Reduction of p-nitrophenol to p-aminophenol using an efficient, cheap and simple technique to prepare spinel ferrites: A comparative study

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ABSTRACT

A successful reduction of p-nitrophenol was carried out on the surface of novel CuFe$_2$O$_4$. Copper ferrite (CuFe$_2$O$_4$) nanoparticles were prepared via simple co-precipitation reaction in presence of a capping agent. The prepared nanoparticles was investigated by DSC (Differential Scanning Calorimeter) and the crystalline structure and size were estimated by XRD (X-Ray diffraction). The experimental results have pointed out the high catalytic activity towards the reduction of p-nitrophenol to p-aminophenol (important intermediate for paracetamol and analgesic drugs) which improved greatly by using polymer as capping agent, where it exhibited several advantages such as low-cost, stability and rapid separation.

Keywords: Reduction, p-nitrophenol, p-aminophenol, spinel ferrites.

INTRODUCTION

Water is available in the universe in huge quantity in the order of 1,400 x$10^6$ km$^3$, only 2.5 % of the global water resources are consisted of fresh water. Among the fresh waters, only about 5 % of them or 0.15 % of the total world waters are readily available for beneficial use, the rest being contained in the polar glaciers or glaciers in altitude. Global freshwater reserves are rapidly depleting and this is expected to significantly impact many densely populated areas of the world. Low to medium income developing regions as well as highly developed countries will face water stress in the future, unless existing water reserves are effectively managed. Although low-and middle-income developing countries currently have low per capita water consumption, rapid increase in population and inefficient use of water across sectors are expected to lead to water shortages in the future. Traditionally, developed countries have high per capita water consumption and need to focus on reducing their consumption through improved water management techniques and practices. By 2025, India, China and selected countries in Europe and Africa will face water scarcity if adequate and sustainable water management initiatives are not implemented. (Martinez-Huitle and Ferro, 2006)

Nitrophenol and its derivatives are some of the most refractory pollutants found in industrial wastewater. They are typically the result of the manufacturing process of insecticides, synthetic dyes and herbicides. The United States Environmental Protection Agency (USEPA) lists nitrophenol as one of the top 114 organic pollutants. (Liu, and Qiao, 2007; Xiong et al., 2019) Aminophenol is an important intermediate in the preparation of several analgesic and antipyretic drugs. It is a strong reducing agent and is used as corrosion inhibitor in paints, photographic developer, and anticorrosion–lubricating agent in fuels. In the dye industry, aminophenol is also used as a wood stain and a dyeing agent for fur and feathers. Because of the aforesaid reasons, it is important to convert nitrophenol to aminophenol. So far, there were many methods for the
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conversion of nitrophenol to aminophenol. Compared with those conversion routes, the method using sodium borohydride as reducing agent in aqueous medium under mild conditions was relatively simple and clean. However, in the absence of suitable catalysts, this reaction proceeds slowly. Therefore, the study for searching efficient catalysts which can catalyze the direct hydrogenation of 4-NP using sodium borohydride becomes more significant from the point of pollution abatement. Nanoparticles have gained much attention for catalysis in recent years because of their high surface-to-volume ratios and unique electronic and surface properties. Many reports are available on the application of metal nanoparticles as catalysts for the reduction of nitrophenols in the presence of NaBH₄. Au, Ag, Pd and Pt (Zhao et al., 2015) nanoparticles are most commonly used as efficient catalysts (Herves et al., 2012) However, the separation of these nano-catalysts from the reaction mixture is an important issue. In order to solve this problem, many researchers are working on the preparation of nanocomposites that combine noble metal with magnetic materials. As the super paramagnetic nature of magnetic materials, the nanocomposite can be separated from the reaction mixture using an external magnet, thus eliminating the need for catalytic filtration, preventing the loss of a catalyst and making the catalyst cost-effective. (Aditya and Pal, 2015; Zhao et al., 2015) Hence, the development of an alternative inexpensive, facile and easy-removal magnetic catalyst for the reduction of nitrophenols is highly desirable in the context of environmental and industrial concerns. As an important class of magnetic materials, the spinel structured ferrites with general formula MFe₂O₄ (M is transition metal, such as Fe, Mn, Cu, and Zn.) (Dey and Goswami, 2020; Frolova, 2020; Goyal and Singhal, 2014; Huang et al., 2020; Liu et al., 2019; Zhang et al., 2019) have been used in many applications. Among the ferrites, CuFe₂O₄ has attracted much fundamental and applied research attention owing to its wide applications in sensors, electronics and catalysts. (Li et al., 2019; Singhal and Namgyal, 2013; Sutar and Patil, 2019; Xiong et al., 2019).

MATERIALS AND EXPERIMENTAL PROCEDURES

1. Materials
Sodium borohydride (NaBH₄) (Sigma-Aldrich, 99%), p-nitrophenol (C₆H₅NO₃), copper chloride (CuCl₂), ferric chloride anhydrous (FeCl₃), silver nitrate (AgNO₃), hydrochloric acid (HCl), sodium hydroxide flakes (NaOH), ammonium hydroxide (35%) (NH₄OH) were all purchased from alpha-chemicals and distilled water was obtained using a 10L 2 step distillation device.

2. Preparation of spinel ferrites nanoparticles
The preparation of copper ferrite active phase and magnetic recycling responsible part of the composite was selected to be a ferro spinel for their stability, super paramagnetism, availability and high catalytic activity regarding nitrophenols reduction. First a three ferro spinel samples (namely copper ferrite, cobalt ferrite and nickel ferrite) were selected from a pool of many ferro-spinels from which the copper ferrite was selected after some comparative trials for being the most active toward the target reaction. Where a simple co-precipitation method were used to prepare all three spinels for this simple comparison in the activity toward the desired reaction, resulting in copper ferrite being the most active of the three selected spinels due to the presence of copper ions in its formula and crystal lattice leading to an improved catalytic activity toward nitrophenols reduction. The preparation process was further improved by the addition of a polymer to further reduce the copper ferrite size and catalytic activity (Ahmed et al., 2008; Amighian et al., 2006; Daigle et al., 2011; Gonzalez-Sandoval et al., 2004; Houshiar et al., 2014; Kundu et al., 2003; Lu et al., 2011). The polymer was also selected from a pool of four polymers for com-
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Comparison and optimization for the selected model reaction, being polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), and polyacrylic acid (PAA), where the most effective polymer in stabilizing the formed particulates was PVP which improved stability and size. Where the 2% weight ratio was selected for the comparison between different polymers.

The simple preparation method done using a mixture containing (1:2) ratio of (copper, cobalt or nickel) and ferric ions which was stirred together first and the appropriate amount of the polymer was then added to the mixture and stirred for 1 hours. A 1M NaOH solution was then added drop by drop to begin the precipitation of the copper-iron double hydroxide until the mixture pH reached a basic pH~10. The mixture was then filtered and washed with copious amount of distilled water to ensure the removal of chloride ions (using silver nitrate AgNO3) and the excess sodium hydroxide. The obtained slurry was then dried in and oven at 100 °C overnight to obtain the powder, which was then crushed into a mortar to ensure size uniformity. The obtained fine powder was then calcinated at 600 °C for 3 hours to ensure polymer removal and the complete transformation of the formed copper-iron double hydroxide to a spinel. The calcinated powder was then crushed again to obtain the final ferrite spinel in powder form.

3. Conversion of p-nitrophenol to p-aminophenol

The purchased p-nitrophenol was first recrystallized using warm water acidified by 1N sulfuric acid and dried at room temperature overnight. Then a 1-liter stock solution of 1x10^{-3}M was prepared using adequate amount of p-nitrophenol and was then diluted to 10^{-4}M for the reduction and conversion of p-nitrophenol to p-aminophenol in the application section.(Feng et al., 2013; Goyal et al., 2014; Li et al., 2012, 2015; Zhang et al., 2011)

RESULTS AND DISCUSSION

1. TG, TGA, DSC analysis

The as prepared double hydroxide powder resulting from the co-precipitation of the ferric ion with copper ions was first analyzed used the Thermogravimetric and differential scanning calorimetry method to select the best calcination temperature specific for the polymer used and the copper spinel. In Figure (1), it was clear that the polymer was nearly completely oxidized in air at around 300 °C – 350 °C (Singh et al., 2011; Tang et al., 2013; Wu et al., 2016; Zhang et al., 2005) which is evident in the TG line as the mass loss stopped after and the transformation of the copper-iron double hydroxide to the copper ferrite nearly finished around 600 °C which was chosen to be the calcination temperature for the rest of the sample (Zakiyah et al., 2015).

Fig.1. TGA, DTG and DSC for copper iron double hydroxide before calcinations
2. XRD analysis

The XRD patterns was used to identify the crystal structure for the different spinel ferrite samples prepared as shown in Figure (2). It was obvious that the pure copper ferrite sample diffraction pattern confirming the formation of copper ferrite with peaks evident at (35.86°, 34.72°, 62.16° and 29.9°) and some minor hematite impurities evident at (33.15°, 54° and 24.1°) (Singh et al., 2015; 2011; Zakiyah et al., 2015; Zhang et al., 2014) from this diffraction pattern the calculated crystallite size for copper ferrite was around 40 nm. Also, it was clear that the diffraction pattern of the copper ferrite sample prepared using 2wt% PAA, which confirm the formation of copper ferrite with peaks evident at (35.86°, 34.72°, 62.16° and 29.9°) and some hematite impurities evident at (33.15°, 54° and 24.1°) (Singh et al., 2015; 2011; Zakiyah et al., 2015; Zhang et al., 2014) and copper oxide as tenorite phase at (35.55° and 38.73°) (Bakhtiari and Darezereshki, 2011; Darezereshki and Bakhtiari, 2011) and minor sodium chloride impurities from washing due to its gel-like texture when dispersed in water which are evident from its main peak at 31.7°, also from this diffraction pattern the calculated crystallite size for copper ferrite was around 10.4 nm, and the diffraction pattern of the copper ferrite sample prepared using 2wt% PAA, which confirm the formation of copper ferrite with peaks evident at (35.86°, 34.72°, 62.16° and 29.9°) (Singh et al., 2015; Singh et al., 2011; Zakiyah et al., 2015; Zhang et al., 2014) and some hematite impurities evident at (33.15°, 54° and 24.1°) (Singh et al., 2015; Singh et al., 2011; Zakiyah et al., 2015; Zhang et al., 2014) and copper oxide as tenorite phase at (35.55° and 38.73°) (Bakhtiari and Darezereshki, 2011; Darezereshki and Bakhtiari, 2011; Sarkar and Dolui, 2015) and minor sodium chloride impurities from washing due to its gel-like texture when dispersed in water which are evident from its main peak at 31.7°, also from this diffraction pattern the calculated crystallite size for copper ferrite was around 10.4 nm which is slightly different from the diffraction pattern of the copper ferrite sample prepared using 2wt% PVP, which confirm the formation of copper ferrite with peaks evident at (35.86°, 34.72°, 62.16° and 29.9°) and some hematite impurities evident at (33.15°, 54° and 24.1°) (Singh et al., 2011, 15; Zhang et al., 2014; Zakiyah et al., 2015) and copper oxide as tenorite phase at (35.55° and 38.73°) (Bakhtiari and Darezereshki, 2011; Darezereshki and Bakhtiari, 2011; Sarkar and Dolui, 2015), also from this diffraction pattern the calculated crystallite size for copper ferrite was around 14 nm.

Fig. 2. XRD pattern to compare different polymers used in the preparation of copper ferrite
3. Reduction of p-nitrophenol

This was a very important optimization step to first select the optimum catalyst for the transformation of the p-nitrophenol to the p-aminophenol used in drug manufacturing. This optimization step was kept simple by reacting each of the candidates with the same amount of the p-nitrophenol in presence of sodium borohydride in this model reduction reaction and measure the time needed to reach 99% reduction for the initial p-nitrophenol concentration used. This was followed by measuring the change in solution absorption spectrum with time using a UV-Vis spectrophotometer. Knowing that the main p-nitrophenol absorption peak was at wavelength = 400nm, which decreased with time and reaction progression and another peak at wavelength = 300nm appeared and increased, this absorption peak was evident for the formation of p-aminophenol (Herves et al., 2012; Aditya et al., 2015).

The model reduction reaction was done using 100mL bottle containing 100mL of 1x10^{-4} M p-Nitrophenol and 0.01g of the selected catalyst stirred well at 700rpm for 5mins, heated to 40°C and maintained for the rest of the reaction then 1mL of a 19wt% solution of sodium borohydride. Then a sample was withdrawn at steady time intervals by a syringe and filtered through a 0.44μm Millipore then measured for absorbance as seen in Figure (3). From the acquired data, the most polymer suitable for catalyst preparation toward the p-Nitrophenol reduction reaction was selected to be Polyvinyl pyrrolidone for its superior stabilization resulting in a more active catalyst for the reduction of p-NP reaction as seen in Table (1).

![Image](image_url)

**Fig. 3.** UV-Vis chart sample to show the decrease in p-Nitrophenol peak at 400nm and the increase in p-Aminophenol peak at 300nm.

**Table 1.** Time for 99% reduction (min) and the constant rats (min^{-1}) for different polymers.

| Polymer | Time for 99% reduction (min) | Pseudo first order kinetics |
|---------|-----------------------------|-----------------------------|
|         |                             | Rate constant (k) (min^{-1}) | R2              |
| Pure    | 20                          | 0.27                        | 0.98            |
| PVP     | 15                          | 0.28                        | 0.97            |
| PVA     | 20                          | 0.24                        | 0.88            |
| PAA     | 300                         | 0.0331                      | 0.93            |
The reaction kinetics was studied under the pseudo first order reaction kinetics as the reaction is originally second order in p-NP and sodium borohydride, but sodium borohydride is always used in excess to accelerate the reaction further as it may take days to occur at a second order same concentration for example. The first order kinetics equation used to calculate the rate constant is as follow:

$$\ln \frac{a}{a-x} = -kt$$

where, a: the initial concentration of the reactant
x: the concentration of product at any given time t
k: reaction rate constant
t: reaction time

From the above equation a linear relationship was plotted for each reaction as seen in Figure (4) from which we can calculate the rate constant (k) of each reaction simply as the rate constant is equal to the slope’s modulus.

![Fig. 4. First order reaction kinetics showing the calculating for rate constant.](image)

A comparison summary for the usage of different polymers to prepare the copper ferrite catalyst used in the reduction of p-Nitrophenol to p-Aminophenol was shown in Figure (5).

![Fig. 5. Usage of different polymers to prepare the copper ferrite catalyst used in the reduction of p-Nitrophenol to p-Aminophenol](image)
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Conclusion

In this work, we have successfully prepared copper ferrite nano material using a simple precipitation method using different polymers to improve the crystallite size and reaction rate constant for further facilitating the reduction of the toxic p-nitrophenol to the more useful and less toxic p-aminophenol.

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