Synthesis, Characterization and Photocatalytic activity of Iron(III)Oxide, Cobalt ferrite and Alkali doped Cobalt ferrite nanoparticles

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Abstract: In the recent decade Nanoparticles (NPs) of transition elements have been researched upon widely for their numerous uses in various fields, varying from biological, catalytic to anti-oxidant applications [1]. Iron (III) Oxide nanoparticles are widely synthesized and are known for their numerous applications. Iron (III) Oxide (Fe_2O_3) in the present work were synthesized by Co-precipitation method. Cobalt Ferrite nanoparticles ($CoFe_2O_4$) have been synthesized and the method which was devised was again Co-precipitation method [8, 9], followed by calcination at 800 ℃ for a period of 3 hrs. [4].The concentration of Cobalt has been taken as 10% and that of Iron Oxide is of 90%in the synthesis of Cobalt ferrite nanoparticles. Further, doping has been carried out with Sodium in Cobalt Ferrite nanoparticles. In the process of doping the concentration of dopant i.e. Sodium has been kept constant while the concentration of Cobalt and Iron Oxide has been varied. Three doped samples have been prepared, in which concentration of Cobalt is 1%, concentration of Sodium is 1%, and as for Iron Oxide it is 98% $Na_{(0.001)}Co_{(0.001)}Fe_2O_{3(0.098)}$ [4]. Sodium Hydroxide (NaOH) has been used as the base to maintain a pH of 11. Polyethylene Glycol has been used as the surfactant. XRD, SEM -EDX and TEM results confirms the formation of Iron Oxide, Cobalt Ferrite nanoparticles and Sodium doped cobalt ferrite nanoparticles. Photocatalytic activity of Iron (III) Oxide, Cobalt Ferrites and sodium doped Cobalt ferrites has been studied by studying the process of degradation of a dye by UV analysis of the samples. The rate of the photocatalytic activity at various quantities of nanoparticles has been discussed in the present work.

Keywords: Nanoparticles, Iron Oxide, Cobalt Ferrites, Co-precipitation, Dopant, Photocatalytic activity.

1.Introduction:

In the recent times nanoparticles of transition metal elements have been used extensively due to their low-cost synthesis, easy availability and for their varied applications. Iron oxide nanoparticles are known widely for their numerous applications. Haematite, Magnetite and Maghemite are the prominent forms of Iron (III)oxide. Accordingly, cobalt ferrite nanoparticles are also well known for their numerous uses in catalytic, biological fields and as anti-oxidants. The category of Cobalt Ferrite nanoparticles is of Spinel Ferrites and they exhibit various unique properties like stability, coercivity, photocatalytic activity, anti-bacterial properties, magnetic properties and so on. In the current paper Photocatalytic activity of the Iron (III)Oxide, Cobalt ferrite nanoparticles and sodium doped cobalt ferrite nanoparticles has been discussed to see the effect of doping on the catalytic activity. The three types of nanoparticles have been prepared to and compared for their photocatalytic activity.

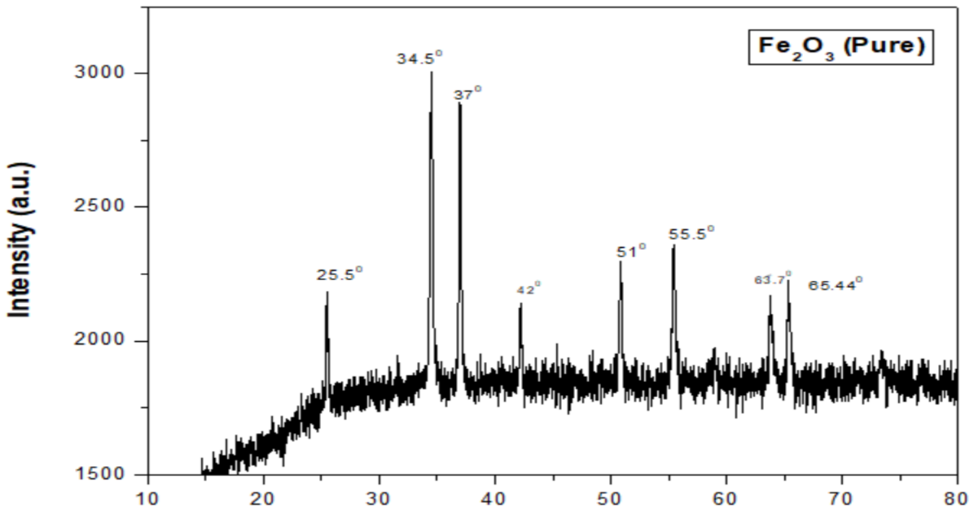
2.Experimental Work

Material and Methods: Co- precipitation method has been used to synthesize the nanoparticles. For the preparation of Iron Oxide (Fe_2O_3) nanoparticles, Iron (III) Nitrate nonahydrate $Fe(NO_3)_3.9H_2O$ has been taken and 0.1M it concentration was prepared. It was subjected to stirring and temperature was maintained at 70°. When temperature was maintained 1ml of PEG (Polyethylene Glycol) was added as a capping agent. Then 40 ml of 1M KOH (Potassium Hydroxide) was added to maintain P_H between 11-12. After this it was subjected to a stirring of 3hrs. The sample was allowed to settle, and was washed with distilled water and ethyl alcohol. It was vacuum dried and was subjected to calcination at 800℃. Similar method was applied for the preparation of Cobalt Ferrite ($CoFe_2O_4$) nanoparticles, $Fe(NO_3)_3.9H_2O$ was taken 0.09M and $Co(NO_3)_2.6H_2O$ was taken 0.01M and a sample of 1M concentration was prepared. PEG was again used as a surfactant same P_H was maintained. A third sample of Cobalt Ferrite was prepared which was doped with sodium. Again a total sample of concentration 1M was prepared in which concentration of Cobalt is 1%, concentration of Sodium is 1%, and as for Iron Oxide it is 98% ($Na_{(0.001)}Co_{(0.001)}Fe_2O_{3(0.098)}$). In this way three samples were prepared for studies.

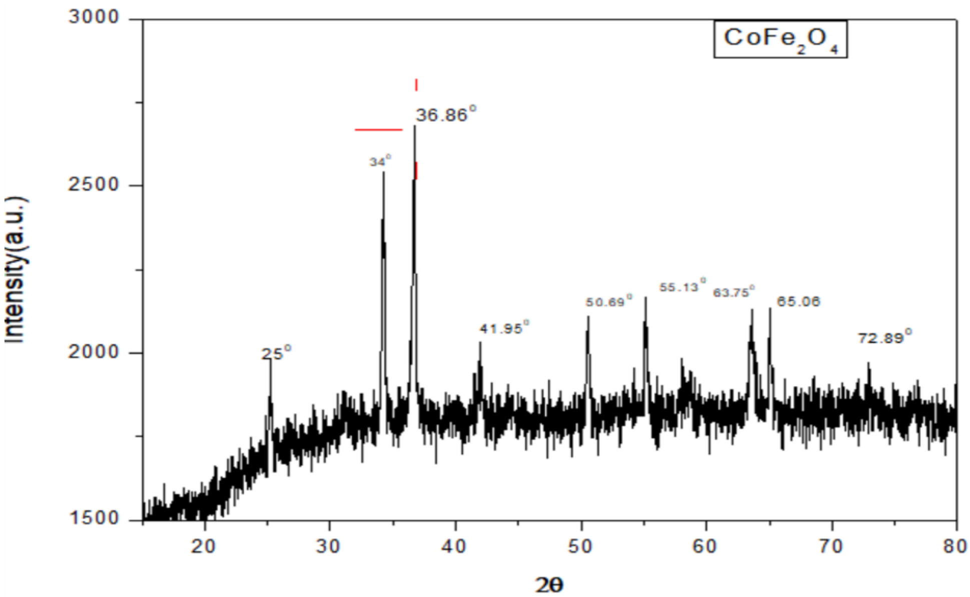
3.Characterization

XRD: The characterization of Iron (III) Oxide nanoparticles was carried out by using XRD technique using a Shimadzu diffractometer using CuK_α radiation over a 2θ radiation of 0 to 80°. XRD confirmed the synthesis of Iron (III) Oxide nanoparticles (Fig.1), Cobalt ferrite nanoparticles (Fig.2) and Sodium Doped Cobalt Ferrite nanoparticles (Fig.3). The peaks corresponding to these nanoparticles were observed respectively.

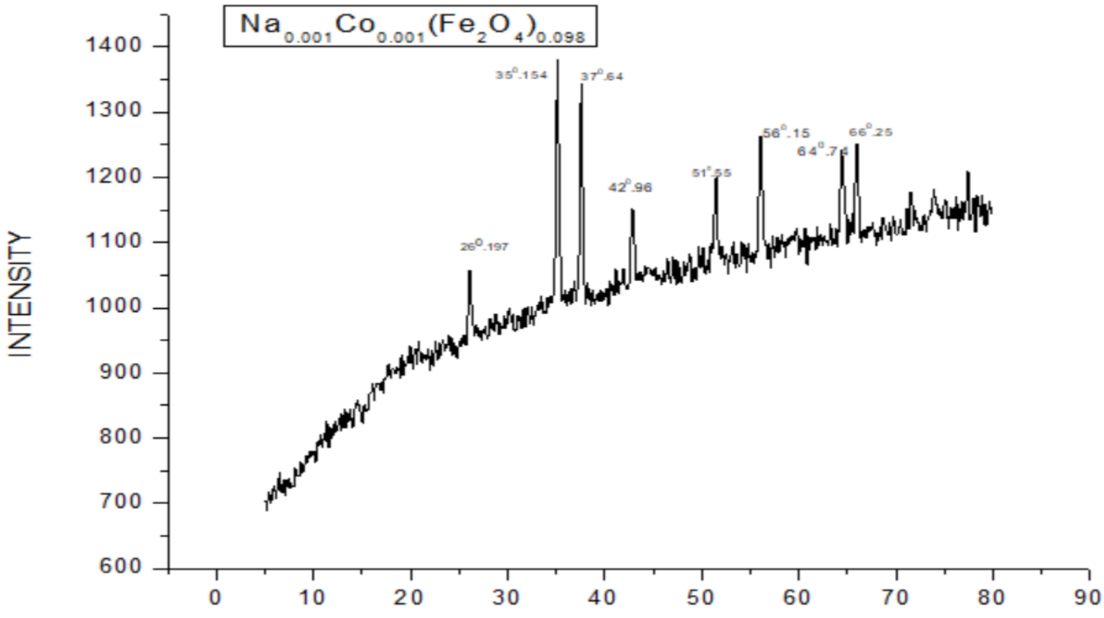
SEM-EDX: The crystallite size , surface morphology and elemental composition of the nanoparticles has been studied by using Field Emission Scanning Electron microscope equipped with Energy Disruptive X-Ray(Fig.4, Fig.5 and Fig.6)



2θ
XRD of Fe_2O_3
Figure 1.



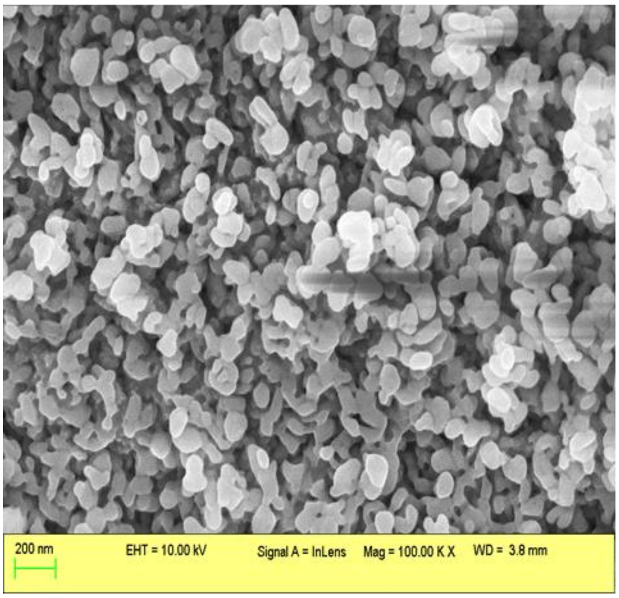
XRD of $CoFe_2O_4$
Figure 2.



2θ

XRD of $Na_{(0.001)}Co_{(0.001)}Fe_2O_{3(0.098)}$

Figure 3.



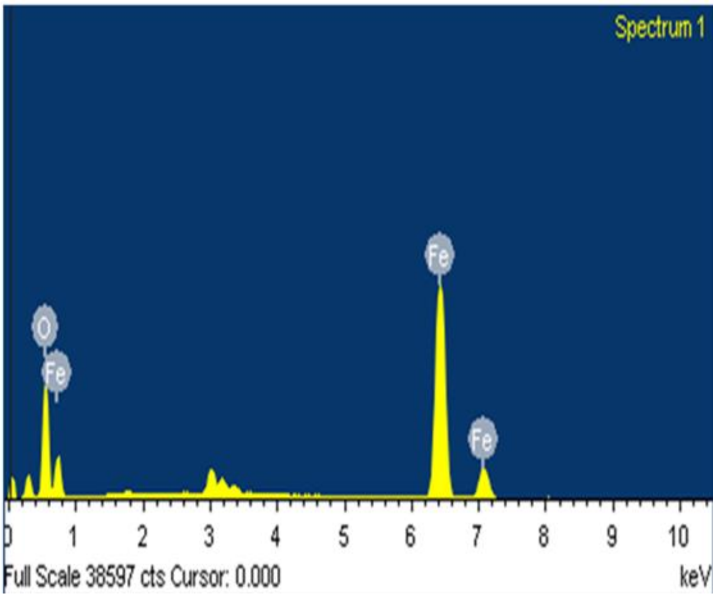
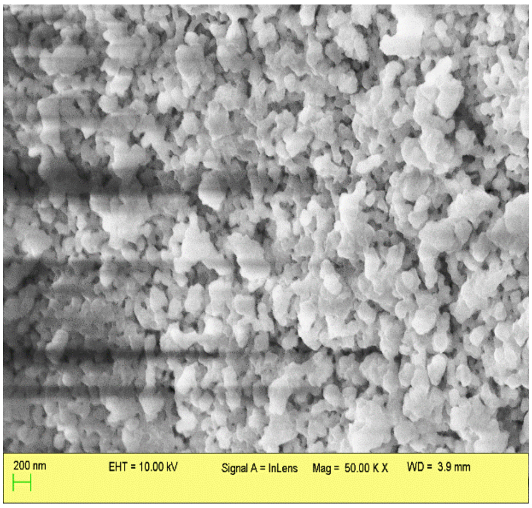


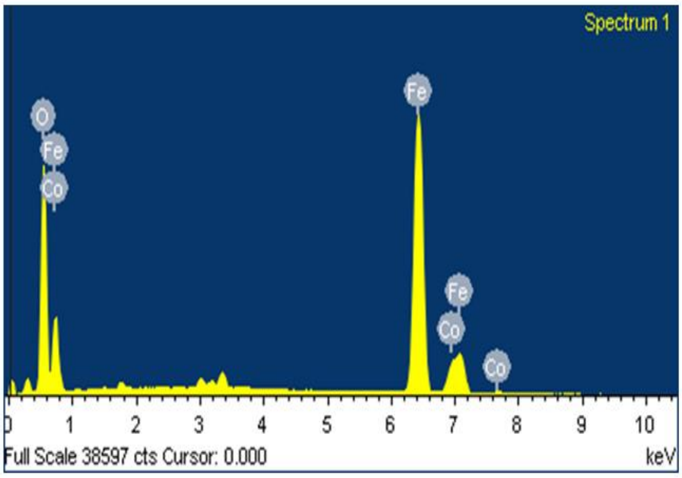
FIGURE 4.

SEM-EDX of Fe_2O_3

SEM-EDX of Iron(III)Oxide (Fe_2O_3)

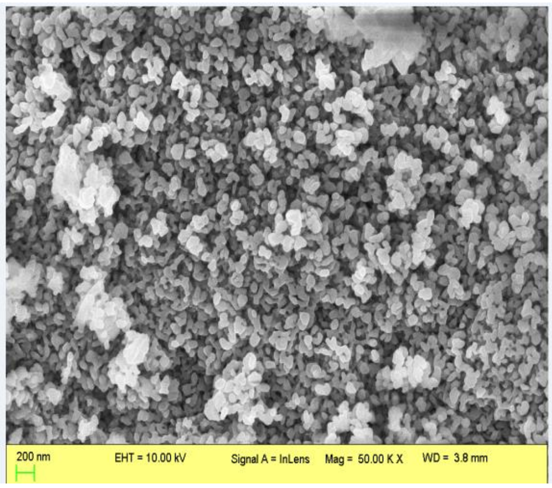
Figure 4.

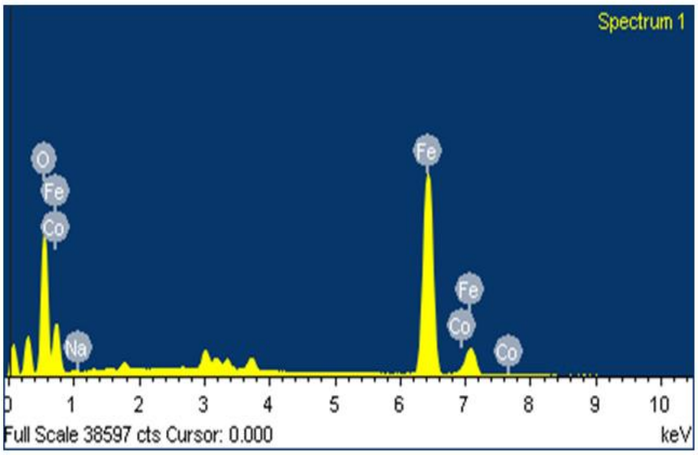




SEM-EDX of $CoFe_2O_4$

Figure 5.





SEM-EDX of $Na_{(0.001)}Co_{(0.001)}Fe_2O_{3(0.098)}$

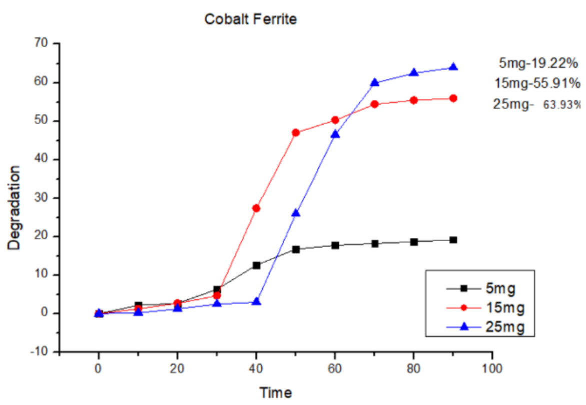
Figure 6.

3.Application

Photocatalytic activity: Photocatalytic activity of iron oxide nanoparticles has been reported widely. They are known to cause photodegradation of dyes. Here, Congo Red dye has been taken and it is studied for photocatalytic degradation with respect to subjecting it to nanoparticles.

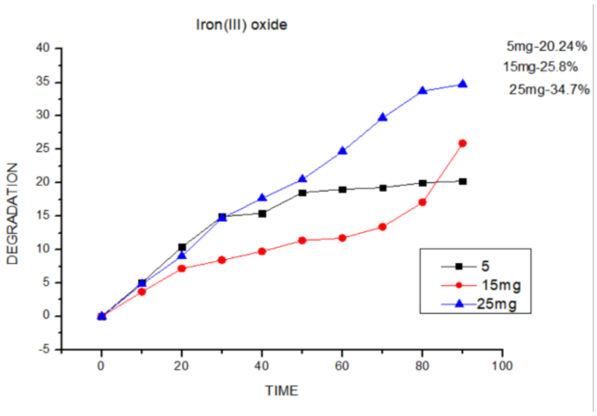
The dye shows absorbance at 498 nm. A high-pressure mercury vapour lamp of almost 125W is used as the source of UV Light.

A photocatalytic chamber was used where the lamp was kept at 6-7 cm above the reaction mixture. A 100 ml of 10 ppm solution of Congo Red dye was prepared and was treated with different quantity (5mg, 15mg, 25mg) of Fe_2O_3/$CoFeO_4$/Na-Cobalt Ferrite nanoparticles. The progress of the reaction was observed by measuring the decrease in absorbance of λ_{max} values for Congo Red dye over an interval of 10 minutes (Fig.7, Fig.8 and Fig. 9, Table 1) and over a total period of 90 minutes [8].



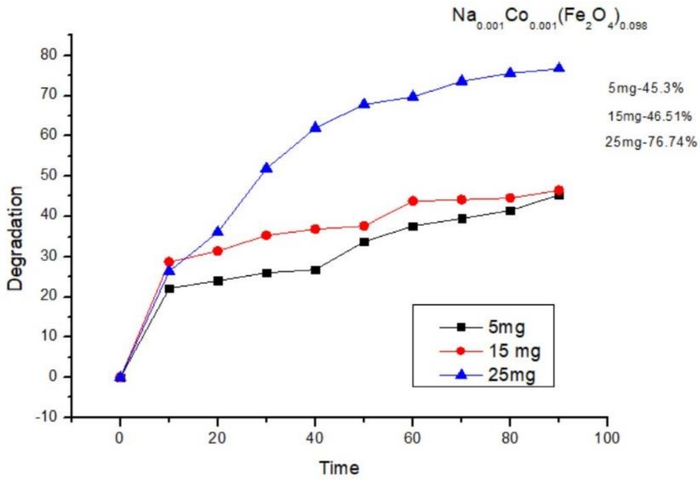
Photocatalytic activity of $CoFe_2O_4$

Figure 7.



Photocatalytic activity of Fe_2O_3

Figure 8.



Photocatalytic activity of $Na_{(0.001)}Co_{(0.001)}Fe_2O_{3(0.098)}$

Figure 9.

4.RESULTS AND DISCUSSION

XRD results confirm the preparation of pure iron(iii) oxide and cobalt ferrite nanoparticles. The decrease in the intensity of most intense peak in respect to pure iron oxide confirms the formation of cobalt ferrite. The sizes of the particles are calculated by using Scherrer formula which is

$D = k\lambda / \beta \cos \theta$

Where D is Crystallite size, k is Scherrer's constant, λ is wavelength of X-Ray, β is Full width half maxima of the peaks and θ is Bragg's diffraction angle. Iron (III) Oxide (pure) shows characteristic peaks at 25.5°, 34.5°, 37°, 42°, 51°, 55.5°, 63.7°, 65.4° [12].The most intense peak's value corresponds to that of Haematite form[12]. The average size particle was found to be 45.11nm. Cobalt ferrite shows peaks at 25°, 34°, 36.86°, 41.95°, 50.69°, 55.13°, 63.75°, 65.06°. The characteristic peak for Iron Oxide is at 34.5°. But when Cobalt was added to prepare Cobalt Ferrite the intensity was reduced and peak was observed at 34°[11]. The average crystal size is found to be 52 nm. If we observe XRD of $Na_{(0.001)}Co_{(0.001)}Fe_2O_{3(0.098)}$,the peaks are observed at 35.154°, 37.64°,42.96°, 51.55°, 56.15°, 64.7°, 66.25° [4] . The intensity of most intense peak is reduced and is observed at 26.197°. The average crystallite size is found to be 60.66 nm.

SEM-EDX : The surface morphology of Iron(III) Oxide nanoparticles was found to be somewhat spherical to irregular (Figure 4).

The surface morphology of $CoFe_2O_4$ was found to be somewhat irregular (Figure 5).

The surface morphology of $Na_{(0.001)}Co_{(0.001)}Fe_2O_{3(0.098)}$ is somewhat spherical. The nanoparticles are agglomerated (Figure 6).

Photocatalytic activity: The photocatalytic activity of Fe_2O_3, $CoFe_2O_4$ and $Na_{(0.001)}Co_{(0.001)}Fe_2O_{3(0.098)}$ synthesized by co-precipitation method by subjecting them to UV lamp(125W) for the degradation of Congo Red Dye. UV visible spectra was recorded from 400-800 nm at an interval of 10 minutes till a total period 90 minutes and the characteristic peak appeared at 498 nm for Congo Red dye. It was observed that the efficiency in photocatalytic activity is affected with doping as is shown in Figure 7, 8 and 9 and Table 1. It has been observed that doping of Cobalt ferrite with sodium leads to maximum degradation activity. It is 76.74% while for Cobalt Ferrite it is 63.93% and for Fe_2O_3, its only 34.7% when 25 mg of sample was used. The percentage of degradation of dye was done using formula:

% Degradation = $(A_O - A_t / A_O) * 100$

Where A_O and A_t are absorbance of pure solution and absorption of reaction mixture at time 't'[8].

The below table confirms this too:

Nanoparticle	Nanoparticle Dosage	Time(min.)	Degradation of Dye (%)
Fe_2O_3 (Iron(III) Oxide)	5mg	90	20.24
	15 mg	90	25.8
	25 mg	90	34.7
$CoFe_2O_4$ (Cobalt ferrite)	5mg	90	19.22
	15mg	90	55.91
	25mg	90	63.93
$Na_{(0.001)}Co_{(0.001)}Fe_2O3_{(0.098)}$ (Sodim doped Cobalt Ferrite)	5 mg	90	45.3
	15 mg	90	46.51
	25 mg	90	76.74

Table 1.

5.Conclusion

Iron(III) oxide (Fe_2O_3) nanoparticles have been formed by co-precipitation method, and after calcination α-Fe_2O_3 (haematite) has been obtained. Cobalt ferrite and copper ferrite nanoparticles have been formed by co-precipitation method and there is decrease in the intensity of most characteristic peaks when iron oxide is doped with cobalt to form cobalt ferrite. Alkali doped (sodium) co ferrite nanoparticles has been prepared by varying concentration of Co, and Iron(III) nitrate .

An important application of photocatalytic activity has been studied and by using sample in milligrams these nanoparticles they act as effective catalysts and thus are suitable easily accessible to accelerate the rate of various reactions. Thus one can check that Photocatalytic activity at various quantities of these three nanoparticles and can decide the type nanoparticle to be used.

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