Use of Some Metal Ferrites in Reduction of 4-Nitrophenol

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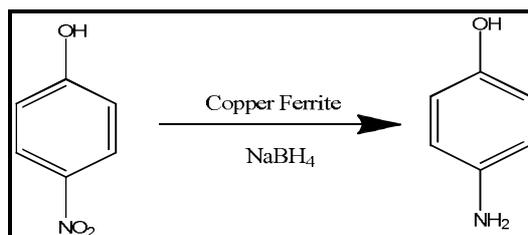**Email:** shubhangvyas@yahoo.com

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ABSTRACT

The noble-metal nanocatalysts are commonly used, but ferrite-based magnetic catalysts are relatively less used. The magnetic copper ferrite, $CuFe_2O_4$ (catalyst) was synthesized via hydrothermal method and it was used to reduce 4-nitrophenol in presence of sodium borohydride. The copper ferrite was analysed by X-ray diffraction spectroscopy (XRD), Energy-dispersive X-ray spectroscopy (EDX), Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR). The reduction of 4-nitrophenol was observed in presence of copper ferrite as catalyst and sodium borohydride as the reductant. The conversion of 4-nitrophenol to 4-nitroamine was monitored by UV-Visible spectrophotometer. The effect of various parameters such as pH, concentration of 4-nitrophenol, and amount of catalyst were studied. The reaction was completed in 6 min in the presence of copper ferrite. It was interesting to note that copper ferrite exhibited higher rate of reduction in presence of zinc or nickel ferrites (combined with cobalt ferrite), may due to synergetic effect.

Graphical Abstract:

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INTRODUCTION

Nitrocompounds are one of the major prime water contaminants as these affect human health because these are endocrine disrupting agents. Although noble-metal nanocatalysts are popular, but the use of magnetic catalysts composed of ferrite materials is limited.

Anantharamaiah *et al.* [**1**] fabricated magnetically recoverable and reusable $MgFe_2O_4/Ag_3PO_4$ composite through a hydrothermal route. Then they used it for reduction of 4-nitrophenol (4-NP) in aqueous medium. The band gap of Ag_3PO_4 was found to be decreased from 2.31 to 1.71 eV in its

composite with $MgFe_2O_4$. They used as-prepared composites as catalyst to drive reduction of 4-nitrophenol using sodium borohydride. It was revealed that this composite exhibited superior catalytic performance over its individual components. This reduction was completed with a 1 min, while same reaction was completed in 15 min on using Ag_3PO_4. This improved catalytic performance of the composite was attributed to a strong electronic coupling between Ag_3PO_4 and $MgFe_2O_4$ that facilitates the transfer of electrons from borohydride to 4-nitrophenol. It was observed that this catalyst was found to be stable even after five consecutive recycles.

Dey *et al.* [2] synthesized copper ferrite nanoparticles (magnetic) via a wet chemical method. It was reported that as-prepared nanoparticles were mesoporous. These copper ferrite nanoparticles exhibited good catalytic property in reduction of 4-nitrophenol with high rate constant and low activation energy. It can be easily separated by magnetic separation and reused again as catalyst many times without any significant loss in its catalytic quality.

Transition metal mixed ferrites, MFe_2O_4 (M = Cu, Mn, Co, or Ni) nanoparticles were synthesised by Gupta *et al.* [3] via co-precipitation method and annealed at 800°C. Their catalytic efficiency was evaluated for the reduction of nitrophenols. It was reported that more than 90% reduction was there on using Cu doped ferrite MNPs as compared to other metal mixed ferrite, which was attributed to the soft behaviour of Cu and higher separation efficiency of the electron-hole pairs. They observed that catalytic activities of these metal ferrites nanoparticles followed the order:

$$CuFe_2O_4 > MnFe_2O_4 > CoFe_2O_4 > NiFe_2O_4.$$

Zhang *et al*. [4] synthesized well-dispersed hollow $CuFe_2O_4$ nanoparticles (H-$CuFe_2O_4$ NPs) using cellulose nanocrystals (CNC) as a support. The catalytic activity of as-prepared H-$CuFe_2O_4$/CNC was evaluated in reduction of 4-nitrophenol in aqueous solution. It was reported that H-$CuFe_2O_4$/CNC catalyst showed an excellent catalytic activity toward the reduction of 4-nitrophenol. This enhanced catalytic activity may be due to introduction of CNC and hollow mesostructure of H-$CuFe_2O_4$ NPs. This catalyst exhibited good conversion efficiency without any significant decrease even after using it for 10 cycles.

Some nanoferrites MFe_2O_4 (M = Ni, Cu, Zn) were synthesized by Goyal *et al*. [5] via sol–gel method. These were then used for reductive transformation of nitrophenols. They employed $NaBH_4$ as mild reducing agent in aqueous medium at room temperature. The ferrites of copper and nickel were found active for this purpose, but zinc ferrite was found to be almost inactive. The rates of reduction for the three isomers of nitrophenols followed the order:

$$2\text{-Nitrophenol} > 4\text{-Nitrophenol} > 3\text{-Nitrophenol}$$

Feng *et al.* [6] prepared and used $CuFe_2O_4$ magnetic nanoparticles (MNPs) high for catalytic reduction of nitrophenol. It was reported that as-prepared $CuFe_2O_4$ MNPs had several benefits such as simplicity, monodispersity, stability, low-cost, and easy magnetic separation, etc. It was revealed that about 95% 4-nitrophenol was reduced to 4-aminophenol within 40 s in the presence of $NaBH_4$.

Gao and Sun [7] developed an efficient and green method to prepare MFe_2O_4 (M Co, Ni, Cu) uniform hollow spheres using polyacrylamide (PAM) as an additive. They used these as-obtained hollow ferrites for catalyzing the reductive transformation of nitrophenols. Out of these three catalysts, $NiFe_2O_4$ and $CuFe_2O_4$ can be reused for at least six runs with a stable conversion efficiency of about 100%, but $CoFe_2O_4$ becomes catalytically inactive just after three cycles. The better catalytic performance of $NiFe_2O_4$ and $CuFe_2O_4$ was attributed to their soft magnetic properties and higher separation efficiency of electron–hole pairs.

Ibrahim *et al.* [**8**] synthesized highly stable and magnetically recoverable MFe_2O_4 (M = Zn, Co, Mn) spinel ferrite nanoparticles. They used sol gel-hydrothermal route for this purpose using polyvinyl alcohol as a surfactant. These were then used as heterogeneous catalysts for the reductive transformation of nitroarenes. It was reported that $MnFe_2O_4$ exhibited the best catalytic performance in the reduction of 4-nitrophenol, 2,4,6-trinitrophenol and 4-nitroaniline and could achieve 100% conversion into the corresponding amino derivatives within 270 sec.

Three metal ferrites ($CuFe_2O_4$, $CoFe_2O_4$, and $NiFe_2O_4$) were synthesized by Ramu *et al.* [**9**] via hydrothermal method, which was followed with calcination process. Toxic nitrocompounds such as 4-nitrophenol, 2,4-dinitrophenol, and 2,4,6-trinitrophenol were degraded in presence of as-prepared materials. It was observed that copper ferrite exhibited excellent removal activity for these nitro compounds by degrading 4-nitrophenol, 2,4-dinitrophenol, and 2,4,6-trinitrophenol in 2, 5, and 10 min, respectively. Day *et al.* [**10**] synthesized nickel ferrite (cube-shaped) nanoparticles. This magnetic nickel ferrite nanocatalyst (NFNC) was 11 nm in size. The catalytic activity of as-prepared NFNC was studied in the reduction of 4-nitrophenol to 4-aminophenol. It was reported that high stability of the catalyst was retained up to 30 cycles.

Two metal-ferrite/maghemite nanocomposites ($NiFe_2O_4/\gamma\text{-}Fe_2O_3$ and $CoFe_2O_4/\gamma\text{-}Fe_2O_3)_3$) were synthesized by El-Subruiti *et al.* [**11**] via doping maghemite with metal salts (nickel and cobalt) followed by reduction of these metal ions using $NaBH_4$. It was observed that as-synthesized nanocomposites exhibited higher catalytic activities for the reduction of 4-nitrophenol and 2-nitroaniline. Titanium dioxide nanotubes (TNTs) were developed by Ibrahim *et al.* [**12**] using TiO_2 P25 as a precursor. Then these nanotubular substrates were wet impregnated with cobalt ferrite to afford $TiO_2/CoFe_2O_4$ (TCF) nanocomposites. It was then used in the photocatalytic reduction of 4-nitrophenol with 94% yield of product within 35 min. It was also revealed that as-prepared nanocomposites exhibited remarkable recycling ability and high-performance stability during this.

Bhatt *et al.* [**13**] prepared visible-light driven SnO_2 quantum dots/TiO_2 nanospheres composite via bottom-up approach. They degraded 2,4,6-trinitrophenol using this as-prepared catalyst. The effect of parameters on rate of degradation was observed such as pH, concentration of dye, amount of semiconductor and light intensity. It was revealed that as-synthesized samples were better photocatalyst than pure TiO_2 nanospheres.

Ahmad *et al.* [**14**] observed that bismuth vanadate is photocatalytically active, and its activity can be enhanced by metal doping such as tungsten. Effect of different operational parameters was studied on the rate of degradation and conditions were optimized as: pH (8.5), amount of photocatalyst (0.10 g) concentration of dye (2.0×10^{-5} M), and light intensity (70.0 mWcm^{-2}). It was proposed that oxygen anion radical was active oxidizing species in this degradation.

MATERIALS AND METHODS

The $CuFe_2O_4$ nanoparticles were prepared via hydrothermal method following a similar method to that of Naidu and Madhuri (2017). In order to synthesize $CuFe_2O_4$, copper and iron nitrates (SRL) (precursor of Cu and Fe) were dissolved in distilled water by maintaining the ratio of nitrates (g): water (mL) as 1:3. Then NaOH (0.28 g) was added slowly to the solution having 1:4 ratio (NaOH: Nitrates). The pH was maintained at 11, mixture was vigorously stirred for 2 h and transferred into a 100 mL Teflon-lined steel autoclave. The sealed autoclave was heat treated at 150°C for 48 h. Copper ferrite nanoparticles were separated from the autoclave and it was washed with acetone and distilled water many times, till pH was decreased to 7, then it was dried at 60°C for 6 h.

RESULTS AND DISCUSSION

X-ray Diffraction (XRD): X-ray diffraction (XRD) patterns of the copper ferrite sample was obtained with D8 QUEST (Bruker) using Cu Ka (λ = 1.5418 Å). An x-ray diffraction pattern is given in figure 1.
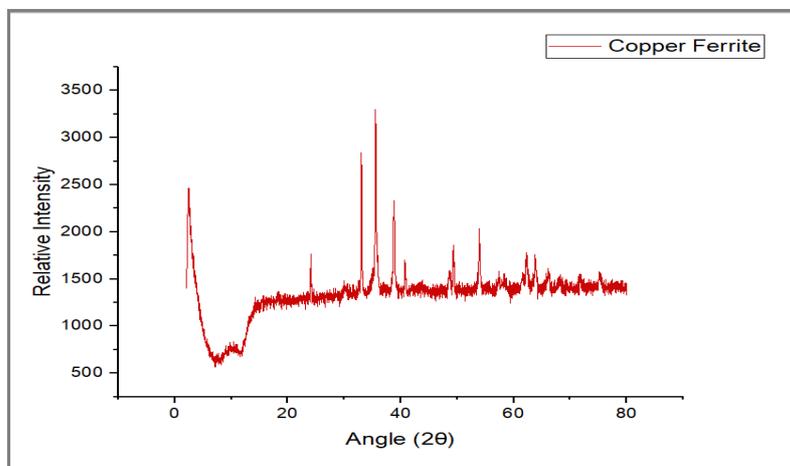

Figure 1. Powder XRD pattern of copper ferrite

Its sharp peaks confirmed that particles of as-prepared sample of copper ferrite were crystalline in nature. The size of these particles were determined using Debye–Scherrer equation

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

Where, D = Crystalline size, K is the Scherer's constant (K = 0.94), λ is the X-ray wavelength (1.54178Å) and β is full width at half maximum (FWHM). The average particle size of the sample was found to be is 29.82 nm.

Field Emission Scanning Electron Microscopy (FESEM): FESEM image of copper ferrite was recorded with the help of (JSM7600F, Jeol). The result is presented in figure 2.
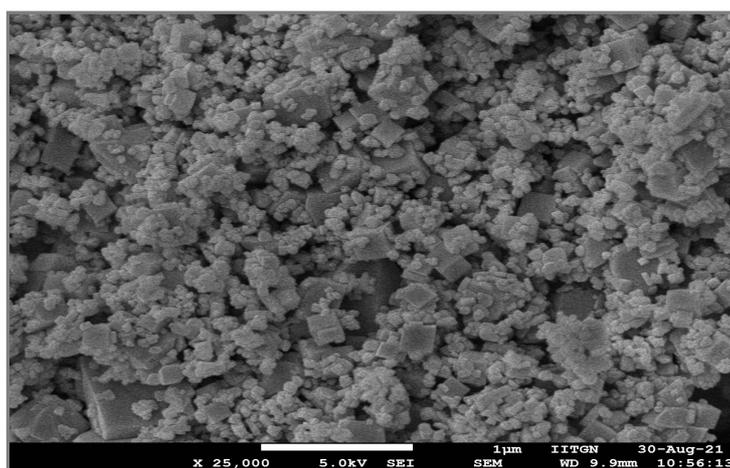

Figure 2. FESEM image of copper ferrite

It was observed that as-prepared copper ferrite was cubic in shape.

Energy Dispersive Spectroscopy (EDS): The copper ferrite sample was also analyzed for its elemental composition using energy dispersive spectroscopy (EDS) (EDX – Oxford INCA Energy 250 EDS) and results are reported in figure 3.
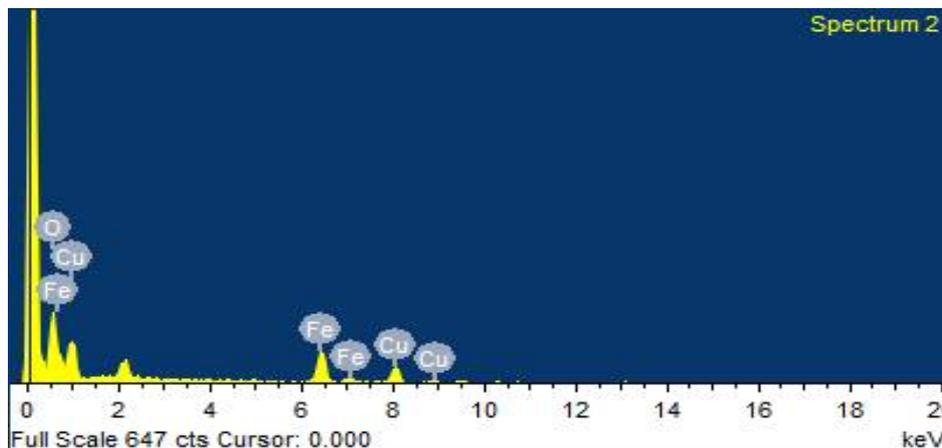

Figure 3. EDS data of copper ferrite.

It was observed that copper ferrite sample contains only copper, iron and oxygen. Therefore, it may be concluded that it does not have any impurity.

FT-IR Spectroscopy (FTIR): The FT-IR spectrum of copper ferrite was recorded with help of (FTIR Spectrometer RX-1) and presented in figure 4.
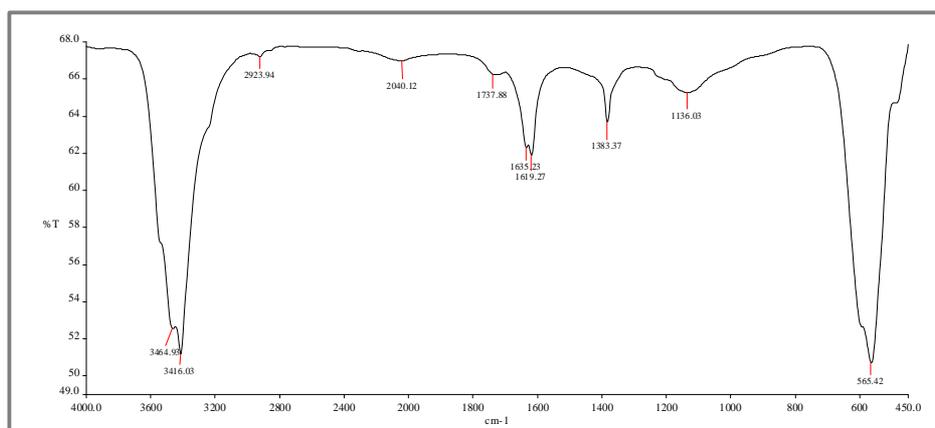

Figure 4. FT-IR spectra of copper ferrite.

The presence of a strong band at 565.42 cm^{-1} indicated the presence of M-O stretching vibration.

Reduction of 4-nitrophenol: Reduction of 4-nitrophenol was carried out with $NaBH_4$ as reducing agent in aqueous medium. The stock solution of 4-nitrophenol (1.0×10^{-3} M) was prepared in doubly distilled water. Working solutions were prepared from this stock solution by diluation. The absorbance was determined by a spectrophotometer (Model UV-1700 Pharmaspec). The desired pH of solution was adjusted by the addition of previously standardized 0.1 N H_2SO_4 and 0.1 N NaOH solutions. The reduction of the solution at various time intervals was measured in terms of absorbance. The effect of various parameters such as pH, concentration of 4-nitrophenol, amount of catalyst, amount of sodium borohydride, and temperature was observed. It was found that negligible reduction was there in absence of catalyst, but the reduction of 4-nitrophenol was completed within 6 min in presence of catalyst.

Effect of pH: The effect of variation of pH was studied in the range of 3.0 to 7.5 and resulted are reported in the table 1.

Table 1. Effect of pH

pH	Rate constant (k) $\times 10^3$ (s^{-1})
3.0	2.10
3.5	3.81
4.0	5.20
4.5	2.93
5.0	1.92
5.5	1.54
6.0	1.20
7.0	0.74
7.5	0.55

It was observed that the reduction of 4-nitrophenol increases in acidic range upto 4.0 and then decreases. The maximum reduction of 4-nitrophenol was found to be at pH 4.0. As the pH was increased, the rate of reduction increases, but on further increase in pH above 4.0, some phenolate ion are also formed. The phenolate ions will face a force of repulsion from negatively charged surface of copper ferrite due to adsorption of OH$^-$ ions. As a result, reduction rate decreases.

Concentration of 4-nitrophenol: The effect of concentration of 4-nitrophenol was observed in the range 3.5×10^{-4} to 7.0×10^{-4} M. The results are reported in table 2.

Table 2. Effect of concentration of 4-nitrophenol

[4-Nitrophenol] $\times 10^4$ M	Rate constant (k) $\times 10^3$ (s^{-1})
3.5	1.10
4.0	2.87
4.5	4.06
5.0	5.20
5.5	1.71
6.0	1.54
6.5	0.99
7.0	0.55

The rate of reduction of 4-nitrophenol increases with increase in its concentration as more molecules are available for reaction, but after a certain limit (5.20×10^{-4} M), its movement to reach active sites of copper ferrite is restricted due to larger concentration of 4-nitrophenol. As a result, a decrease in rate of reduction was observed.

Amount of NaBH$_4$: The effect of concentration of sodium borohydride was observed from 0.8×10^{-3} M to 2.0×10^{-3} M. The results are reported in table 3. The freshly prepared NaBH$_4$ was prepared by dissolving 0.3782 g in 25 mL of water and it was added to the 4-nitrophenol solution (5.0×10^{-4} M) drop wise. It was observed that the color of solution changed from yellow to orange, may be due to formation of phenolate ion. But, after some time, it reverts back to its original yellow color. Then 0.005 g catalyst was added and its affect was studied.

Table 3. Effect of NaBH$_4$

(NaBH$_4$) $\times 10^3$ M	Rate of constant(k) $\times 10^3$ (s^{-1})
0.8	1.02
1.0	1.39
1.2	1.60
1.4	2.12
1.6	3.08
1.8	4.13
2.0	**5.20**

The rate of reduction increases with increase in concentration of $NaBH_4$. Maximum rate could be achieved with $2.0 \times 10^3 M$. It is all due to fact that at larger concentrations, more molecules of reductant are available and hence, the higher rate of reduction.

Effect of amount of catalyst: The amount of catalyst is also likely to affect the reduction of 4-nitrophenol. Therefore, the amount was varied from 0.002 to 0.010 g. The results are reported in table 4.

Table 4. Effect of amount of copper ferrite

Amount of copper ferrite (g)	Rate constant $(k) \times 10^3$ (s^{-1})
0.002	1.61
0.003	2.37
0.004	3.62
0.005	5.20
0.006	4.68
0.007	3.31
0.008	2.06
0.009	1.15
0.010	0.97

It was observed that as the amount of catalyst was increased, the rate of reaction increases reaching an optimum value for 0.005 g, but it decreases on further increase in amount of copper ferrite. It can be attributed to the fact that on increasing the amount of catalyst, more active sites are available, resulting in higher rate of reduction, but after attaining maximum value, there was a decrease in rate of reduction due to saturation of active sites.

Effect of Light: The reduction of 4-nitrophenol was also observed in the presence of light (with and without catalyst) (Table 5).

Table 5. Effect of light

Effect of Light	
Without copper ferrite	With copper ferrite
$8.92 \times 10^{-5} s^{-1}$	7.41×10^{-3} s^{-1}

The rate of reduction was very much slower in absence of catalyst but a fast reduction was observed in the presence of copper ferrite. It may be due to degradation of 4-nitrophenol along with its reduction as the copper ferrite is a photocatalyst also.

Effect of temperature: The effect of temperature was observed on the rate of reduction of 4-nitrophenol in the range 303-313 K (with or without catalyst). The results are reported in table 6 and figure 5

Table 6. Effect of temperature

Catalyst	Temperature (K)	Rate constant $(k) \times 10^3$ (s^{-1})
With catalyst	303	5.20
	308	7.07
	313	11.22
Without catalyst	303	0.07
	308	0.12
	313	0.20

The plot of log K v/s 1/T is linear, which indicates that the reaction followed Arrhenius law. The energy of activation was calculated as Ea= 43.98 KJ mol^{-1} (without catalyst) and 33.69 KJ mol^{-1} (with

catalyst), which clearly indicated that energy of activation in presence of catalyst was less as compared to without catalyst.
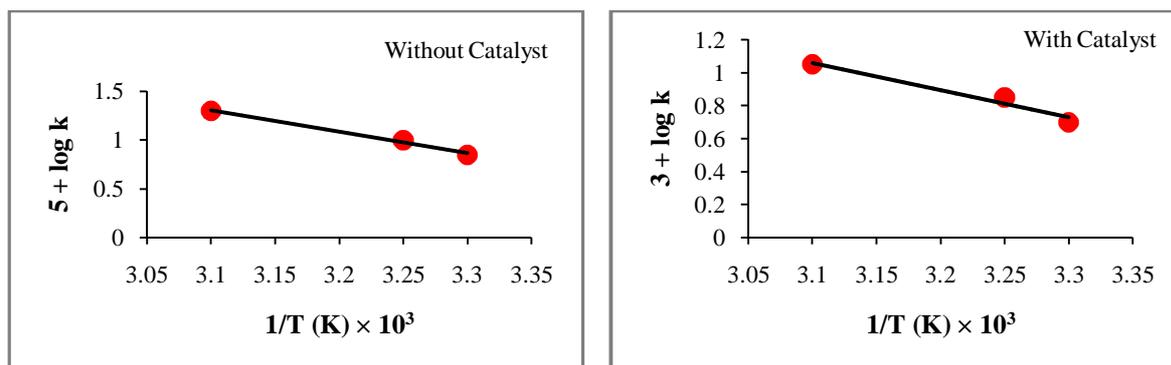

Figure 5. Arhenius plots (log k vs 1/T)

Effect of combination of ferrites: The effect of mixing other ferrites (zinc and nickel ferrites) with copper ferrite was also observed. It was quite interesting to note that the rate of reduction of 4-nitrophenol in presence of zinc and nickel ferrite was quite low, i.e. 9.9×10^{-5} and 8.58×10^{-5} s^{-1}, but there was a sudden rise in the rate of reduction as 8.43×10^{-3} and 4.81×10^{-3} s^{-1} respectively, when these were used with copper ferrite as a catalyst. It may be like a synergetic effect between two ferrites. The product was confirmed as 4-aminophenol because of the presence of a new peak at 305 nm in UV-Vis spectrum of the product, which is characteristic of 4-aminophenol.

APPLICATION

Photocatalysis has emerged as an active field of research, which has numerous applications such as solar cells, photosplitting of water, waste water treatment, antimicrobial activities, photoreduction of carbon dioxide, etc. and it will open up many new avenues in a few decades from now.

COCLUSION

Nitroaromatic compounds are already known endocrine disrupting agents and these are explosive in nature also. Water is polluted by the presence of such nitroaromatics. An effort has been made to reduce toxic 4-nitrophenol by sodium borohydride catalyzed by copper ferrite and its combination with zinc and nickel ferrites. The reaction was completed in 6 min in presence of copper ferrite, but in much shorter period, when copper ferrite was used with these ferrites. The conversion of toxic nitro compounds to their corresponding amino products can be considered a favorable step towards reducing pollution load on water as amino compounds are much more less toxic than their counter nitro compounds.

ACKNOWLEDGEMENT

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