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Effect of nucleating agents and stabilisers on the synthesis of Iron-Oxide Nanoparticles-XRD analysis

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Abstract. Iron nanoparticles were made by using the modified coprecipitation technique. Usually the characteristics of synthesised particles depend upon the process parameters such as the ratio of the iron ions, the pH of the solution, the molar concentration of base used, type of reactants and temperature. A modified coprecipitation method was adopted in this study. A magnetic stirrer was used for mixing and the morphology and nature of particles were observed after synthesis. Nanoparticles were characterised through XRD. Obtained nanoparticles showed the formation of magnetite and maghemite under citric acid and oxalic acid as stabilisers respectively. The size of nanoparticle was greatly affected by the use of different types of stabilisers. Results show that citric acid greatly reduced the obtained particle size. Particle size as small as 13 nm was obtained in this study. The effects of different kinds of nucleating agents were also observed and two different types of nucleating agents were used i.e. potassium hydroxide (KOH) and copper chloride ($CuCl_2$). Results show that the use of nucleating agent in general pushes the growth phase of nanoparticles towards the end of coprecipitation reaction. The particles obtained after addition of nucleating agent were greater in size than particles obtained by not utilising any nucleating agent. These particles have found widespread use in medical sciences, energy conservation and electronic sensing technology.

Keywords: nanoparticles; iron oxide; maghemite; magnetite; X-ray diffraction; nucleating agents; stabilisers

1. Introduction

Massart (1981) first discussed the preparation of magnetite nanoparticles using a base solution with iron salts. In last decade, preparation of iron oxide nanoparticles has been extensively studied, not because of its scientific interest but because of the technological advances it is making, Laurent *et al*. (2008). Literature (Hafeli *et al*. 1997, Han *et al*. 2000, Lu *et al*. 2007, Mohammed M. Rahman 2011) reports that these particles found extensive applications in sensing technology, biomedical applications, storage media, water cleaning, magnetic inks. There are various ways to prepare iron oxide nanoparticles such as the coprecipitation method, the thermal decomposition method, the micro-emulsion method and the hydrothermal synthesis method. Details on each process can be found in Drbohlavova *et al*. (2009), Guo *et al*. (2001), Gupta and Gupta (2005),

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Kim *et al*. (2001), Mehta *et al*. (2012), Ramimoghadam *et al*. (2014).

The coprecipitation method is one of the most utilised methods used to prepare iron oxide nanoparticles (Han *et al*. 2000, Lu *et al*. 2007, Drbohlavova *et al*. 2009, Gupta and Gupta 2005, Kim *et al*. 2001, Businova *et al*. 2011, Hoa *et al*. 2009, Scherer and Figueiredo Neto 2005, Song *et al*. 2011, Wei *et al*. 2012, Wu *et al*. 2008) due to its flexibility to modify the process parameters. Varying the parameter of the process affects the final product. The available process parameters are the molar ratio of the iron salts, the pH of solution, the nucleating agents and types of base used. In the coprecipitation method, molar solutions of iron salts of chlorides or sulphates are treated with a molar solution of a base in accordance with the following reaction (Gupta and Gupta 2005).

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O$$

pH of solution governs the reaction chemistry and dictates the end product. To prepare the magnetite particles the pH of the solution should be greater than 10; otherwise, the particles will oxidise to maghemite (Hoa *et al*. 2009, Song *et al*. 2011, Wei *et al*. 2012).

Necessary research is being carried out in this field to reduce the particle size which influences the magnetic properties critical in applications Hafeli *et al*. (1997), Besra and Liu (2007). The present study focuses on the use of nucleating agents and stabilisers to influence particle size. In this study, the modified coprecipitation method is used to synthesize iron oxide nanoparticles. Strong base and weak acid is used to affect the nucleation and growth stages of iron oxide nanoparticles formation. Obtained particles were then characterised through XRD. The Scherer formula was used for particle size determination.

2. Experimental

2.1 Materials

All chemicals purchased were lab grade. NH_4OH was purchased from Merck. $FeCl_2$ and $FeCl_3$ were obtained from Daejong, Korea. Citric acid, oxalic acid, copper chloride and potassium hydroxide were obtained from Sigma-Aldrich.

2.2 Method

In the present study, iron oxide nanoparticles are prepared using the modified coprecipitation method. Four different batches were prepared by altering the process parameters.

1. Samples were prepared by altering process parameters of the coprecipitation technique. Iron salt solutions with a molar ratio of 2:1 were used with NH_4OH as a base. After precipitation, particles were decanted thrice and the obtained nanoparticles were dried.

2. In Samples 1 and 2 stabilisers were used as citric acid and oxalic acid, respectively. The effect on size was observed and the nature of obtained particles was studied using XRD. Normal temperature conditions were used. Stabilisers were added to the decanted particles and were magnetically stirred for a half hour.

3. In Samples 3 and 4 nucleating agents were introduced in the base solution as 1M $CuCl_2$ and 1M KOH before addition of iron salt solution. The effect on the size of the particles and nature was observed following modified coprecipitation method.

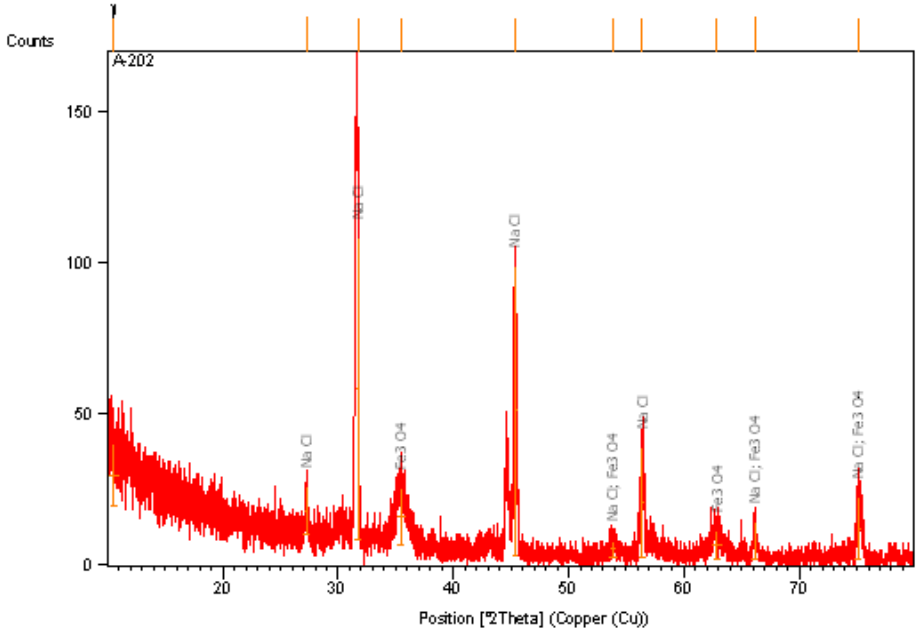

Fig. 1 Sample XRD diffractogram showing the formation of Fe3O4 using citric acid as stabiliser

2.3 X-ray diffraction

X-ray diffraction measurements were carried out on X'pert Pro using Cu Kα radiation. Powdered samples were placed on the sample holder. XRD data was collected in the range of 0 to 80 degrees. Calculations were performed using High score software. The average particle size was estimated by using the Scherer formula. The line width of most intensive peaks was considered for calculation purposes.

3. Result and discussion

The XRD technique was used to identify the size and nature of the obtained particles. Sample 1 was stabilised using citric acid and the XRD pattern (Fig. 1) confirmed the formation of magnetite nanoparticles with size of up to 18 nm (Scherer Formula, Eq. (1)). Sample 2 was stabilised using oxalic acid and the particle size obtained was upto 50 nm, XRD pattern (Fig. 2) confirmed the formation of maghemite.

$$\tau = (K\,\lambda)/(\,\beta \mathrm{Cos}\,\theta) \tag{1}$$

where,

τ is the mean size of the particles,
K is a dimensionless shape factor=0.9
λ is the X-ray wavelength=1.54×10^{-10} A^{o}
β is the line broadening at half the maximum intensity (FWHM)
θ is the Bragg angle

Table 1 Listing of process parameters and effects observed on obtained particles

Sample	Process parameter	β (Degree)*	2θ (Degree)*	Size of particle (nm)	Nature
1	Stabilisation using citric acid	0.7872	35.4195	18	Magnetite (Fe3O4)
2	Stabilisation using oxalic acid	0.2755	35.5893	52	Maghemite (Fe2O3)
3	Stabiliser citric acid and nucleating agent KOH	0.4723	35.4731	31	Magnetite (Fe3O4)
4	Stabiliser citric acid and nucleating agent $CuCl_2$	0.5510	35.7359	26	Magnetite (Fe3O4)

*Note: β and 2θ values were obtained from diffractograms

Samples 3 and 4 were stabilised using citric acid and nucleating agents as KOH and $CuCl_2$ were used respectively. In both cases, citric acid supported the formation of magnetite but the particle size difference was close as 30 nm and 25 nm respectively (Figs. 3-4). Process modifications and effects observed are listed in following Table 1.

XRD analysis in Figs. 1-4 shows the formation of different types of iron oxide nanoparticle under the influence of different types of nucleating agents and stabilisers. One feature common in all diffractograms is the high impurity content in form of sodium chloride (NaCl). To analyse this problem, Sample no. 2 was taken since it was available in bulk amount (yield was high) and was continuously decanted using distilled water and a magnet. A small amount of the sample was analysed using XRD. Fig. 5 shows the diffractogram of the pure sample; no impurity can be

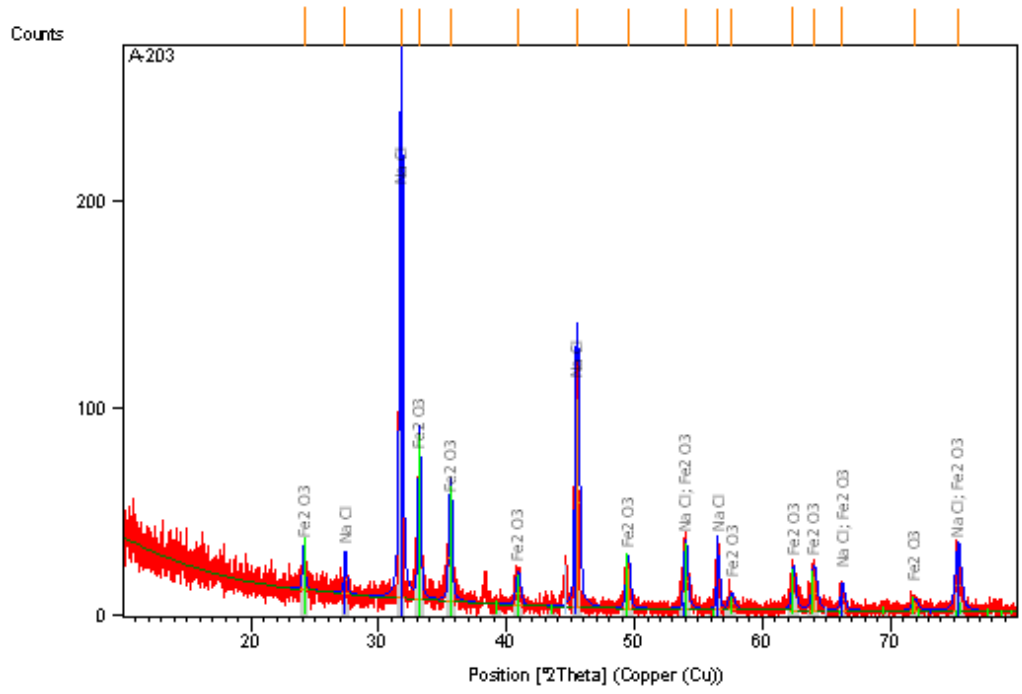

Fig. 2 Sample XRD diffractogram showing the formation of Fe2O3 using oxalic acid as stabiliser

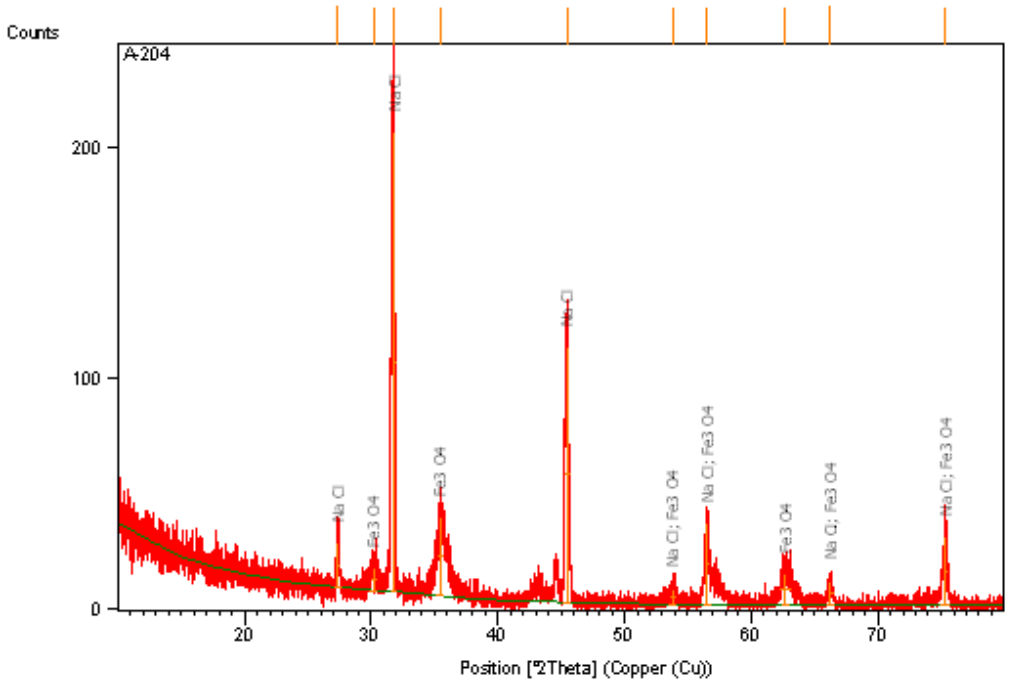

Fig. 3 Sample XRD diffractogram showing the formation of Fe3O4 using citric acid as stabiliser as potassium hydroxide as nucleating agent

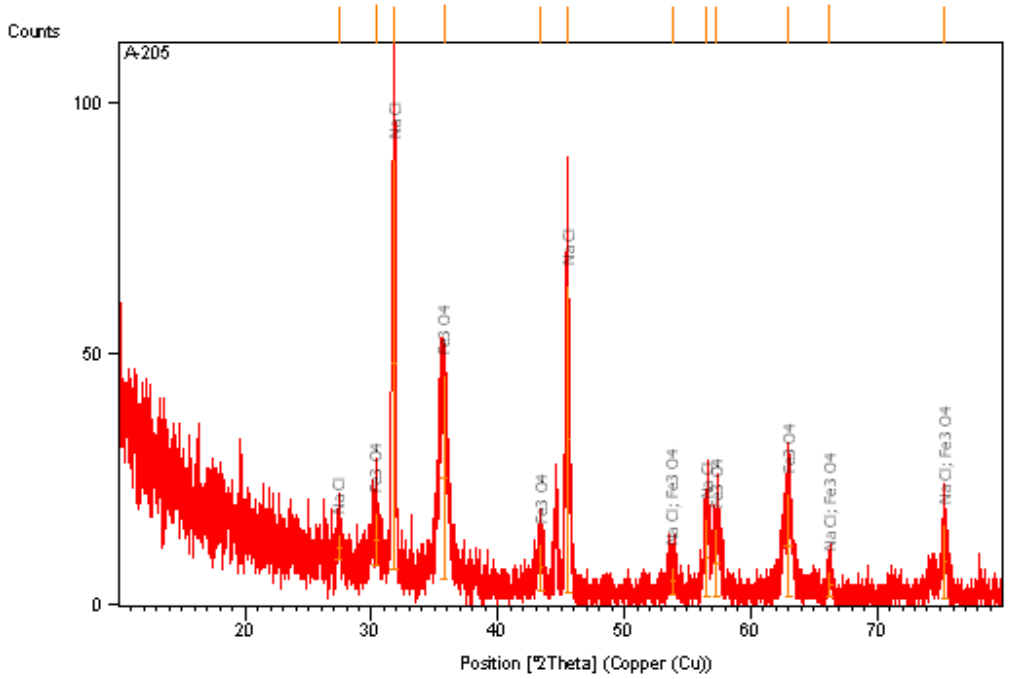

Fig. 4 Sample XRD diffractogram showing the formation of Fe3O4 using citric acid as stabiliser and copper chloride as nucleating agent

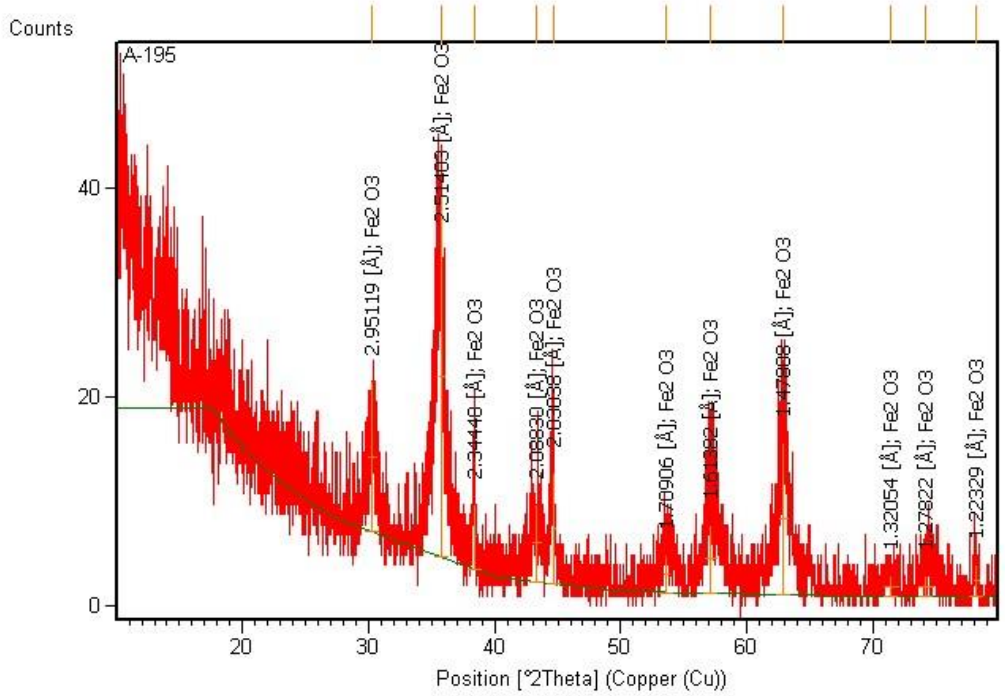

Fig. 5 A Sample XRD diffractogram showing the formation of Fe_2O_3, stabilisation using oxalic acid (sample refined by several stage of decanting using Distilled water)

attributed to this sample. Thus to observe the pure XRD spectrum, the sample should be decanted enough but this will affect the total yield of the synthesis system.

4. Conclusions

XRD results confirmed the formation of nanoparticles. Citric acid stabilised particles were lesser in size during the study than particles obtained under oxalic acid as a stabiliser. It appears that citric acid promotes the formation of magnetite particles by resisting further oxidation of magnetite particles since oxalic acid as a stabiliser promoted the formation of maghemite. The particle size difference under different stabilisers also reflected that the use of citric acid reduces the particle size (in this case up to 18nm) while oxalic acid increased the particle size by 50 nm.

Samples 3 and 4 were prepared under citric acid as a stabiliser while KOH and $CuCl_2$ were used as nucleating agents. The data infers that in both cases magnetite particles were obtained, with a size difference not too wide i.e., 26 nm and 31 nm in each case respectively. Results indicated that the addition of nucleating agent pushed the reaction chemistry towards more growth. In sample 1 when no nucleation agent was used, a particle as small as 18 nm was obtained but when the nucleating agent was introduced particle size increased by at least 30%.

In summary, citric acid should be used as stabiliser as it promotes the formation of magnetite nanoparticles particles.

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