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Impact of Cobalt to NaOH/KOH Ratio on Properties of Cobalt Ferrites in Co-precipitation and Reverse Micelles Methods

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Abstract

Cobalt ferrite ($CoFe_2O_4$) nanoparticles were synthesized by co-precipitation and reverse micelle methods with different ratios of cobalt to sodium hydroxide (NaOH) or potassium hydroxide (KOH) (reagent). This study investigates the influence of reagents and varying cobalt to NaOH/KOH ratio on the completion of reactions and structural properties of cobalt nano-ferrites. All the samples were subjected to X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, transmission electron microscope (TEM), thermogravimetric-differential thermal analysis, and vibrating sample magnetometer (VSM) studies to elucidate the impact of methods and reagents on structural and magnetic properties. From the as-prepared sample by co-precipitation method, the ferrite formation is observed to be completed, and the XRD pattern of the material has shown single phase spinel structure. The X-ray patterns of as-prepared samples by reverse micelles indicate a hindering mechanism to ferrite formation from the ingredients. TEM images of cobalt ferrite samples prepared by co-precipitation and reverse micelle method using NaOH, KOH show particle size in range 9 to 18 nm. The VSM study shows the saturation magnetization values ranging from 34.56 emu/g to 61.18 emu/g for the prepared samples. This shows the different methods of nanoparticle synthesis that lead to different particle sizes and magnetic properties. Antibacterial activity was tested for the synthesized nanoparticles with two-Gram positive and two-Gram negative bacteria. Out of all the compounds tested, only samples prepared by reverse micelle using KOH showed significant antibacterial activity. The other three samples showed no zones of inhibition. Among the four test isolates for same sample, maximum zone of inhibition was observed for *Staphylococcus* sp.

Keywords

Cobalt ferrite, Co-precipitation, Reverse micelles, Particle size, Antibacterial activity, Zone of inhibition

Introduction

Nanotechnology involves manipulating matter on an atomic or molecular scale, typically at the nanometer scale. It's a multidisciplinary field that merges science and engineering, aiming to understand, control, and utilize materials and devices at the nanoscale. Here are some key aspects. Nano-engineered materials have enhanced properties, like increased strength, conductivity, or flexibility, which find applications in various industries from aerospace to construction.

The properties of ferrites are extremely sensitive to the method of processing and the number of additives present in the ferrite system. The particle size is a key parameter in altering the properties as each property is interrelated to a characteristic length scale. Hence, the control of particle size in ferrites is required by exploiting suitable preparation methods, heat treatment and compositional effect in order to achieve the best trade-off between various parameters [1].

Wet chemical process is widely used for synthesizing small sized nanoparticles. Advantages of wet synthesis over other traditional routes includes minimum particle size distribution, good control of the final powder, excellent interaction on the atomic scale, stoichiometries for getting homogeneity, simple equipment, low energy consumption, and processing time. Additionally, there are also general advantages of wet syntheses over the other bulk approaches that includes enhanced control of the particle size, shape, and uniformity [2-4].

Cobalt ferrite displays distinct physical and mechanical characteristics making them useful in nanomedicine areas [5, 6]. Cobalt ferrite belongs to the family of hard magnetic material with a high coercivity, and a high curie temperature. It is chemically stable and a good electrical insulator [7-9]. These notable properties make cobalt ferrite a very promising candidate for a wide range of medical applications that include magnetic drug delivery, radio frequency hyperthermia and magnetic resonance imaging [10-12].

Hence, for present investigations cobalt ferrite was selected and synthesized in co-precipitation and reverse micelles methods with different ratios of cobalt to NaOH/KOH (precipitating reagents).

Materials and Method

Synthesis

Cobalt(II) nitrate $Co(NO_3)_2.6H_2O$ and Iron(III) nitrate $(Fe(NO_3)_2.6H_2O)$ are taken in the required proportions and separately dissolved in deionized water. Then the resultant cationic solutions are then mixed and stirred for an hour to produce a homogeneous solution. The resultant solution is known as the precursor, and it is employed for the following processing techniques.

In the co-precipitation method, NaOH or KOH is weighed in the required proportions and dissolved in distilled water to prepare one molar solution (Figure 1). This is added dropwise into the precursor while stirring vigorously and heating at 70 °C on a magnetic stirrer. As the pH reaches between 10.2 and 10.5, the entire solution comes to a standstill indicating the initiation of reaction among the constituents. After the reaction is completed and the cobalt ferrite is formed, stirring is resumed again. After complete NaOH and KOH are transferred, the heating and stirring process is stopped and the solution is kept aside till cobalt ferrite precipitates at the bottom [13, 14].

In the reverse micelle method, we have prepared two microemulsion systems (Figure 2). This was prepared by mixing water, sodium dodecyl sulfate, 1-butanol, and n-hexane in the required ratio. After one hour, a clear transparent solution was observed, signifying that a stable micelle was formed. The

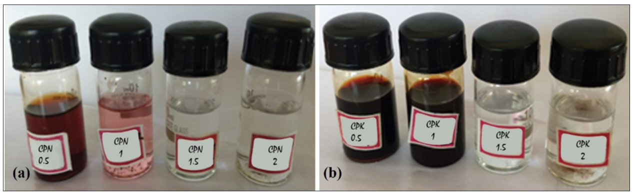

Figure 1: Samples prepared by co-precipitation method with **(a)** NaOH and **(b)** KOH.

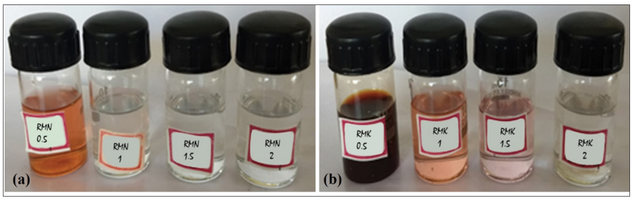

Figure 2: Samples prepared by reverse micelle method with **(a)** NaOH and **(b)** KOH.

precursor solution is dissolved in one of the microemulsion systems and in the other microemulsion, 5 M different ratio of cobalt to NaOH/KOH (reagent) solution was added. The resultant two microemulsions were mixed together and then magnetically stirred for one hour. Cobalt ferrite is precipitated within the reverse micelle nanoreactors [15, 16].

The precipitates that were obtained from the above methods were meticulously washed in distilled water. Using a hot air oven, the product was dried for 6 h at a temperature of 110 °C to remove the water contents. The dry powder (as-prepared sample) was then homogeneously mixed for 10 min in an agate mortar and pestle for further investigation.

The samples with ratio of (cobalt:NaOH/KOH) 1:0.5, 1:1, 1:1.5, and 1:2 was prepared using co-precipitation method and named as CPN0.5/CPK0.5, CPN1/CPK1, CPN1.5/CPK1.5, and CPN2/CPK2.

The samples were prepared using reverse micelle method with ratio of (cobalt:NaOH/KOH) 1:0.5, 1:1, 1:1.5, and 1:2 was named as RMN0.5/RMK0.5, RMN1/RMK1, RMN1.5/RMK1.5, and RMN2/RMK2.

It is well-reported that reaction initiation and completion depend on the pH of the solution [17]. It is rarely reported about the quantity of NaOH and KOH required to attain a particular pH. In this study, we bring out a relation between the quantity of NaOH/KOH and metal nitrate for the completion of the reaction. In the above images, the presence of unreacted cobalt and iron nitrates is indicated by the colored solution, while the transparent solution indicates the completion of the reaction.

Samples labelled CPN0.5, CPK0.5, CPK1 and RMK0.5 did not yield any dried precipitated powders. Also, it is observed that the samples with a ratio of cobalt:NaOH/KOH in the proportion of 1:2 displayed a complete reaction with the formation of a clear precipitate of cobalt ferrite. While in all the other ratio samples, there was an observation of incomplete reaction. This indicates that the reagent quantity which is twice the proportion of cobalt results in a complete precipitative reaction.

Characterization techniques

The dried powder (as-prepared) was structurally characterized by irradiating with Cu-K_{α} radiation (λ = 1.5406 Å) using a Breuker advanced 80 X-ray diffractometer. The dried powder was also examined under the TEM (Model JOEL JEM 200CX) at the electron accelerating voltage 120 kV to record the bright field micrograph and corresponding selected area electron diffraction pattern. The dried powder was made in the form of a pellet using potassium bromide for recording the room temperature infrared spectrum using a Perkin Elmer 5DX 1650 FTIR spectrometer in the range from 400 cm^{-1} to 4000 cm^{-1}. The magnetic hysteresis measurement was done using a VSM (115 PAR-EG&G Model) at an external maximum magnetic field of 20 kOe.

Antibacterial activity

The antibacterial activity of cobalt ferrite nanoparticles was tested using Agar well diffusion assay method [18]. The test organisms *Escherichia coli*, *Bacillus* sp., *Staphylococcus* sp., and *Pseudomonas* sp. were grown overnight in Luria-Bertani broth to get 10^6 CFU/ml. Agar plates were pre-seeded with 100 µl of overnight-grown bacteria test cultures. Gels were punched using a sterile cork width of 8 mm bore diameter. Agar wells were loaded with 10 µl of test compounds, while Streptomycin was used as the positive control and sterile distilled water as a negative control. The agar plates were incubated for 24 h at 37 °C. We recorded zones of inhibition after incubation. The experiment was done in triplicates and the standard deviation was recorded.

Results and Discussion

FTIR analysis

To ensure the completion of precipitative reaction, the dried precipitated powder was subjected to FTIR spectra studies (Figure 3 and figure 4). Both absorption bands corresponding to octahedral and tetrahedral sites were seen in samples marked CPN2, CPK2, RMN2, and RMK2.

The characteristics band observed in all the samples around 600 cm^{-1} corresponds to stretching vibration of metal at tetrahedral site (M_{tet}-O) bond and the band around 420 cm^{-1} corresponds to the intrinsic stretching vibration of the metal at octahedral site (M_{oct}-O) bond [19]. The observed positions of the bands in our study confirm the formation of a spinel structure. The other important peaks observed around 1381 cm^{-1}, 3400 cm^{-1} and 1600 cm^{-1} are attributed to the aromatic C-N stretching, H-O-H stretching and bending vibrations of the absorbed water molecules, respectively. The additional peaks observed at approximately at 2920 cm^{-1} and 2854 cm^{-1} are due to asymmetric νas(C-H) and symmetric ν(C-H), respectively [20, 21].

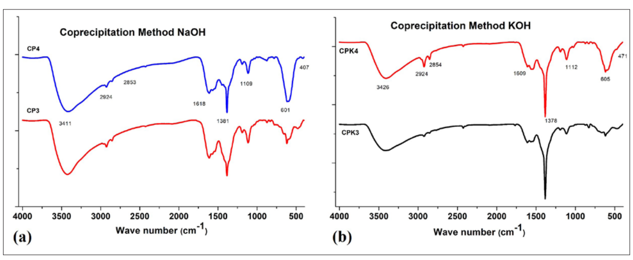

Figure 3: FTIR pattern of as prepared cobalt ferrite synthesized by co-precipitation method with **(a)** NaOH and **(b)** KOH.

As prepared samples with a ratio of cobalt:NaOH/KOH 1:2 and labelled as CPN2, CPK2, RMN2, and RMK2 were only considered for further analysis as it is observed that these samples displayed completed reactions.

XRD analysis

In samples prepared by co-precipitation method, the ferrite formation is observed completed in the as-prepared samples and XRD pattern of the material (Figure 5) has shown single phase spinel structure. Using the Debye-Scherrer formula, the crystallite sizes were calculated as 15.32 nm and 11.90 nm for CPN2 and CPK2 samples respectively for the 311 peaks of the XRD.

In sample prepared by reverse micelle method, start of ferrite growth has been evidenced from the diffraction peaks at angles of 36.5°, 35.7° (311 plane) and 63.48°, 63.0° (440 plane) in both the samples with RMN2 and RMK2 (Figure 6). The XRD patterns also indicate the necessity of further heat treatment to complete the required ferrite formation.

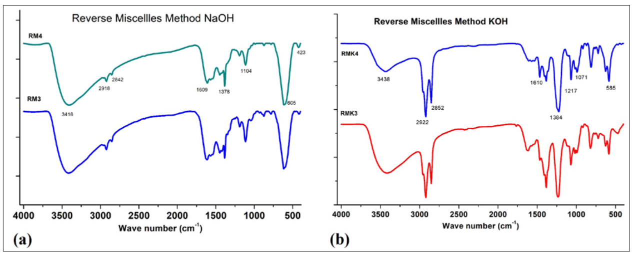

Figure 4: FTIR pattern of as prepared cobalt ferrite synthesized by reverse micelle method with **(a)** NaOH and **(b)** KOH.

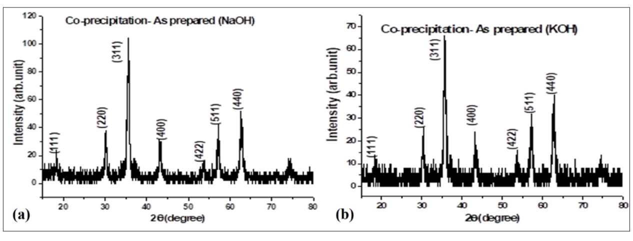

Figure 5: XRD patterns of as-prepared cobalt ferrite samples labelled **(a)** CPN2 and **(b)** CPK2.

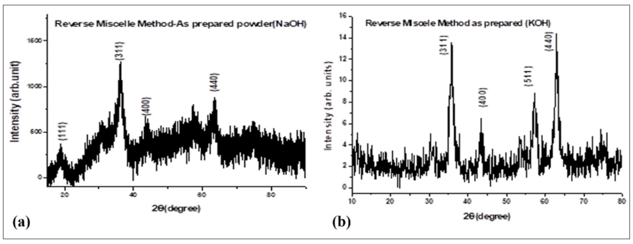

Figure 6: XRD patterns of as-prepared cobalt ferrite samples labelled **(a)** RMN2 and **(b)** RMK2.

The XRD patterns of the as-prepared samples by reverse micelles method indicate a hindering mechanism to ferrite formation from the ingredients. This might be due to micelle formation by anionic surfactant sodium dodecyl sulfate in the reverse micelle method.

The pre-sintering of the as-prepared sample at high enough temperatures to decompose the polymer chains and several organic compounds are expected to produce the desired nano-crystalline cobalt ferrite.

Particle size

As the properties of the end product depend on particle size, it is always desirable to produce the ferrite material with a smaller crystallite size coupled with higher magnetization. From the TEM images, it is clear that powders contain a good number of extremely small size particles and the average particle size obtained from corresponding histograms lies in the range of 9 - 18 nm. Particle size for a given sample can been estimated from TEM are displayed in figure7a - 7b and figure 8a - 8b [22].

Specific saturation magnetization

The room temperature hysteresis loops of all the prepared samples are shown in figure 9. The specific magnetic parameters like saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c), measured from the hysteresis loops are listed in table 1. When compared to reverse micelle samples, samples obtained through co-precipitation had greater saturation magnetization and coercivity. The high M_s value obtained in the co-precipitation method may be due to the large particle size as reported in earlier studies [23].

Antibacterial activity

In figure 10 and figure 11 for this study, for samples CPN2, CPK2, RMN2, and RMK2 labelling was used as NaCP, KCP, NaRM and KRM.

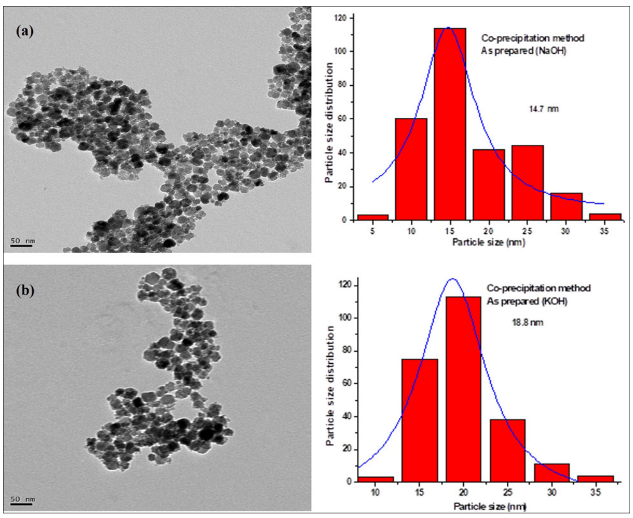

Figure 7: TEM images and particle size distribution histograms of cobalt ferrite samples prepared by co-precipitation method **(a)** NaOH and **(b)** KOH.

The antibacterial property was performed using agar well assay with two-Gram positive organisms *Bacillus* sp. and *Staphylococcus* sp. and two-Gram negative organisms *E. coli* and *Pseudomonas* sp. were tested for cobalt ferrite powder prepared by co-precipitation, and reverse micelle methods using NaOH and KOH nanoparticles. Of all the compounds tested, only the RMK2 sample showed significant antibacterial activity for all four test isolates with a maximum zone of inhibition for *Staphylococcus* sp. while the other three samples showed no zones of inhibition. These results are promising as the RMK2 sample can be used as a targeted therapeutic agent against Methicillin-resistant *Staphylococcus aureus* (MRSA) strains which are otherwise resistant to antibiotics.

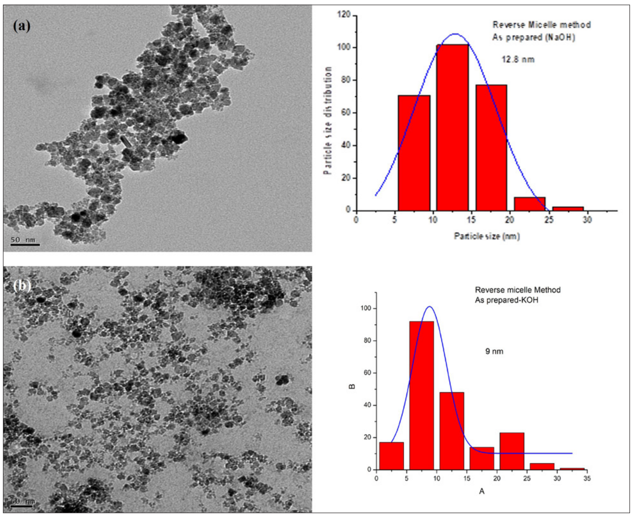

Figure 8: TEM images and particle size distribution histograms of cobalt ferrite samples prepared by reverse micelle method **(a)** NaOH and **(b)** KOH.

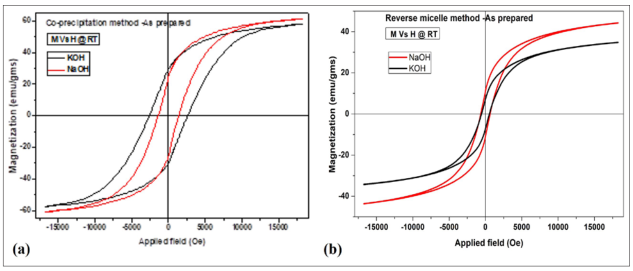

Figure 9: Room temperature hysteresis loops of the as-prepared cobalt ferrite powder by **(a)** co-precipitation and **(b)** reverse micelle method using NaOH and KOH.

Table 1: Room temperature magnetic properties of as-prepared cobalt ferrite powder by co-precipitation, reverse micelle method using NaOH and KOH.

Sample	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	M_r/M_s
CPN2	61.18	21.63	1398	0.35
CPK2	57.82	27.72	2615	0.48
RMN2	43.95	8.82	646	0.25
RMK2	34.56	5.8	540.3	0.25

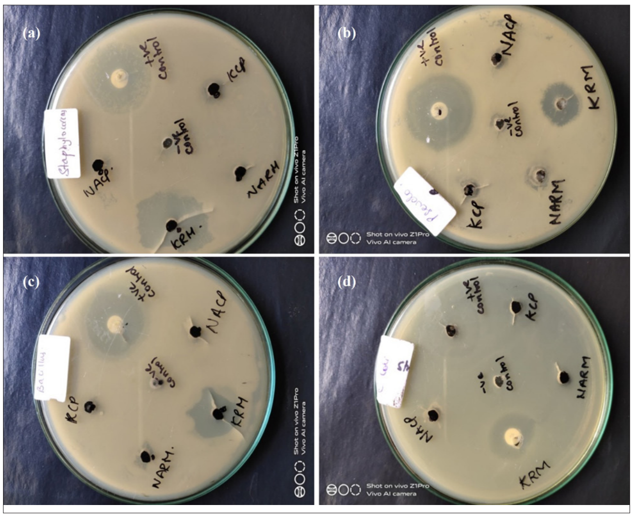

Figure 10: Inhibition zone measurements for cobalt ferrites **(a)** KRM, **(b)** KCP, **(c)** NaRM, **(d)** NaCP against *Bacillus* sp., *Staphylococcus* sp., *E. coli*, and *Pseudomonas* sp.

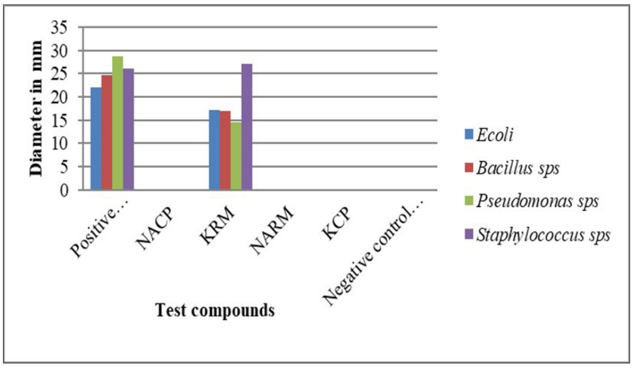

Figure 11: Antibacterial activity of test compounds using Gram-positive and Gram-negative bacteria.

Conclusion

The above work is a preliminary study to understand the suitable quantity of precipitating reagent required for the preparation of cobalt ferrite nanoparticles. In this study, we establish a relationship between the quantity of NaOH/KOH and metal nitrate for the completion of the reaction. It is observed that the samples with a ratio of cobalt:NaOH/KOH in the proportion of 1:2 displayed a complete reaction. The XRD patterns obtained from co-precipitation samples using NaOH and KOH showed a single-phase spinel structure. Both XRD and FTIR studies suggest that the samples prepared by the reverse micelle method require further heat treatment. From TEM images the average particle sizes are in the range of 9 to 18 nm. The smaller the particle sizes of the as-prepared material, the greater is the possibility of improving the material's qualities by heat treatment. The samples prepared by co-precipitation have higher saturation magnetization, and coercivity but greater particle size when compared to the reverse micelle method. The increased crystallinity found in the co-precipitation sample might be another cause resulting in higher saturation magnetization. Of all the samples prepared, RMK2 shows significant antibacterial activity with a maximum zone of inhibition for *Staphylococcus* sp. These results are promising as the RMK2 sample can be used as a targeted therapeutic agent against MRSA strains which are otherwise resistant to antibiotics. In summary, cobalt ferrite nanoparticles with high saturation magnetization and smaller particle size are always sought and helpful for biological applications.

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None.

Conflict of Interest

None.

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