_a = N_b$, no shape anisotropy is there and its contribution can be neglected if the particles in general possess a spherical shape.

The anisotropy arising out of the stress created can also play a role in increasing the coercivity of a material as the stress induces magnetostriction, which increases the anisotropy there by contributing an increase in the coercivity of the sample.

Stress anisotropy can be mathematically expressed as

$$H = h(3\lambda_{si}\sigma/M_s), \quad (4)$$

where λ_{si} is the magnetostriction, and σ the stress.

Out of the three major anisotropies contributing to the coercivity, only crystal anisotropy or magneto-crystalline anisotropy is intrinsic to the material and all others are induced anisotropies. In any crystal, the direction of easy magnetization is the direction of spontaneous domain magnetization in the demagnetized state. Because of the applied field doing work against the anisotropy force to turn the magnetization away from the easy direction there must be energy stored in the crystal and this energy is termed as magneto-crystalline energy.

Magneto-crystalline anisotropy is mainly due to spin-orbit coupling neglecting the contributions from spin-spin and orbit-lattice coupling as they are too strong to be changed even by large applied fields and so isotropic.

The magneto-crystalline anisotropy can be mathematically expressed as

$$H = h(2K_1/M_s), \quad (5)$$

where K_1 is the anisotropy constant, assuming K_2 is small and applying conditions of minimum energy.

In cubic crystals like Fe_3O_4 there are more than one easy axis of magnetization there by reducing

the magneto-crystalline anisotropy. But in a hexagonal crystal like cobalt, there is only one magnetic easy axis, which is directed along the hexagonal 'c' axis. So the anisotropy and hence the coercivity is very high in case of a uniaxial crystal like cobalt which possess a positive K_1 value.

It is in this context that incorporation of Co in a polymer matrix consisting of $\gamma-Fe_2O_3$ assumes significance. It is envisaged that the incorporation of cobalt into the lattice of $\gamma-Fe_2O_3$ in the polymer matrix will significantly modify the coercivity because of its magneto-crystalline anisotropy there by offsetting the finite size effects of the particle media on the coercivity of the matrix.

Here ion-exchange method is used for the preparation of magnetic nanocomposites, which is a chemical method in which polystyrene polymer beads are used as nonmagnetic polymer matrix. The polystyrene matrix is chosen because of the large number of pores and these pores restrict the growth of the magnetic inorganic component and the size anisotropy induced will hence be a minimum. These composites can be synthesized by weak ion exchange process as well as strong ion exchange process employing hydrogen peroxide or hydrazine hydrate as oxidizing agents, out of which the strong ion exchange process is chosen here [9]. In the present system, as the pore size is the limiting size for the growth of the $\gamma-Fe_2O_3$ nanoparticles, which is inherent for a system of polystyrene beads, the coercivity cannot be controlled by the size anisotropy contribution.

In the case of $\gamma-Fe_2O_3$ nanoparticles, the shape cannot be controlled in the ion exchange process and the $\gamma-Fe_2O_3$ particles formed are assumed to be spherical. So the size anisotropy contribution is neglected here, as it cannot be controlled in a system of nanoparticles. So in order to increase the coercivity of a sample, it is desirable to dope it with a material, which possess a large uniaxial symmetry for which cobalt is the best candidate.

In our present investigation, attempts are made to acquire expertise on the synthesis of these single domain superparamagnetic magnetic nanocomposites whose average size lies in the limits 60 and 90 Å, and gain control over its magnetic properties so as to tailor materials for potential applications. Attempts are made to explain the magnetization

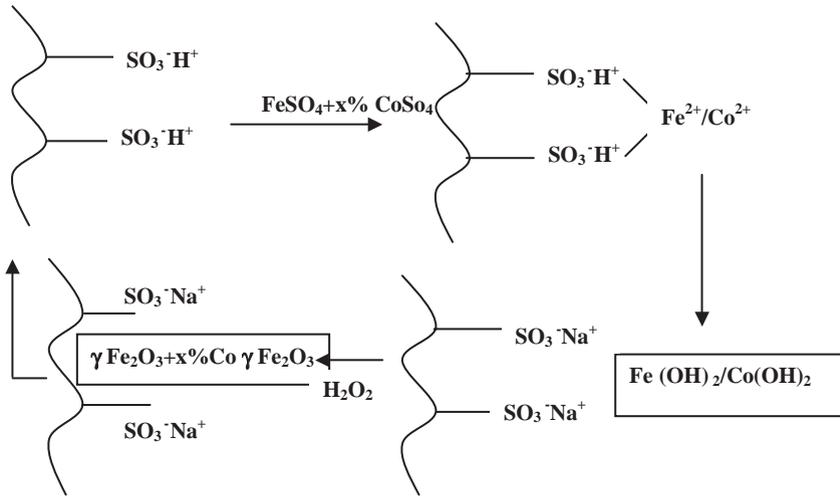


Fig. 1. The schematic diagram of ion exchange process.

and coercivity behaviour of these composites at the nanolevel. Our motivation is to study the effect of cobalt doping in a matrix containing $\gamma\text{-Fe}_2\text{O}_3$ and the effect of cycling in the amount of Co/Fe in the matrix. It is also intended to modify the existing method of ion exchange process to incorporate cobalt in the atomic percentage range in order to tune the coercivity of the fine particles.

2. Experimental techniques

2.1. Synthesis of magnetic nanocomposites

The samples were synthesized by ion exchange process using sulphonated polystyrene which was supplied in the spherical beads' shape. The details are cited elsewhere [11]. Cycling was effected using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution. The ion exchange cycling was carried out both at room temperature and at a higher temperature of 65°C for the determination of the change in magnetization with the cycling temperature. The schematic diagram of a typical ion exchange process is depicted in Fig. 1.

2.2. Doping

Doping with Co was carried out using the same ion exchange process previously described using

CoSO_4 in the appropriate molar ratio. Doping was effected in the atomic percentage 1–10%. The cycling was carried out using CoSO_4 and upto the tenth cycle for each atomic percentage of cobalt.

2.3. XRD studies

The cycled nanocomposites were powdered with HEBM (High Energy Ball Milling) process for 3 min in a high-energy ball milling unit in an aqueous medium for which FRITSCHE PULVERISSETTE (P-7) PLANETARY MICRO MILL was employed and the samples were dried to obtain them in the powder form. The time and speed (200 rpm) of ball milling is kept low in order to avoid the structural changes imparted by the HEBM on the samples. The XRD spectra of the samples were recorded using an X-ray diffractometer (Rigaku D-max-C) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The particle size was estimated by employing Debye–Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta},$$

where λ is the wavelength of X-ray used, β the FWHM of the XRD peak with highest intensity, D the particle diameter and θ the glancing angle.

2.4. VSM studies

The magnetic characterization of the composites containing γ -Fe₂O₃ and Co γ -Fe₂O₃ were carried out by using vibrating sample magnetometry (VSM) (model: EG & G PAR 4500). The saturation magnetization (M_s), retentivity (M_r) and coercivity (H_c) were measured at room temperature.

2.5. Iron and cobalt content estimation

The nanocomposite samples were analysed by Atomic Absorption Spectroscopy (AAS) for the determination of exact percentage of iron in the samples. From the relative intensities of the absorption lines, the percentage of iron in the polymer globules can be determined. The samples were analysed for each and every cycle of ion exchange in order to determine whether there is an increase in iron content with cycling. The same method is employed for the measurement of exact percentage of cobalt that has got incorporated to the composite sample. Estimation was carried out for samples with Co in the atomic percentage 1, 2, 4, 6 and 10 for representative ion exchange cycles 1 and 10.

3. Results and discussions

The ion exchange resin used for the synthesis of these nanoparticles were transparent (slightly golden) to the visible light. The ion exchange cycling effected composites with decreasing transparency and the finally cycled samples (9th cycle) are slightly brownish in colour.

The X-ray diffraction pattern indicates that the composites exhibit semi-amorphous nature due to the presence of large polymer content of the host matrix polystyrene and the particle size, calculated by employing Debye Scherrer's formula, lies in the range 70–85 Å for all the synthesized samples. The cycling of iron resulted in an increase in the crystallinity. The detected phases were that of γ -Fe₂O₃ only with no detectable impurity peaks. Representative X-ray diffraction spectrum is depicted in Fig. 2.

The iron content measurements by atomic absorption spectroscopy indicate an increase in

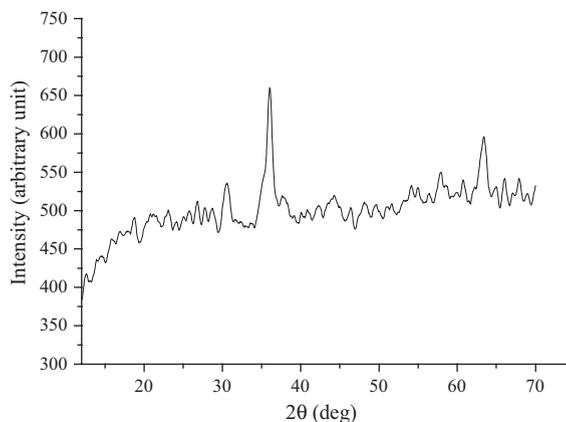


Fig. 2. Representative XRD spectrum of γ -Fe₂O₃ polystyrene magnetic nanocomposites.

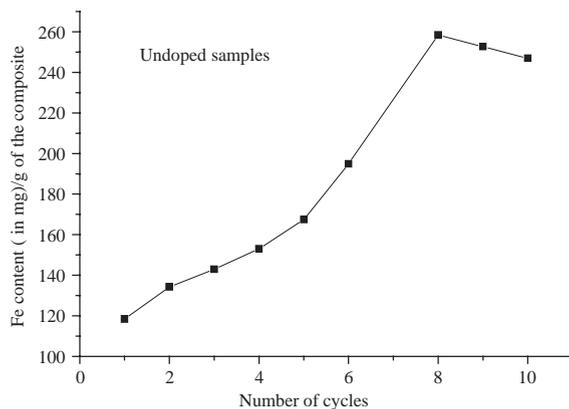


Fig. 3. Fe content in different cycles of ion exchange with Fe²⁺ ion.

iron content with cycling of ferrous sulphate and this attains a saturation for cycle 8 and after that a slight decrease in iron content is observed on further increase in Fe cycling. This result is analogous to the one reported [9]. The saturation may be the result of occupation of all the vacant sites inside the polymer matrix by the Fe²⁺ ions and their subsequent oxidation to gamma Fe₂O₃. Further increase in the cycling process may push out some of the gamma Fe₂O₃ molecules previously occupied in the vacant sites. A graph plotted with the iron content against number of ion exchange cycles is shown in Fig. 3.

The magnetization studies using vibrating sample magnetometer show that the undoped

magnetic nanocomposites synthesized by ion exchange process are low hysteresis ones with remanence and coercivity almost zero. The hysteresis loops for the undoped samples are depicted in Fig. 4.

A graph plotted with the saturation magnetization vs. no. of ion exchange cycles (Fig. 5) shows a similar behaviour as in Fig. 3.

It is observed that the iron content and magnetization increases if the cycling is carried out in higher temperature instead of room temperature. The samples that were left for ion exchange for 4 h at a temperature of 65 °C possess a saturation magnetization comparable or even higher than the samples allowed for ion exchange for 24 h. The representative hysteresis loops (Fig. 6) clearly shows that the ion exchange process as well as the yield of γ -Fe₂O₃ is higher at 65 °C, which is evident from the magnetisation curve (Fig. 6). Remanance and coercivity have near zero value for all samples showing their superparamagnetic nature in general. Mössbauer spectroscopic observations also shows that there is reduction of ferrimagnetism. The details are cited elsewhere [9]. A more clear evidence of superparamagnetism is obtained by the fitting of magnetization curve for Langevin's function (Fig. 7).

From the magnetization measurements, an increase in magnetization with increase in iron content is observed up to cycle number 8 and then it decreases. This behaviour is analogous to the iron content estimation result in which there is a

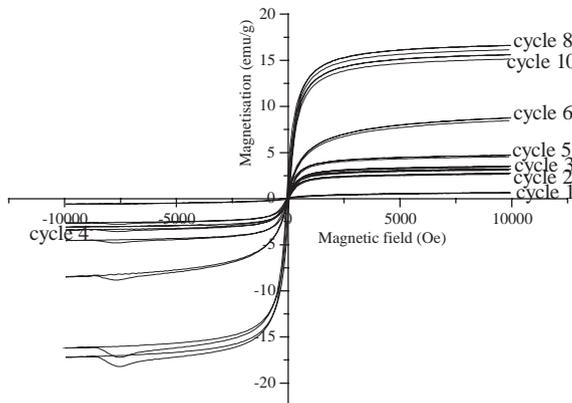


Fig. 4. Hysteresis loops of undoped samples in different cycles of ion exchange with Fe³⁺ ion.

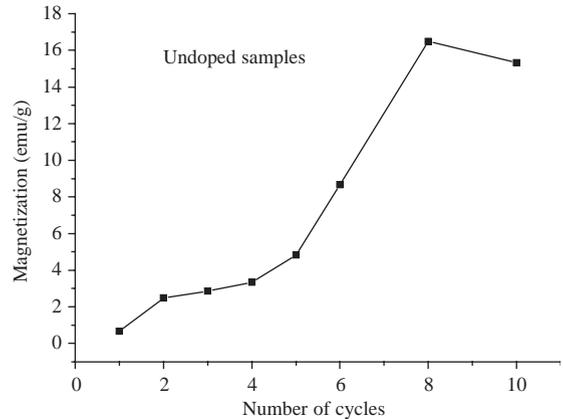


Fig. 5. Saturation magnetization in different cycles of ion exchange with Fe³⁺ ion.

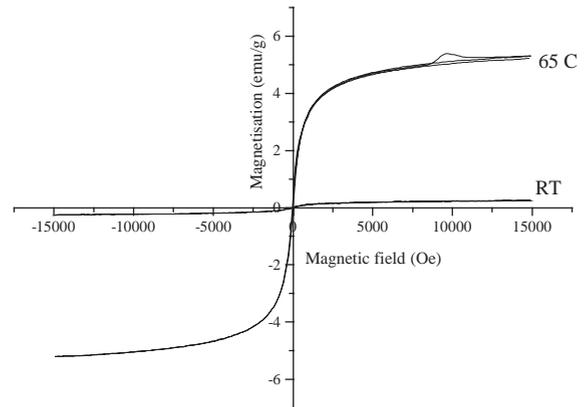


Fig. 6. Representative hysteresis loop showing increase in magnetization with increase in temperature of ion exchange cycling.

slight decrease in the content of iron after the 8th cycle. This confirms the absence of α -Fe₂O₃ phase in the sample in a detectable amount. The X-ray analysis also shows no additional peaks. The magnetization reaches a maximum of 17 emu/g and then decreases slightly for undoped samples. This can be explained on the basis of Neel's two sublattice theory.

The available pores in the polymer network is such that if all the pores are filled and saturated, weight percentage of γ -Fe₂O₃ will be 25% in the polymer matrix.

In 1 g of the composite, 250 mg of γ -Fe₂O₃ is there if all the pores are filled and saturated.

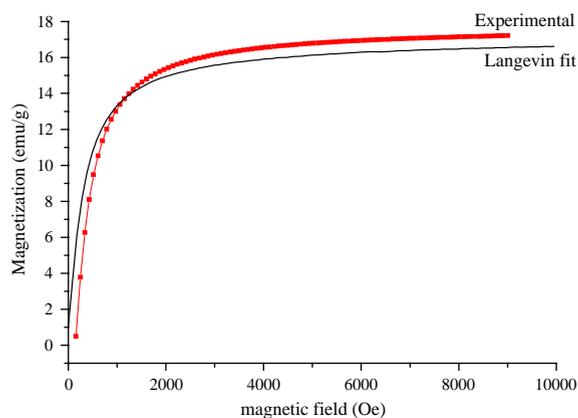
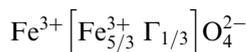


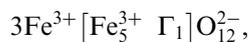
Fig. 7. Langevin's curve fitting for magnetization.

Molecular weight of $\gamma\text{-Fe}_2\text{O}_3$ is 160. Hence the number of molecules of $\gamma\text{-Fe}_2\text{O}_3$ in 1g of the composite could be calculated as $9.41 \times 10^{20}/\text{m}^3$. From the Langevin curve fitting, the number of moments is also around $9.7 \times 10^{20}/\text{m}^3$ confirming the superparamagnetic nature of the particles in general.

Maghemite is one of the most important magnetic materials. This compound has a vacancy ordered spinel structure and is prepared generally by oxidizing magnetite Fe_3O_4 . The Fe ions are in the trivalent state and a fraction of the cation sites are vacant. The structure of gamma ferric oxide can be written as



or



where Γ represents vacancies which are exclusively found on the octahedral sites. By the Neel's two sublattice model, the saturation magnetization of $\gamma\text{-Fe}_2\text{O}_3$ is calculated as

$\mu = \mu_A - \mu_B = 2 \times 4$ (effective difference of ions in the sites \times moment of Fe^{3+} ions) and saturation magnetization M_s in emu/g is $(5585 \mu/\text{Mol Wt}) = 69.8125$ emu/g.

If all the pores are filled and saturated, then the expected magnetization is $69.8 \times 1/4 = 17.4$ emu/g. So in the samples cycled 8 times (ion exchange) the maximum theoretical magnetization is achieved.

Analysis of the results of Atomic Absorption Spectroscopy (AAS) carried out on the doped

samples suggests that the cobalt content increases in the sample in each cobalt cycling. The samples with cobalt in the atomic percentage 1%, 2%, 4%, 6% and 10% with respect to $\gamma\text{-Fe}_2\text{O}_3$ were also investigated by AAS for the estimation of cobalt content. The cobalt content estimation shows an increase with addition of cobalt percentage indicating the proper ion exchange and doping. So doping is made easy with in situ addition of the cobalt salt along with an iron salt maintaining proper pH and temperature, which are optimized.

The magnetization studies of the doped samples show an increase in coercivity of the doped samples and the detectable change in coercivity of the sample is noted for higher cobalt doping, i.e., 4%, 6% and 10%. Representative magnetization curves are shown in Fig. 8 and 9. The variation of coercivity with percentage of cobalt is depicted in Fig. 10

It may be noted that the coercivity of the nanocomposites containing cobalt and $\gamma\text{-Fe}_2\text{O}_3$ enhanced from 20 to 300 Oe by cobalt doping. It is obvious from the figure that the coercivity increases almost linearly with increase in cobalt in the low doping regime. But the increase in coercivity is not that high for higher doping.

One of the probable reasons for this special behaviour in higher doping is that although there is a higher cobalt content the ion exchange process may not be complete and some amount of cobalt may still exist in the unionized state itself.

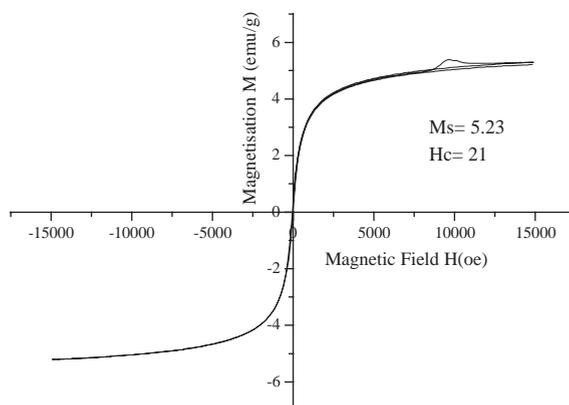


Fig. 8. Representative hysteresis loop of the sample with Co (0.304% as determined by AAS).

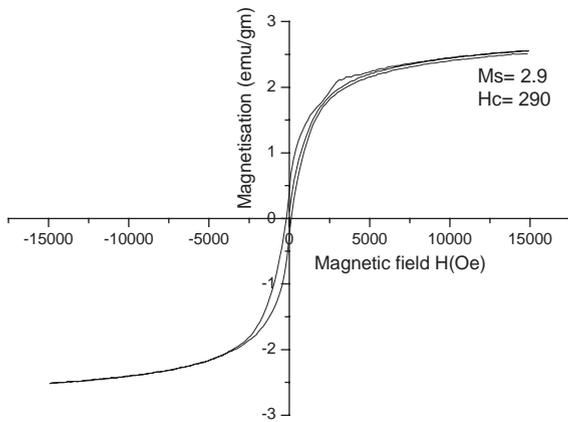


Fig. 9. Representative hysteresis loop of the sample with Co 1.484%.

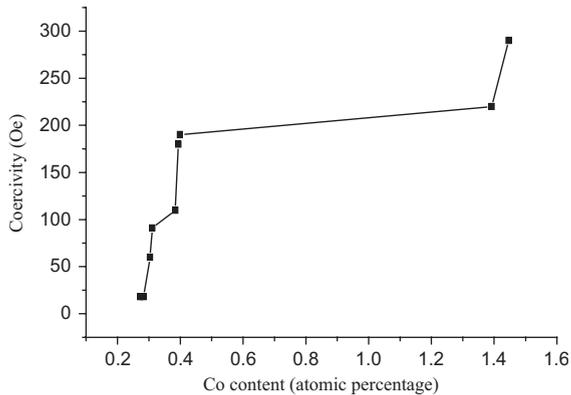


Fig. 10. The variation of coercivity with percentage of Co (as determined by AAS).

γ -Fe₂O₃ particles can be prepared in both acicular (needle like) and spherical form. Needle shaped γ -Fe₂O₃ particles can be synthesized by using complexing media [12] or by starting from Geothite [13]. But in the ultrafine regime, the normal tendency of the particles is to be in spherical shape, so that the contribution from the size anisotropy arising from the needle like shape of the particles is a minimum. In our present system, γ -Fe₂O₃ is trapped inside the pores of polymer network by chemical route and these pores, which are spherical, limit the growth and shape of the nanoparticles. There are also various reports ensuring the spherical shape of the particles in their ultrafine form. Vassiliou et al.

reported the transmission electron microscopy images of these samples showing the spherical nanoparticles [14]. Thus the contribution of the shape anisotropy towards the increase in coercivity is not considered here. Hence it is assumed that the coercivity enhancement is due to the magneto-crystalline anisotropy introduced by the dopant cobalt. However the contribution of shape anisotropy can be further checked by electron micrograph studies.

Thus in magnetic nanoparticles, the increase in coercivity for probable applications can be obtained by the addition of an element/crystal possessing large magneto-crystalline anisotropy for which cobalt is the best candidate. Ion exchange method can be successfully employed for tuning both magnetization and coercivity of the samples. The decrease in magnetization caused by the doping is due to the exchange of iron with cobalt in the occupied states. The magnetization can be increased by ion exchange cycling with iron, which enable to fill the vacant sites for the doped samples. Thus complete tuning of the magnetic parameters is possible by a combination of the ion exchange cycling and appropriate cobalt doping.

4. Conclusion

The undoped magnetic nanocomposites synthesized by ion exchange process is superparamagnetic in nature with remanence and coercivity almost zero. The magnetization can be increased by cycling process in which more vacant sites in the polymer matrix can be made occupied by the maghemite molecules. The addition of cobalt, which possesses large magneto-crystalline anisotropy, is found to increase the coercivity of the samples. It is evident from the magnetization measurements that there is a cation redistribution, which changes the magnetization, which is already reported for ultrafine particles of spinel ferrites. Thus the magnetization and coercivity can be successfully tuned by doping in the nanocomposites for possible device applications. The method of strong ion exchange resin can be adopted for the incorporation of cobalt into the matrix containing γ -Fe₂O₃. Cycling of iron and cobalt

can be achieved to obtain an optimum magnetization M_s and H_c of the matrix. The incorporation of cobalt in the lattice modifies the coercivity and this is useful for tailoring the coercivity of nanocomposites whereby this offsets the finite size effect on the coercivity.

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