Enhanced catalytic reduction of p-nitrophenol on nanoscaled metal hexacynoferrate

A dissertation submitted in the partial fulfillment of
the requirement for the degree of
Bachelor of Science
in
Chemistry

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DECLARATION

This thesis entitled "**Enhanced catalytic reduction of p-nitrophenol on nano scaled metal hexacyanoferrate**" is my original work and adheres to ethical research guidelines. All external sources are properly cited. This work is done under the supervision of **Dr. Mamta Latwal and Dr. Shefali Arora** from **Department of chemistry, Applied Sciences Cluster, School of Advanced Engineering, University of Petroleum & Energy Studies, Dehradun, India.**

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I certify that, **Tanu Parashar** has prepared his project entitled "**Enhanced catalytic reduction of p-nitrophenol on nano scaled metal hexacyanoferrate**" for the award of **B.Sc. (Hons) Chemistry,** under our guidance. She has carried out the work at the **Department of Chemistry, School of Advanced Engineering, University of Petroleum & Energy Studies, Dehradun, India.**

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Abstract

Enhanced catalytic reduction of nitroaromatic compound by using transition metal containing catalyst are in much demand. Overall, the research into copper hexacyanoferrate for p-NP reduction is driven by the desire of catching a sustainable, efficient and cost-effective method for environmental remediation and organic transformation. Initially precious metals (Au, Ag, Pt, Pd etc.) are used, which are expensive. Therefore, CuHCF NPs are a good green alternative for this reduction and it is a potentially efficient catalyst at converting 4-NP into 4-AP. Studying this process helps us in understanding the factor that makes a good catalyst and could lead to further development and optimization of this particular catalyst and similar ones.

CuHCF NPs were synthesized using an eco-friendly method (co-precipitation method). Synthesized particles were characterized by different techniques like FTIR (Fourier Transform Infrared) spectroscopy, XRD (X-Ray Diffraction) and CHNS analyzer. The result showed that CuHCF achieved a maximum conversion of 100% for p-NP into 4-AP in the aqueous medium with the reducing agent $NaBH_4$ at room temperature. This conversion rate was comparable to Au nanoparticles and it exhibited excellent reusability in successive 7 cycles.

Abbreviations

MHCF = Metal Hexacyanoferrate

CuHCF = Copper Hexacyanoferrte

ZnHCF = Zinc Hexacyanoferrate

NiHCF = Nickel Hexacyanoferrate

NPs = Nanoparticles

4-NP = 4-Nitrophenol

p-NP = p-Nitrophenol

4-AP = 4-Aminophenol

p-AP = p-Aminophenol

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CHAPTER 1
INTRODUCTION

The 4-NP is an important raw material for the production of dyes, pharmaceuticals, pesticide and insecticides. It is hazardous and toxic pollutants which widely exists in untreated industrial wastewater. While being exposed to the environment p-nitrophenol causes ecological health risk. 4-NP is highly stable and soluble in water, due to its high solubility and toxicity, 4-NP is hard to biodegrade and decomposed. Many traditional water purification methods for removing 4-NP like Absorption, Microbial degradation, catalytic degradation and electrochemical treatment are not effective. These techniques are energy consuming and requires more cost.

So, it is important to developed a mild treatment method to remove p-nitrophenol. Catalytic reduction is one of the most promising Technology for the degradation and removal of pollutants under mild conditions.

Many researchers have showed that 4-NP can be converted into 4-AP, because 4-AP is lesser toxic than 4-NP and it can be used as an intermediate which can be used further for the preparation of important pharmaceutical drugs, such as Paracetamol, Polymers, Corrosive lubricants and dyes.

1.1 Transition Metal Hexacyanoferrates: -

These are the very important stable co-ordination compound. Various metals like Iron, Copper, Cobalt, Zinc, Nickel hexacyanoferrates have drawn attention of many reseacher's nowdays, due to their good solid-state chemistry. Transition Metal hexacyanoferrates have the general formula $M_h[Fe(CN)_6]_n.xH_2O$ (where x, n and h are stoichiometric numbers, M = transition metal cations). Here are some examples of transition metal hexacynoferrates along with their chemical formulas.

1. Copper (II) hexacyanoferrate - $Cu_2[Fe(CN)_6]._nH_2O$
2. Nickle (II) hexacyanoferrate – $Ni_2[Fe(CN)_6]._nH_2O$
3. Zinc (II) hexacyanoferrate – $Zn_2[Fe(CN)_6]._nH_2O$
4. Cobalt (II) hexacyanoferrate – $Co_2[Fe(CN)_6]._nH_2O$
5. Manganese (II) hexacyanoferrate – $Mn[Fe(CN)_6._nH_2O$

In these formulas, the transition metal ions M (II) can vary, leading to different transition metal hexacyanoferrates with distinct properties and applications. Additionally, the value of the n in the formula represents the number of water molecules associated with the compound's structure, which can vary depending on the synthesis conditions.

1.2 Methods of synthesis: -

Nanoparticles can be synthesized by physical, chemical and biological means. These are the chemical methods, which are mentioned below in detailed.
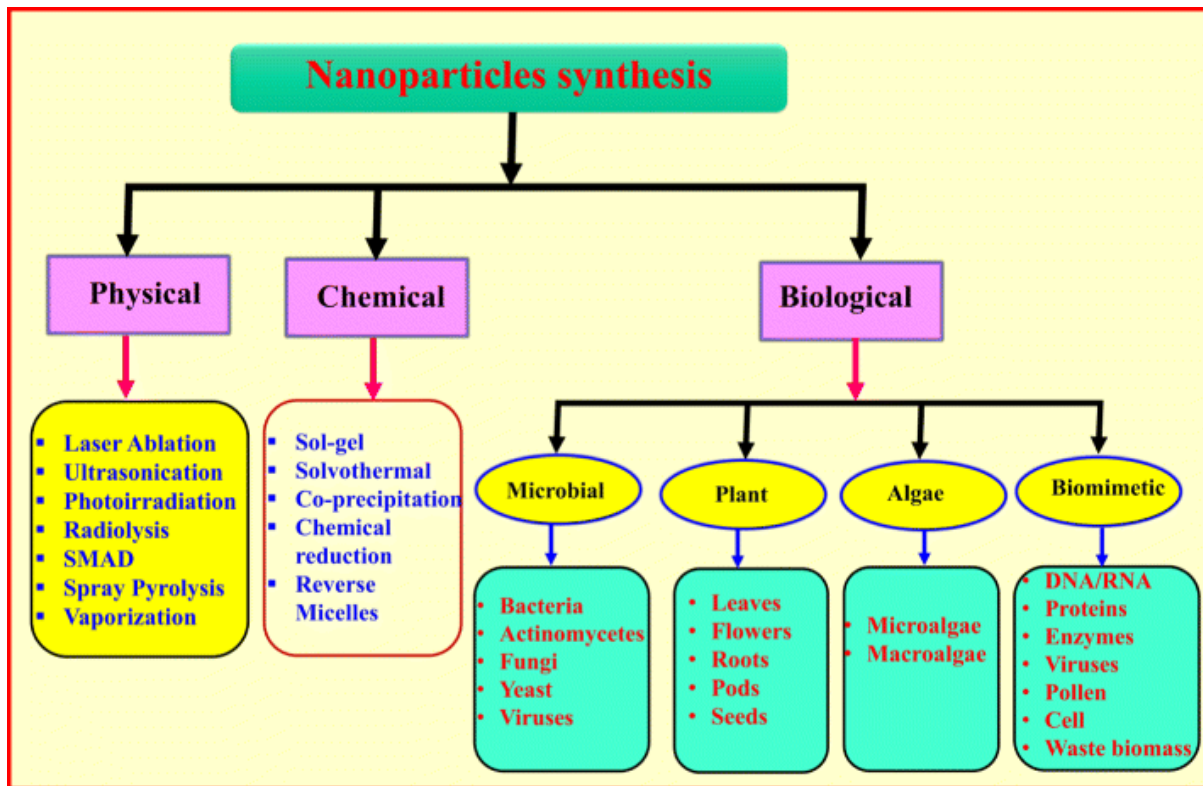

Figure 1: Ref:- https://www.wikipedia.org/

1.2.1 Sol-gel Method

The Sol-gel method involves nanoparticles in a liquid solvent to form a sol. This sol undergoes gelation, forming a three-dimensional network through chemical cross-linking or bonding. After aging to enhance stability, the gel is dried to remove the solvent, crucial for solid material formation. Optionally, calcination may follow to induce further structural transformations. Sol-gel synthesis enables precise control over composition, morphology, and structure, making it indispensable in ceramics, coatings, sensors, and catalysis.

1.2.2 Solvothermal

The solvothermal method involves heating a reaction mixture in a sealed container under high pressure and temperature. This promotes nucleation and growth of nanoparticles. Control over parameters such as temperature, pressure, and reaction time allow precise tuning of nanoparticle size, shape, and crystallinity. Solvothermal synthesis is particularly useful for producing nanoparticles with uniform properties and high purity. The method finds applications in various fields including catalysis, materials science, and nanotechnology. Its versatility and ability to produce complex nanostructures make it a valuable tool for advanced research and development efforts.

1.2.3 Co-precipitation Method

The co-precipitation method involves mixing aqueous solutions of soluble salts containing desired metal ions. The addition of a precipitating agent induces the formation of insoluble metal hydroxides or oxides, leading to nanoparticle formation. Control over reaction conditions like pH, temperature, and stirring rate influences nanoparticle properties. This method offers simplicity, scalability, and versatility in nanoparticle synthesis. It is widely employed in diverse applications such as catalysis, magnetic materials, and biomedical fields. Its ability to produce nanoparticles with tunable properties makes it a valuable tool in materials science and nanotechnology research

1.2.4 Chemical Reduction

Chemical reduction employs a reducing agent to convert metal ions into metallic nanoparticles. This process allows for control over nanoparticle size, shape, and composition. It finds wide applications in catalysis, electronics, and biomedicine due to its versatility and ability to produce tailored nanoparticles.

1.2.5 Reverse Micelles

Reverse micelles are microscopic balls with a twist: water inside, and oil outside. Surfactant molecules act as a soap bubble, trapping water in a nonpolar solvent. These tiny spheres can solubilize water-insoluble materials, making them valuable in drug delivery and other fields

Table 2: Synthesis of different MHCF Nanoparticles using different methods.

Metal Hexacyanoferrate Nanoparticle	Mode of Synthesis	References
Iron hexacyanoferrate nanoparticles	• By microemulsion technique (W/O). • synthesis of PB Nanocubes from a single-source precursor using sonochemical method. • Synthesis with single precursor.	Vaucher et al.,2002 [9,10] Wu et al.,2005 [11,12] Jia et al.,2007 [13]
Copper hexacyanoferrate nanoparticles	• Synthesis by film preparation of copper hexacyanoferrate nanoparticles. • By co-precipitation method.	Chen et al.,2007 [14] Ali et al.,2011 [8]

Cobalt hexacyanoferrate nanoparticles	• synthesis using EDTA stabilizer. • By Solgel method.	Qu et al.,2006 [7] Berrettoni et al., [15]
Nickel hexacyanoferrate nanoparticles	• Synthesis using Nickel nitrate and EDTA surfactant.	Qu et al.,2006 [7]

Many metal hexacyanoferrates were synthesized using these techniques over the last two-three decades. The detailed literature is shown in Table 1.

1.3   Copper hexacyanoferrate nanoparticles

Copper hexacyanoferrate nanoparticles act as catalysts for various redox reactions, including the oxidation of organic compounds and the reduction of pollutants. Their nanostructured morphology and high surface area enhance catalytic efficiency and stability. These nanoparticles exhibit promising potential in environmental remediation and wastewater treatment processes. Their facile synthesis methods and tunable properties make them attractive for industrial catalysis applications. Ongoing research aims to explore their catalytic mechanisms and optimize their performance for diverse chemical transformations.

1.3.1 Catalytic property

Copper hexacyanoferrate nanoparticles demonstrate remarkable catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol. Through a redox reaction, the copper ions in the catalyst facilitate the conversion of the nitro group to an amino group on the phenolic ring. This catalytic process occurs under mild reaction conditions and proceeds efficiently in aqueous environments. The reaction kinetics can be monitored spectrophotometrically, with the color change from yellow to colorless indicating the reduction process. This catalytic system offers a green and sustainable approach for the synthesis of 4-aminophenol, contributing to the development of environmentally friendly chemical processes
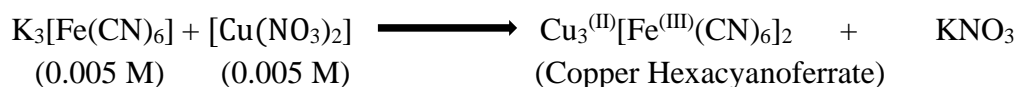
CHAPTER 2
EXPERIMENTAL DETAILS

2.1 Synthesis of CuHCF NPs

2.1.1 Chemicals Used: - The chemicals used for the synthesis of CuHCF nanoparticles are Copper (II) Nitrate purchased from Merck, Potassium Hexacyanoferrate i.e. $K_3[Fe(CN)_6]$ from Merck, Potassium Chloride purchased from Avantor and Ethylenediaminetetracetic acid i.e. EDTA obtained from Molychem. All chemicals used as it is given in the laboratory and preparation of solution takes place in distilled water

2.1.2 Synthesis :-

CuHCF is synthesized as per the following reaction:-

$$K_3[Fe(CN)_6] + [Cu(NO_3)_2] \longrightarrow Cu_3^{(II)}[Fe^{(III)}(CN)_6]_2 + KNO_3$$
$$(0.005\ M) \qquad (0.005\ M) \qquad \qquad (Copper\ Hexacyanoferrate)$$

Ali et al. (2011) proposed an environmentally friendly method for synthesizing CuHCF nanoparticles known as the co-precipitation method. In this method, two solutions were prepared of 0.005M: Solution (A) containing 0.658g of Potassium Hexacyanoferrate and 0.149g of KCl in 400g of distilled water, and Solution (B) containing 0.724g of copper(II) nitrate and 0.876g of EDTA in 600g of distilled water, in specific ratios. Solution (A) was prepared by dissolving Potassium Hexacyanoferrate and KCl in distilled water, while Solution (B) involved dissolving copper(II) nitrate and EDTA in distilled water. These solutions were mixed slowly over several hours (5-6 hours) using a burette, with Solution (B) added dropwise to Solution (A) on a magnetic stirrer. The reaction occurred at room temperature, and after complete mixing, the mixture was left undisturbed for 24 hours, resulting in a colour change indicating the formation of CuHCF nanoparticles. The nanoparticles were then separated by centrifugation, filtered, and dried in an oven. Care was taken during the filtration process to avoid contamination with filter paper particles.
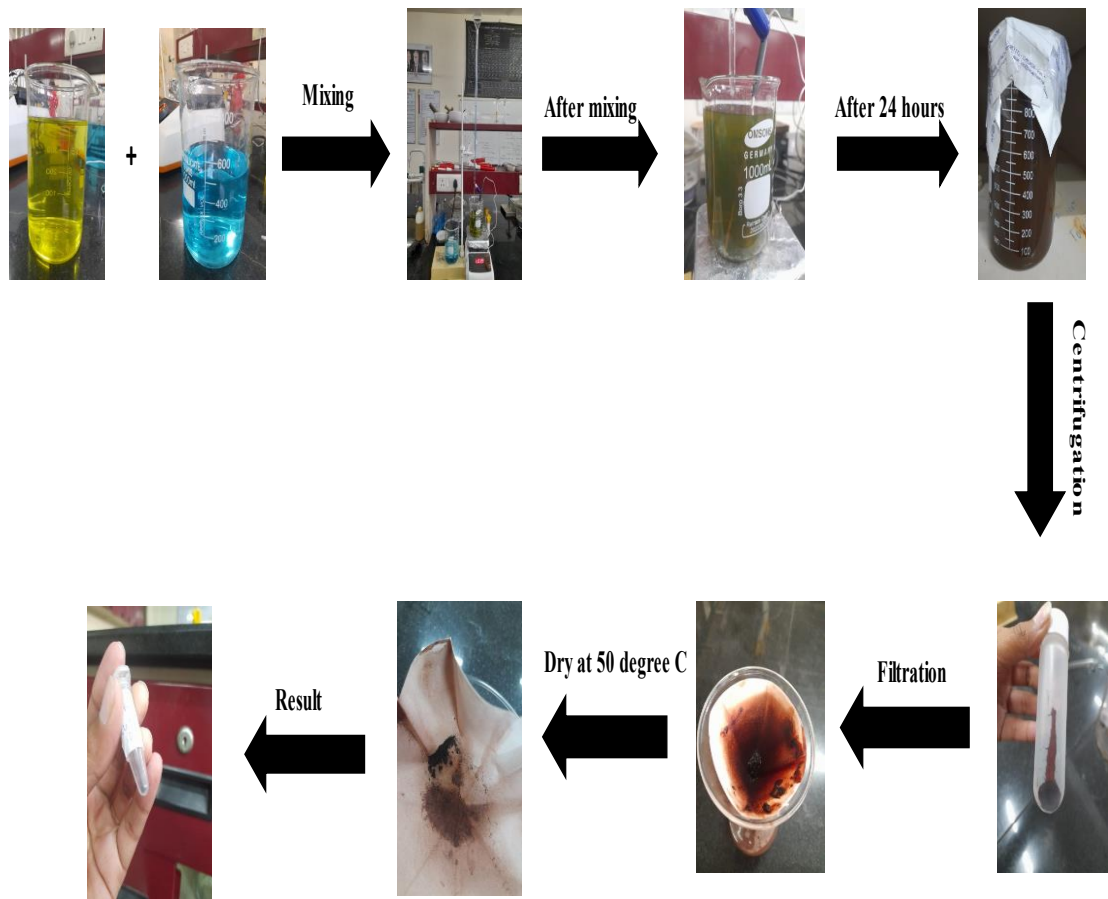
Figure 2:- Methodology of CuHCF Nanoparticles synthesis

2.2   Characterization of CuHCF NPs

2.2.1 XRD:-

X-ray diffraction (XRD) is a technique used to analyze the crystalline structure of materials. By bombarding a sample with X-rays, it produces diffraction patterns, revealing information about its atomic arrangement. XRD is crucial in various fields, including materials science, chemistry, and geology. It helps identify phases present in a sample and determine their crystalline structures. This technique aids in understanding material properties and guiding manufacturing processes. The size of the crystallites within the compound was determined using the Debye-Scherrer equation. This equation correlates the broadening of peaks in X-ray diffraction patterns to the size of nanoparticles. It is expressed as:

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

Where D represents the crystallite size, K is the Scherrer constant (0.98), λ is the X-ray wavelength, θ is the Bragg angle (measured in radians), and β is the full width at half maximum (FWHM) of the peak.

The analysis of copper hexacyanoferrate nanoparticles was conducted using a Bruker X-Ray Diffractometer, capturing the pattern within the 2θ range of 10-80 degrees. The wavelength of the X-ray radiation was set at 1.54 Å.

Figure 3 :- X-Ray Diffractrometer

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2.2.2 FTIR:-

FTIR spectroscopy utilizes the principle of measuring the absorption of infrared light by molecules to identify functional groups and molecular structures in a sample. It distinguishes between different regions: the functional group region (4000-1500 cm^-1), where specific bonds absorb light, providing information about chemical functionalities, and the fingerprint region (1500-500 cm^-1), which offers a unique pattern for each molecule, aiding in identification. This technique is crucial in various fields like chemistry, pharmaceuticals, and materials science for its ability to provide rapid and non-destructive analysis of samples, offering insights into molecular composition and structure.

Functional groups within the synthesized compound were identified through analysis using a Perkin Elmer Spectrometer (refer to Figure 4). To facilitate this, CuHCF NPs were blended with moisture-free potassium bromide (KBr) to form a thin pellet. This choice was motivated by KBr's optical transparency in the mid-infrared region, allowing radiation to pass through while being absorbed by the sample. The pellet was compressed under 5 psi pressure using a hydraulic press. Spectral examination covered the range of 400 cm^-1 to 4000 cm^-1, with the aim of discerning the presence of any organic coatings on the surface of the nanoparticles.

Figure 4 :- Fourier Transform Infrared Spectrometer

2.2.3 CHNS Analyzer :-

CHNS analyzers, also known as elemental analyzers, determine the carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) content in a sample. The principle involves combustion of the sample in a high-temperature environment to convert the elements into their respective oxides or gases. These gases are then separated and quantified using techniques such as gas chromatography or thermal conductivity detection. Typically, the detection ranges for each element are as follows:

➢ Carbon (C): 0.1% - 100%
➢ Hydrogen (H): 0.1% - 100%
➢ Nitrogen (N): 0.1% - 100%
➢ Sulphur (S): 0.1ppm – 5%

CHNS Analyzers are widely used in various fields, including environment analysis, pharmaceuticals, and materials science, for their ability to provide accurate elemental composition data in solid, liquid, and gas samples.

Figure 5 : *CHNS (O) Elemental Analyzer*
Ref:- https://www.wikipedia.org/

2.2.4 Sonicator :-

To prepare the nanoparticles for UV-Vis Spectroscopy, a sonication process is necessary due to their natural insolubility in water. Figure 5 illustrates this step, wherein the nanoparticles are sonicated for 15 minutes. Sonication helps disperse the nanoparticles uniformly in the solvent, facilitating accurate UV-Vis spectral analysis.

Figure 6 : Sonicator

2.3 Reduction of 4-nitrophenol to 4-aminophenol with CuHCF NPs as a catalyst.

2.3.1 Chemicals Used: -

The reaction utilized p-nitrophenol and NaBH4, both procured from Merck. These chemicals were employed in their as-received state from the laboratory, without additional purification. Solutions were prepared using distilled water.

2.3.2 Reaction Procedure: -

The reaction was conducted directly within the cuvette. A solution containing 3.6×10^{-3} M of p-nitrophenol and a 1M aqueous solution of Sodium Borohydride (NaBH4) was prepared. Initially, 122 µL of p-nitrophenol, along with 3.2 ml of distilled water, was added simultaneously to the cuvette, and the absorbance was measured using a UV-Vis spectrophotometer within the range of 200-800 nm. Subsequently, 175 µL of NaBH4 was added to the same cuvette containing the p-nitrophenol solution, and the new absorbance was recorded. Finally, 17.5 µL of CuHCF solution was added to the cuvette, and absorbance readings were taken at various time intervals. The entire reaction was carried out at room temperature.

Due to the insolubility of CuHCF NPs in water, they were sonicated for 15 minutes. For this, 10 mg of CuHCF NPs were added to a water sample bottle containing 10 ml of water and subjected to sonication. The resulting colloidal solution of nanoparticles was utilized for the reduction reaction.

CHAPTER 3
RESULTS AND DISCUSSION

3.2.6 Characterization of CuHCF NPs

3.3.1 XRD: -
Figure 7 displays the graph representing the resulting Copper Hexacyanoferrate nanoparticles. The presence of sharp peaks suggests a highly crystalline structure, which aligns with previous findings [20]. The face-centered cubic (fcc) lattice structure, typical of Prussian blue and several other transition metal hexacyanoferrates, is likely exhibited by the Copper Hexacyanoferrate nanoparticles.
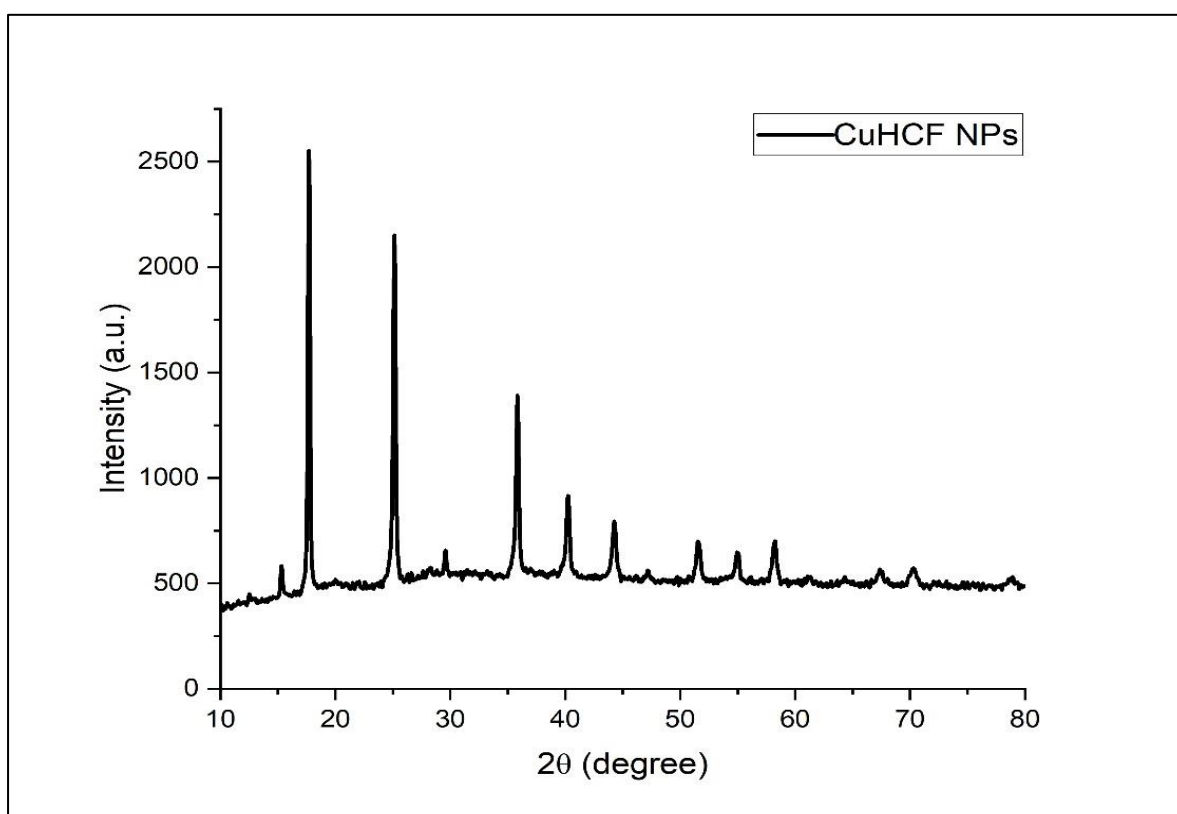

Figure 7 :- XRD pattern of CuHCF NPs

1.3.2   FTIR:-

The IR spectrum graph of CuHCF NPs, depicted in Figure 8, reveals distinct features. A sharp peak at 2106 cm^{-1} is notably present, characteristic of the C≡N group within the unit. Furthermore, bands ranging from 480 to 596 cm^{-1} correspond to Fe-C stretching within the [Fe(CN)6] entity. Additionally, a broad band spanning from 3300 to 3600 cm^{-1} indicates hydrogen bonding, likely originating from water molecules within the lattice's interstitial sites. A H-O-H bending peak at 1632 cm^{-1} further supports this observation. These findings are consistent with previous research [21].
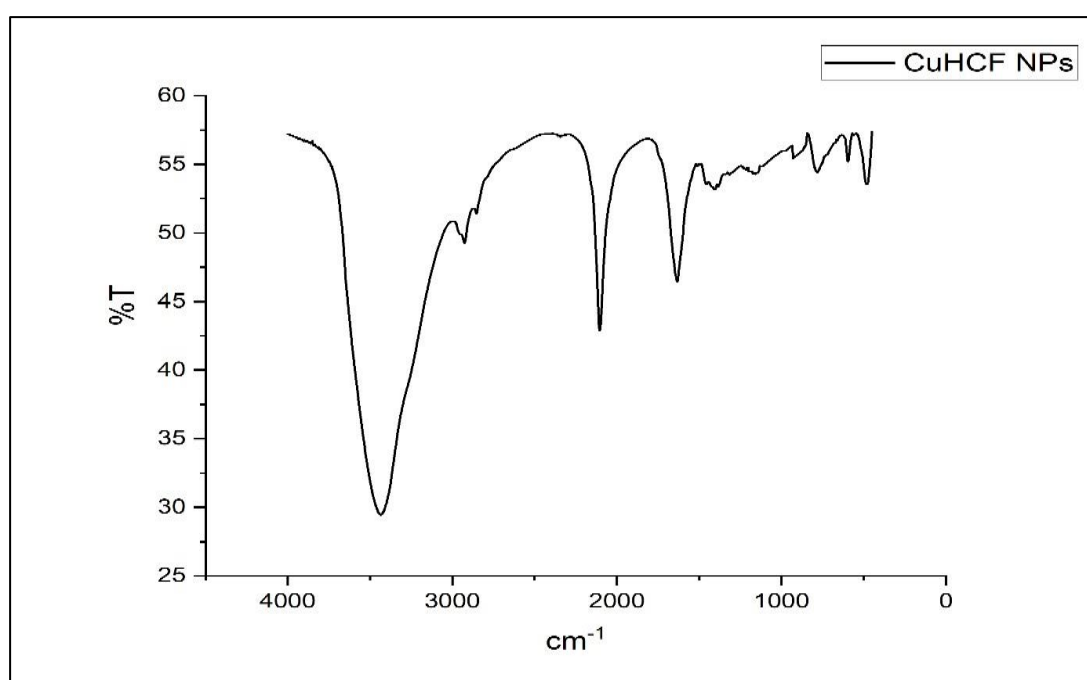

Figure 8 : *FTIR spectra of CuHCF NPs*

1.3.3   CHNS Analyzer:-

The results for CHNS clearly indicate the presence of Carbon (C) , Hydrogen (H) and Nitrogen (N) in the synthesized compound. The amount of Carbon, Hydrogen and Nitrogen present is shown in Table 2 given below.

Table 2: CHNS results for the synthesized compound.

Sample Name	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Sulphur (%)
CuHCF	21.3774	17.9041	3.0787	0.0000

3.4   Reduction of 4-nitrophenol

3.4.1   Reduction without catalyst

sodium borohydride (NaBH4) can reduce 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by donating hydride ions. The reduction reaction involves the conversion of the nitro group (-NO2) to an amino group (-NH2). Here's the chemical equation for the reaction:
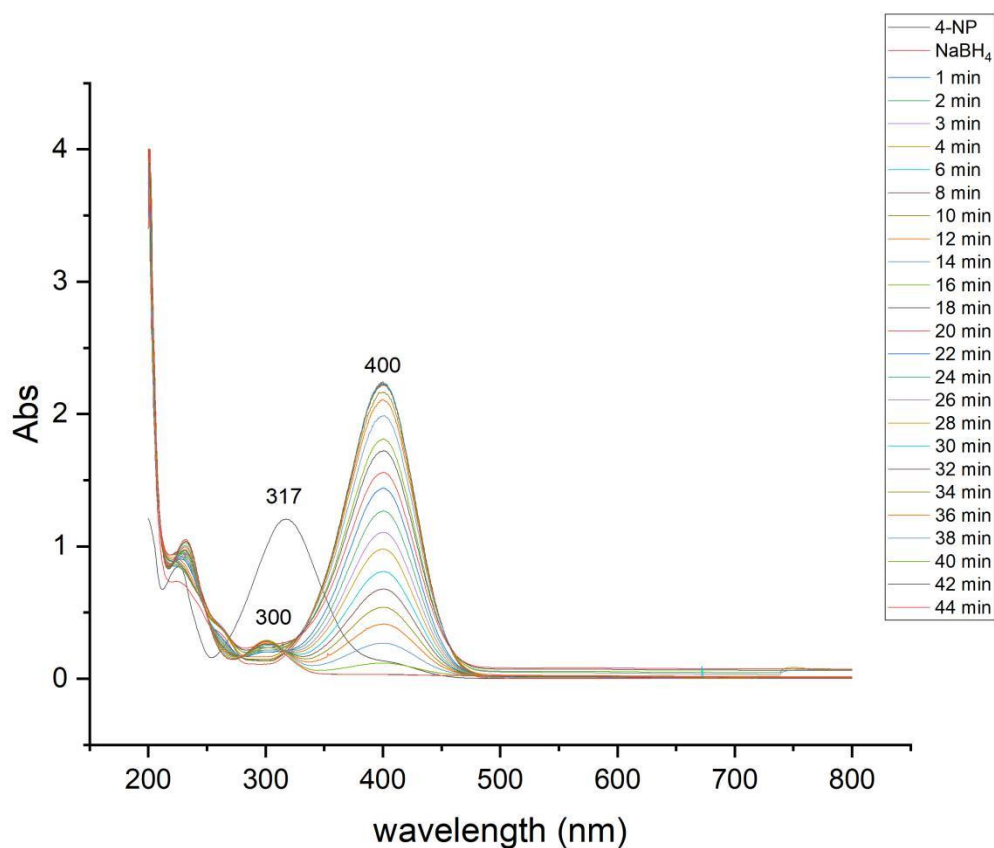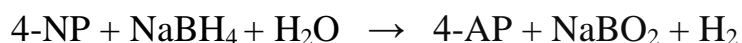
$$4\text{-NP} + NaBH_4 + H_2O \quad \rightarrow \quad 4\text{-AP} + NaBO_2 + H_2$$

Figure 9 : *UV–visible spectra of p-NP and p-AP during reduction reaction with reducing agent NaBH$_4$*

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3.2.2 Reaction with catalyst :-

The reduction reaction, monitored using a UV-Vis Spectrophotometer within the 200-800 nm range, exhibits time dependence. Initially, 4-nitrophenol demonstrates a distinct peak at 317 nm in an aqueous medium. However, upon addition of Sodium Borohydride (NaBH4), a bathochromic shift (red shift) occurs, shifting the peak from 317 nm to 400 nm due to the formation of p-nitrophenolate ion in an alkaline environment.

Consequently, a prominent peak is observed at 400 nm. Upon introduction of CuHCF, a reduction in absorbance at 400 nm is noted, indicating the initiation of the reaction. Within two minutes, a minor peak at 400 nm is observed, alongside a new peak corresponding to p-aminophenol at 300 nm. By the third minute, the peak for p-nitrophenol at 400 nm disappears entirely, with a complete peak for p-aminophenol detected at 300 nm. This signifies the complete reduction of p-nitrophenol to p-aminophenol in the presence of copper hexacyanoferrate acting as a catalyst. These results are illustrated in Figures 10 and 11 below.
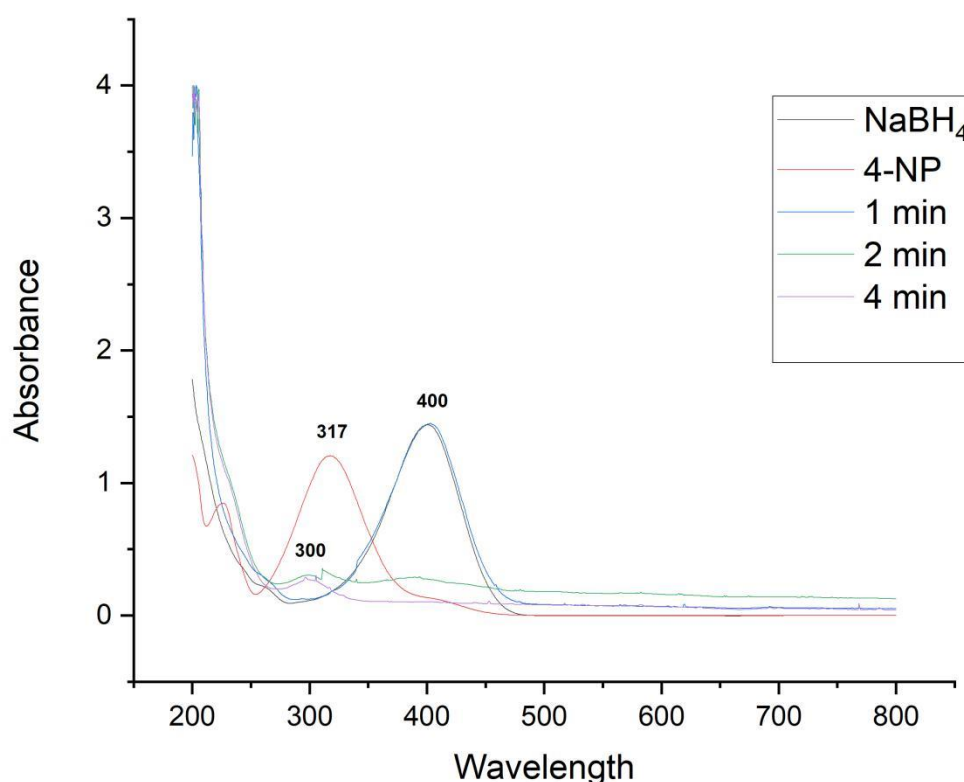

Figure 10 : *UV–visible spectra of p-NP and p-AP during reduction reaction with CuHCN NPs as catalyst*
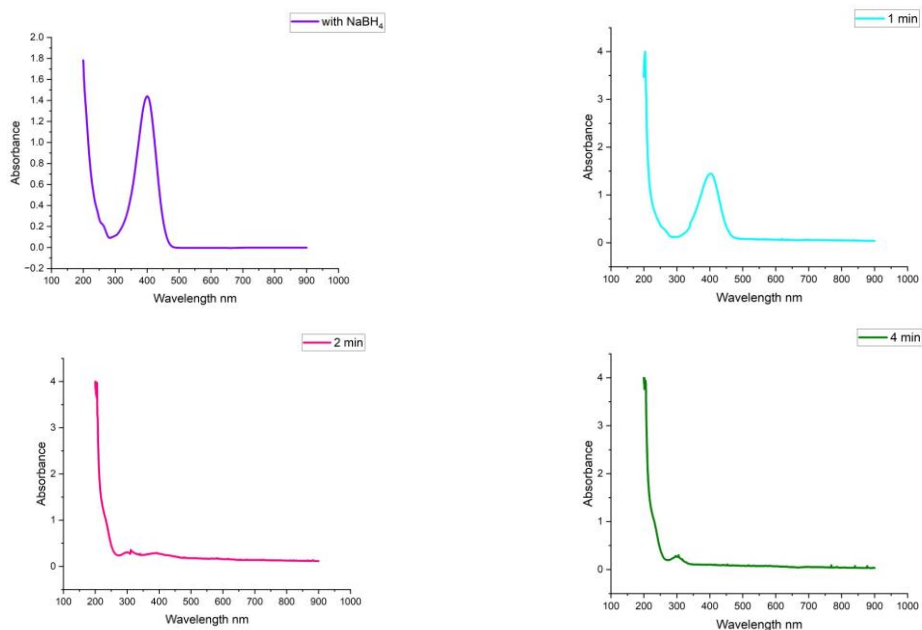
Figure 11 : *UV–visible spectra of p-NP and p-AP during reduction reaction with CuHCF NPs as catalyst at different time intervals.*

3.2.3 General Mechanism for the Reduction Reaction:

In the aqueous medium, NaBH4 dissociates into Na+ and BH4-. BH4- reacts with water to form borate ions and hydrogen ions. These hydrogen ions play a crucial role in the hydrogenation process of the nitro group in 4-nitrophenol, converting it to 4-aminophenol. Initially, the hydrogen ions attach to the two oxygen atoms of the nitro group in 4-nitrophenol, leading to the formation of 4-nitrosophenol by removing water. Subsequently, the double bond between oxygen and nitrogen in 4-nitrosophenol is broken, facilitating hydrogenation and resulting in the formation of 4-hydroxylamine. Further hydrogenation occurs, followed by the condensation of water molecules with the formed 4-aminophenol, resulting in the final product. This reaction pathway is depicted in Figure 10 [23].
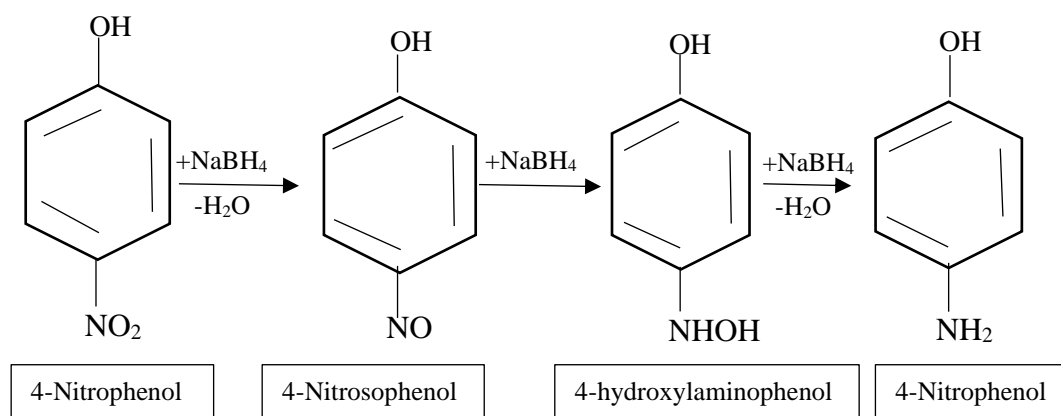
$$BH_4^- + 2H_2O = BO_2^- + 4H_2$$
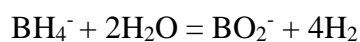
Figure 12 :- *General reaction mechanism for the reduction of 4-nitrophenol to 4-aminophenol using NaBH$_4$ in aqueous medium*

3.2.4 Expected Mechanism for the Reduction Reaction using catalyst.

Upon addition of CuHCF NPs to the mixture of 4-nitrophenol, water, and sodium borohydride, all these substrates swiftly diffuse to the catalyst's surface. As sodium (Na+) ions are inserted into the mesopores of the catalyst, the oxidation state of neighboring metal centers undergoes alteration. While the synthesized compound typically features Cu2+ and Fe3+ ions, the introduction of Na+ ions may lead to a change in some of these ions' oxidation states.

$$Cu^{2+}[Fe^{+3}(CN_6)]_2 + 2Na^+ + 2e^- \longrightarrow K_2Cu^{+2}[Fe^{+2}(CN_6)]_2 \qquad [21]$$

This indicates the presence of a pair of Fe+2/Fe+3 within the crystal structure of the catalyst. Similarly, a combination of Cu+/Cu2+ is also found in the lattice, facilitating efficient electron transfer during the reaction.

The CuHCF catalyst facilitates the transfer of electrons from the electron donor BH4-, which is adsorbed on its surface, to the nitro group of 4-nitrophenol, acting as an acceptor, via the metal ion pairs present in the lattice. Hydrogen ions are provided by the polar protic solvent, aiding in the reduction reaction and resulting in the synthesis of 4-aminophenol. The rapid detachment of freshly generated 4-aminophenol creates a free surface.

3.2.5 Comparison between Nano-size metal catalysts in terms of their catalytic performance for the reduction of p-nitrophenol

Copper Hexacyanoferrate demonstrates superior catalytic efficiency for the reduction reaction compared to other nanoparticles, completing the process in just four minutes, the fastest reported in the literature. This advantage is highlighted in Table 3. The excellent catalytic properties of CuHCF NPs can be attributed to its remarkable solid-state chemistry, characterized by increased mesopores within its cubic structure, facilitating faster adsorption and desorption phenomena. Additionally, copper's high conductivity, in comparison to other non-precious metals, aids in the exchange of electrons from the nucleophile ($NaBH_4$) to the electron acceptor (NO_2) of p-nitrophenol through easily accessible ion pairs (Cu^+/Cu^{2+}) and (Fe^{2+}/Fe^{3+}). [19]

Table 3: Comparison between Nano-size metal catalysts in terms of their catalytic performance for the reduction of p-nitrophenol

Nanoparticles	Concentration (µg/L)	%Conversion	Time Taken (min)	References
Gold Nanoparticles (Au NPs)	-	100	5	M.A. Bhosale et al., 2013 [23]
Palladium Nanoparticles (Pd NPS)	22	98	9	S. Chatterjee and S.K. Bhattacharya et al., 2021[24]
Platinum Nanoparticles (6 nm)	-	97	60	S. Pandey and S.B. Mishra et al., 2014 [22]
Platinum Nanoparticles (9 nm)	-	93.7	70	S. Pandey and S.B. Mishra et al., 2014 [22]
Tin-Oxide Nanoparticles	-	98	40	F Naaz et al., 2020 [25]
Copper Hexacyanoferrate NPS	17.5	100	4	PRESENT

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CHAPTER 4
CONCLUSION

Copper Hexacyanoferrate Nanoparticles are produced through a straightforward and environmentally friendly approach known as the co-precipitation method. The resulting compound displays a high degree of crystallinity and is presumed to possess a face-centered cubic (fcc) structure. Its remarkable catalytic performance suggests it acts as a heterogeneous catalyst, swiftly converting p-nitrophenol to p-aminophenol in an aqueous environment using Sodium Borohydride as the reducing agent. Notably, this synthesized compound not only demonstrates favorable properties but also exhibits faster catalytic activity compared to other metal nanoparticles.

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