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USE OF SOME METAL FERRITES IN THE REDUCTION OF 2,4,6-TRINITROPHENOL

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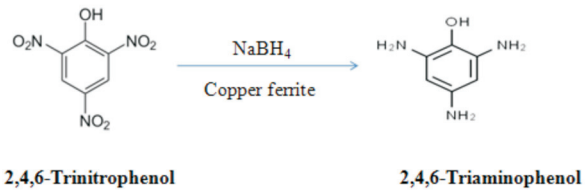
ABSTRACT

The noble-metal Nanocatalyst are widely used, but ferrite-based magnetic catalyst are rarely used. The magnetic copper ferrite, $CuFe_2O_4$ catalyst was synthesized by hydrothermal method and used to reduce 2,4,6-trinitrophenol 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 2,4,6-trinitrophenol was observed in presence of copper ferrite as catalyst and sodium borohydride as the reductant. The conversion of 2, 4, 6-trinitrophenol to 2, 4, 6-triaminophenol was monitored by UV-Visible spectrophotometer. The effect of various parameters such as pH, concentration of nitro compound, and amount of catalyst were studied. The reaction was completed in 8 min in the presence of copper ferrite. It was interesting to note that copper ferrite exhibited higher rate of reduction in present of zinc and nickel ferrites, may due to synergetic effect otherwise they show very slow reduction.

KEY WORDS : Copper ferrite, Reduction, 2,4,6-Trinitrophenol, Catalyst, Picric acid

GRAPHICAL ABSTRACT



2,4,6-Trinitrophenol **2,4,6-Triaminophenol**

INTRODUCTION

Environmental pollution has become a worldwide problem and currently water pollution is the most serious global concern. A large amount of organic wastes are regularly discharged into water bodies without treatment or little treatment, causing serious environmental pollution. Nitro compounds are the major contaminants of water and these are considered prospective endocrine disrupting agents.

Highly stable and magnetically recoverable spinel metal ferrites (M = Zn, Co, Mn) nanoparticles were synthesized (Ibrahim *et al*., 2016). They used polyvinyl alcohol as a surfactant. It was reported that $MnFe_2O_4$ exhibited the best performance in the reduction of 2,4,6-trinitrophenol (2,4,6-NP) with 100% conversion into amino derivatives in 270 sec with rate constant equal to 0.01061, 0.01134 and 0.01355 s^{-1}, respectively. The enhanced catalytic activity of $MnFe_2O_4$ was attributed to increase in pore radius and pore volume.

The 4-nitrophenol, 2,4-dinitrophenol, and 2,4,6-trinitrophenol were removed over magnetic copper, nickel and cobalt ferrites (Ramu *et al*., 2021). Out of these three catalysts, copper ferrite exhibited excellent removal performance and it was observed that 4-nitrophenol, 2,4- dinitrophenol and 2,4,6-trinitrophenol were completely removed in 2, 5, 10 min, respectively.

The $NiCo_2O_4$ nanoparticles were prepared using *Bryophyllum pinnatum* (Lam) Oken leaf extract (BPLE) as capping and hydrolyzing agents (Yulizar *et al*., 2022). The average particle diameter of nickel cobaltite was found to be 25.84 nm. The catalytic performance of nanoparticles was evaluated in the

reduction of 2,4,6-trinitrophenol and it was found that 96.03% trinitrophenol could be reduced within 24 min. The higher efficiency of this catalyst was attributed to the effective electron relay between borohydride ions and trinitrophenol. It was also claimed that these nanoparticles retained their activity even upto to four cycles.

The Au nanoparticles were prepared by photoreduction using chitosan-Au (III) hydrogel system (Wu *et al*., 2015). The as-prepared Au nanoparticles were then used for reduction of a number of nitroaromatic compounds in prescence of sodium borohydride. As-prepared Au nanoparticles exhibited good stability and reusability. It was revealed that highly explosives (2,4,6-trinitrophenol and 2,4,6-trinitrotoluene) could also be reduced by $NaBH_4$ using this catalytic system.

As SnO_2 quantum dots/TiO_2 nanospheres composite may be an excellent candidate as a photocatalyst, because of its high specific surface area, high tunability, strong visible-light absorbing ability, and semiconductive properties, so SnO_2 quantum dots/TiO_2 nanospheres composite was prepared (Bhatt *et al*., 2019). It was reported that photocatalytic activity of as-synthesized samples for reduction of picric acid was higher than only TiO_2 nanospheres.

Silver nanoshell coated cationic polystyrene beads were synthesized (Jana and Pal, 2007). As-prepared silver coated resin beads were used as catalyst to reduce 4-nitrophenol by sodium borohydride. It was revealed that the catalyst can be recycled for a number of times. The activity of this solid catalyst was examined towards the reduction of, 2- nitrophenol, 3- nitrophenol and 2,4,6-trinitrophenol.

A catalytic method was developed to reduce nitrophenols using gold nanoparticles decorated-ZIF-11 (Au/ZIF-11) composite (Malik and Nath, 2021). They synthesized three Au/ZIF-11 composites (Au0.1Z, Au0.2Z and Au0.3Z) through direct reduction of $HAuCl_4$ (0.1 to 0.3 mM) using sodium borohydride in the suspension of pre-synthesized ZIF-11. It was reported that spherical and uniformly distributed gold NPs were having average particle size of 7.35 ± 0.95 nm. It was observed that sample of Au0.2Z exhibited high catalytic efficiency towards the reduction of 2-nitrophenol, 3- nitrophenol, 4- nitrophenol, as well as 2,4,6-trinitrophenol. It was also reported that catalyst Au 0.2Z can be reused up to 5 cycles retaining its conversion efficiency (> 90%).

A coprecipitation method was used to prepare cobalt doped graphitic carbon nitride-based catalyst ZIF-67/g-C_3N_4 (ZIF-CN) (Roy *et al.*, 2021). It was then used for the reduction of nitrophenols in presence of sodium borohydride. The diameter of nanoparticles was in the range of 5–10 nm, which were embedded in the conductive g-C_3N_4 (gCN) layer. It was reported that as-synthesized catalyst exhibited excellent reduction of 4-nitrophenol, 2,4-dinitrophenol, and 2,4,6-trinitrophenol. It was observed that reduction rate of 4–nitrophenol over this composite was about 3.8 and 7.3 times than that with pristine ZIF-67 and gCN, respectively. This as-synthesized ZIF-CN catalyst can be reused for at least for ten cycles without any sigminficant loss in its catalytic activity.

MATERIALS AND METHOD

$CuFe_2O_4$ nanoparticles were prepared via hydrothermal method. 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 (g) was added slowly to the solution in 1:4 (NaOH : Nitrates) ratio. 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. The product in the autoclave was washed with acetone and distilled water many times, till pH was decreased to 7. Copper ferrite nanoparticles were separated from the autoclave and dried at 60 °C for 6 h.

Characterization of Copper Ferrite

X-Ray Diffraction (XRD)

X-ray diffraction patterns is given in Fig. 1.

X-ray diffraction (XRD) patterns of the as-synthesized sample was obtained with D8 QUEST (Bruker) using Cu Ka (λ = 1.5418 Å). 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 known as the Scherer's constant (K = 0.94), λ is the X-ray wavelength (1.54178Å) and β is full width at half maximum (FWHM).

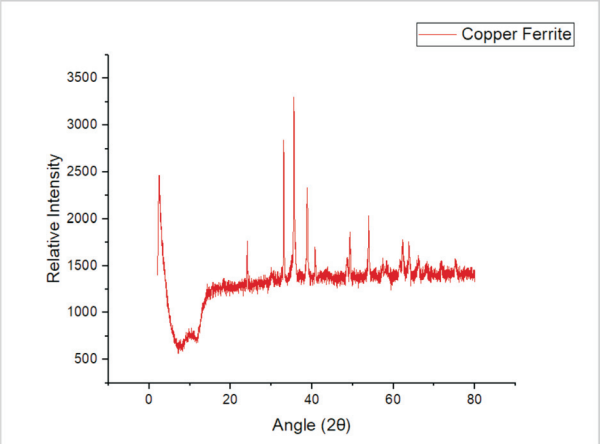


Fig. 1. Powder XRD pattern of copper ferrite

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 is presented in Fig. 2.

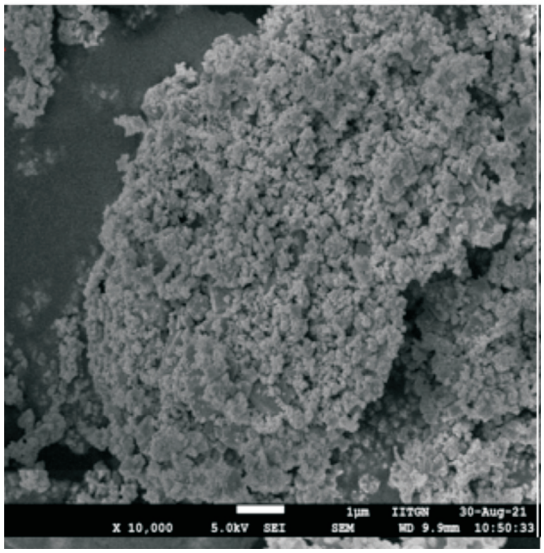


Fig. 2. FESEM image of copper ferrite

It was observed that as-prepared copper ferrite was having structure like a pumice stone.

Energy Dispersive Spectroscopy (EDS)

The copper ferrite sample was also analyzed for its elemental composition using energy dispersive spectroscopy (EDS) and results are reported in Fig. 3.

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.

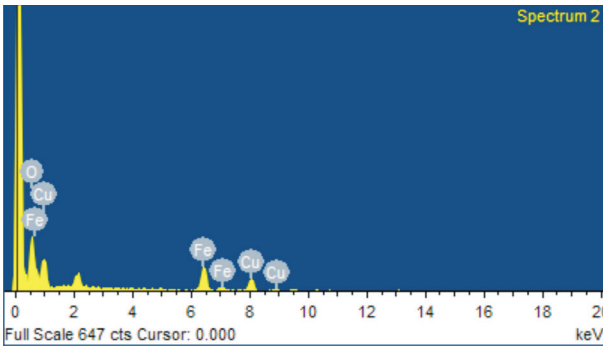


Fig. 3. EDS data of copper ferrite

FT-IR Spectroscopy (FTIR)

The FT-IR spectrum of copper ferrite is presented in Fig. 4.

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

Reduction of 2,4,6-nitrophenol

Reduction of 2,4,6-nitrophenol was carried out with $NaBH_4$ as reducing agent in aqueous medium. The stock solution of 2,4,6- trinitrophenol (picric acid) (1.0×10^{-3} M) was prepared in doubly distilled water. Working solutions were prepared from this stock solution as and when required. 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 sulphuric acid and 0.1 N sodium hydroxide 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 2,4,6-trinitrophenol, amount of catalyst, amount of sodium borohydride, light, and temperature was observed. It was found that no reduction was there in absence of catalyst, but the reduction of 2,4,6- trinitrophenol was completed within 8 min in presence of catalyst.

Effect of pH

The effect of variation of pH was studied in the range of 4.0 to 8.0 and resulted are reported in the Table 1.

It was observed that the reduction increases in acidic range and decreases in the basic range. The maximum reduction of 2,4,6-trinitrophenol was found to be at pH 5. As the pH was increased, the rate of reduction increases, but on further increase in pH above 5.0, some phenolate ion are also formed. The phenolate ions will face a force of repulsion from negatively charge surface of copper ferrite due

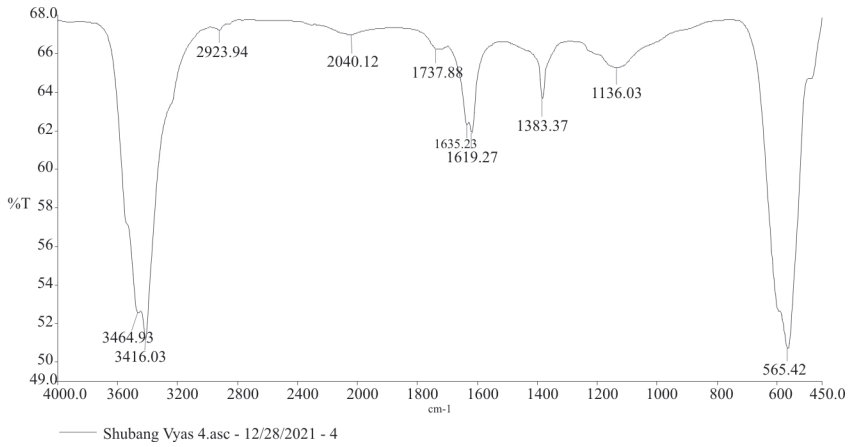


Fig. 4. FT-IR spectra of copper ferrrite

Table 1. Effect of pH

pH	Rate constant (k) × 10^4 (s^{-1})
4.0	8.32
4.5	9.01
5.0	11.23
5.5	8.72
6.0	6.05
6.5	4.66
7.0	3.28
7.5	2.91
8.0	1.0

Table 2. Effect of concentration of 2,4,6-trinitrophenol

[2,4,6-trinitrophenol] × 10^4 M	Rate constant (k) × 10^4 (s^{-1})
0.71	4.62
0.83	5.75
0.90	8.56
1.00	11.23
1.12	9.72
1.20	6.50
1.28	5.04
1.39	4.71

to adsorption of OH^- ions. As a result, reduction rate decreases.

Concentration of 2,4,6-trinitrophenol

The effect of concentration of 2,4,6-trinitrophenol was observed in the range 7.10 × 10^{-5} to 1.39 × 10^{-4} M. The results are reported in Table 2.

The rate of reduction of 2,4,6-trinitrophenol increases with increase in its concentration as more molecules are available for reaction, but after a certain limit (1.0 × 10^{-4} M), its movement to reach active sites of copper ferrite is restricted due to larger concentration of 2,4,6-TNP. As a consequence, a decrease in rate of reduction was observed.

Amount of $NaBH_4$

The efect of concentration of sodium borohydride was observed from 0.76 × 10^{-3} to 3.40 × 10^{-3} M. The results are reported in Table 3. The freshly prepared $NaBH_4$ was prepared by dissolving 0.3782 in 25 ml of water and it was added in the 2,4,6-trinitrophenol solution (1.0 × 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 some amount of catalyst was added. No reaction was observed in absence of copper ferrite.

Table 3. Effect of $NaBH_4$

($NaBH_4$) × 10^3 M	Rate of constant (k) × 10^4 (s^{-1})
0.76	2.05
1.13	3.28
1.51	4.26
1.89	6.44
2.26	7.61
2.64	9.27
3.02	11.23
3.40	8.46

A similar effect was also observed in case of increasing the concentration of sodium borohydride resulting in decreases in rate of reaction.

Effect of amount of catalyst

The amount of catalyst is also likely to affect the reduction of 2,4,6- trinitrophenol. Therefore, the

amount was varied from 0.003 to 0.009 g. The results are reported in Table 4.

Table 4. Effect of amount of copper ferrite

Amount of copper ferrite(g)	Rate constant (k) $\times 10^4$ (s^{-1})
0.003	2.79
0.004	4.10
0.005	6.41
0.006	8.22
0.007	11.23
0.008	9.1
0.009	6.4

It was observed that as the amount of catalyst was increased, the rate of reaction increases reaching an optimum value for 0.007 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 slight decrease in rate of reduction due to saturation of active sites.

Effect of Light

The reduction of 2,4,6-trinitrophenol 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
3.5×10^{-5} (s^{-1})	1.56×10^{-3} (s^{-1})

The rate of reduction was little slow in absence of catalyst but a fast reduction was observed in the presence of copper ferrite. It may be due to degradation of 2.4.6 –trinitrophenol 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 2,4,6 –trinitrophenol in the range 303-313 K (with or without catalyst). The results are reported in Table 6 and Fig. 5.

The reaction followed Arrhenius law. The activation parameters have been calculated as Ea= 47.86 KJ mol^{-1} (without catalyst) and 23.93 KJ mol^{-1} (with catalyst), which clearly indicated that energy

Table 6. Effect of temperature

	Temperature (K)	Rate constant (k) $\times 10^4$ (s^{-1})
With Catalyst	303	16.10
	308	17.96
	313	27.02
Without Catalyst	303	2.5
	308	3.2
	313	4.68

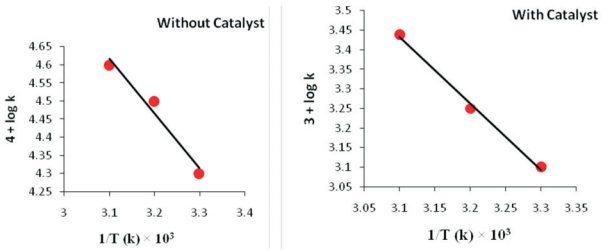


Fig. 5. Arhenius plots (log k vs 1/T)

of activation was decreased to almost half of the original in presence of catalyst.

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 2,4,6–trinitrophenol in presence of zinc and nickel ferrite was quite low, i.e. 2.53×10^{-5} and 3.02×10^{-5} s^{-1} of zinc and nickel ferrite, but there was a sudden rise in the rate of reduction 2.05×10^{-3} and 0.99×10^{-4} s^{-1}, respectively, when these were used with copper ferrite as a catalyst It may be like a synergetic effect between two.

The product was confirmed as 2,4,6-triaminophenol because of the production of a new peak at 305 nm in UV-Vis spectrum of the product, which is characteristic of 2,4,6-trinitrophenol (Veerakumar *et al.*, 2017).

CONCLUSION

Nitroaromatic compounds are known endocrine disrupting agents and some of them are explosive in nature also. Water is polluted by the presence of such nitroaromatics. An effort has been made to reduce toxic 2,4,6-trinitrophenol by sodium borohydride catalyzed by copper ferrite and its combination with zinc and nickel ferrite. The reaction was completed in 8 min in presence of copper ferrite, but in much shorter period, when copper ferrite was used with these ferrites. The

conversion of toxic nitro compound to their amino products can be consider a favorable step to reduce pollution load on water as corresponding amino compounds are much more less toxic than their counter nitro compounds.

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