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UV-VIS, FTIR AND XRD CHARACTERIZATION OF *SYNTHESIZED* MAGNETIC COBALT (Co_3O_4) NANOPARTICLE USED IN CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

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ABSTRACT

Magnetic cobalt nanoparticles have many applications, including magnetic drug targets, catalysis. This paper focuses on synthesis, characterization and study of magnetic cobalt (Co_3O_4) nanoparticle's catalytic properties in the decomposition of hydrogen peroxide as well as order of the reaction. In this study, magnetic cobalt Co_3O_4 nanoparticles was synthesized using co-precipitation method. FT-IR spectrum of Co_3O_4 nanoparticles showed significant absorption peaks at 564.96 cm^{-1}, 662.83 cm^{-1}, 2923.98 cm^{-1} and ~3532 cm^{-1}/~3413.61 cm^{-1} corresponding to Co-O stretching vibration mode, bridging vibration of O-Co-O bond which indicates the presence of crystalline Co_3O_4, $–CH_3$ stretching vibrations and –OH stretching and bending modes of water respectively absorbed by the sample. The UV-Visible absorption spectroscopy showed an absorption peak at about 300 nm. XRD patterns of the prepared Co_3O_4 nanoparticles revealed that it was amorphous. The XRD of the calcined Co_3O_4 nanoparticle showed that cobalt oxide has cubic phase structure. The peak positions (2θ = 18.89°, 31.21°, 36.81° 38.40°, 44.79°, 49.10° and 55.65° which are associated with the plane 111, 220 ,311, 222 400, 330 and 422. The average crystallite size of Co_3O_4 was determined using Debye-Scherer relation. The crystallite size of Co_3O_4 was found to be 37.1 nm. The decomposition of hydrogen peroxide was studied using Co_3O_4 catalyst at room temperature using gasometric technique. It was observed that as the concentration of catalyst increase more oxygen gas was generated during the reaction. Decomposition of H_2O_2 showed that prepared Co_3O_4 nanoparticles could be used as suitable catalysts for decomposition of hydrogen peroxide in industries, research institutes.

Keywords: gasometric, synthesis, catalyst, calcination, spectroscopy

INTRODUCTION

According to Aliya et al., (2021), the development of modern chemistry is currently proceeding in several priority areas including investigations focused on the synthesis, stabilization and application of transition metal nanoparticles which are widely used in chemical, physical, engineering and biomedical processes. A special place among known transition metal nanoparticles is occupied by cobalt nanoparticles, since they are used for highly important targets such as creation of new catalysts, magnetic devices or carriers of drug delivery. Nanotechnology investigates electrical, optical and magnetic activity and structural behavior at the molecular and sub-molecular level. It has the potential to revolutionize a wide variety of medical and biotechnology tools and procedures, making them more portable, cheaper, safer and easier to use (Jhilirani *et al.,* 2020). Nanoparticles are used in various fields of industrial production, such as solar cells and oxide fuel cells for energy storage, from medicine to cosmetics and clothing, optics, catalysts, sterilization, electronics, sensor technology, biological labeling and the treatment of some types of cancer (Saba, 2015).

Nanotechnology plays an important role in various applications. Most researchers have focused their research on bimetallic nanoparticles due to their different synthetic modes or mechanisms such as chemical, physical and biosynthetic methods. These nanoparticles are of great interest due to their enormous application potential and catalytic activity. Currently, there is a focus on synthesizing bimetallic nanoparticles using various natural sources due to their advantages of being non-toxic to humans and the environment (Roopan *et al.,* 2013). Nanotechnology is a small science, very small. It is the use and manipulation of matter on a small scale. At this size, atoms and molecules have different functions, offering a variety of surprising and interesting applications (Jhilieni *et al.,* 2020).

Research in nanotechnology and nanoscience has developed rapidly in recent years in a wide range of product areas (Sovanla *et al.,* 2011). Playing a key role in developing innovative methods of manufacturing new products for suitable existing production facilities, reformulating new materials and chemicals with improved performance, and reducing energy and material consumption and reduce environmental impact and remediation. Nano-catalysts are expected to be a fertile area recently synthesized by various methods. Current applications and research on the use of nano-catalysts in wastewater management, textile industry, agriculture and medicine were also reviewed (Kandasamy *et al.,* 2015).

Prema et al., (2018) synthesized and characterized cobalt oxide nanoparticles using a microwave method. The synthesized nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), UV-Vis spectroscopy, photoluminescence (PL), and scanning electron microscopy (SEM). Hongyan et al., (2014) successfully synthesized Co_3O_4 nanoparticles by a novel, simple and environmentally friendly carbon-assisted process using cotton wool. Structural and morphological characterization was performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The constituents of samples obtained at different temperatures were determined

by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Furthermore, this simple synthetic strategy was shown to be extendable to the preparation of other metal oxide materials such as Fe_3O_4.

Sharifi et al., (2013) synthesized Co_3O_4 nanoparticles by calcination of cobalt hydroxide. The nanoparticles can be easily prepared by $Co(NO_3)_2.6H_2O$ and various reactants. The effect of calcination temperature on the structure and morphology of nanoparticles is investigated. This indicates that larger nanoparticles were produced at higher temperatures. Decomposition of H_2O_2 showed that calcination at 300°C led to higher activity. Kumar et al., (2019) synthesized Co_3O_4 nanoparticles by a sol-gel method using green chemistry. The cobalt oxide nanoparticles thus produced were characterized by UV-visible, FTIR, XRD and TEM techniques. FTIR spectroscopy was performed to know the synthesis conditions. UV-visible spectroscopy was performed for the optical characterization of the metal nanoparticles.

Sharifi et al., (2015) studied the application of iron manganese oxide nano-catalysts in the decomposition of hydrogen peroxide. It was an iron-manganese oxide nanocomposite. These nanocomposites were produced with different catalyst beds. Polyvinylpyrrolidone was used as a capping agent to control nanoparticle aggregation. Nano-catalysts were identified by FT-IR, XRD, and SEM. Catalytic activity of samples prepared by coprecipitation method was higher than samples prepared by other methods. Nanoparticles which are used for recording media, their magnetic characters crucially depend on the shape, size and purity of them. Now adays metal-oxide nanoparticles due to their unusual optical, magnetic and electronic properties, which are quite different from the bulk, being a subject of interest. Cobalt nanoparticles are hard magnetic material having high coercivity and moderate magnetization (Priyanka *et al.,* 2022)

According to Hakimeh and Dawood (2023), magnetic Co_3O_4 nanoparticles were used as a catalyst with high activity and stability in the synthesis of tetrahydrobenzo[b]pyran derivatives. The reaction was carried out in water as it is an environmentally friendly solvent, using a low loading of Co_3O_4 nanoparticles at room temperature. In addition, the catalyst was recovered and reused several times with no notable decrease in its activity. According to him, different magnetic nanoparticles, the cobalt oxide nanoparticles are very interesting for researchers due to their unparalleled properties such as good performance, high specific surface area, easy synthesis, high thermal and mechanical stability and easy magnetic separation.

There are various methods in which nanoparticles can be produced such as; co-precipitation synthesis, thermal decomposition, hydrothermal synthesis, sol-gel synthesis, microemulsion synthesis, sono-chemically assisted, micro-wave assisted, biological synthesis routes, surface coating, silica coating, carbon-based coating, metallic coating, polymer coatings, amongst all the methods co-precipitation which is straight forward, well known, cheap, effortless and creates abundant magnetic nanoparticles was used (Jesus *et al.,* 2022). This research studied the effectiveness of using non-toxic, inexpensive and environmentally friendly method of nanoparticle production for use in research institutions and industries, that improves the rate of production and reduce the cost of production.

Among different magnetic nanoparticles, cobalt oxide nanoparticles are very interesting due to their high chemical stability, good reactivity, high surface area, excellent semi-conductivity, easy synthesis, high catalytic performance and superior magnetic properties (Hakimeh and Dawood 2023). The presented work is about cobalt nanoparticles synthesis, characterization and their catalytic properties. Characterization of cobalt nanoparticles was done by FTIR, UV-vis and XRD. Particle size using XRD characterization was calculated by Debye-Scherrer method (Priyanka *et al.,* 2022).

MATERIALS AND METHODS

Preparation of Sodium Carbonate Solution

1 M Na_2CO_3 solution was prepared by suspending 26 g of sodium carbonate in a 250 ml standard volumetric flask and was filled up to its mark with distilled water.

Synthesis of Co_3O_4

The synthesis of magnetic cobalt nanoparticles was carried out according to the method described by Ramzan and Saeed (2019) and Andrey et al., (2022) by co-precipitation method described as follows; 2.5 g of $CoCl_2.6H_2O$ was dissolved in deionized water stirred magnetically for 20 mins. After stirring, 20 ml sodium carbonate solution (1 M) was added to the above solution. The mixtures were stirred for 5 hours at 60 °C at the end light purple color precipitate was collected by centrifugation at 30,000 rpm. The precipitate was washed three times with deionized water and absolute alcohol respectively. The collected precipitate was dried in an oven at 80 °C for 12h. The obtained product was calcined in an electric furnace for 3 hours at 500 °C.

Ultraviolet-Visible Spectrophotometer

The supernatant liquid was characterized using UV-Visible Spectrophotometer model 6705 for the wavelength between 200 to 1000 nm. Maximum absorption wavelength was determined by placing each aliquot sample in quartz cuvette operated at a resolution of 1nm, using deionized water as the blank or reference solvent. The samples were placed in 1 x 1 cm quartz cell (Akinsiku *et al.,* 2018 and Agbaje *et al.,* 2023).

Fourier Transform Infrared Spectrophotometer

The synthesized Co_3O_4 nanoparticles was characterized using Fourier Transform Infrared Spectroscopy (PerkinElmer Spectrum Version 10.03.09) to determine the various absorptions for functional groups. This was done also to determine the functional groups that were involved in the bio-reduction process.

Catalytic Decomposition of Hydrogen Peroxide H_2O_2 Using Co_3O_4 Nanoparticles

3 ml of hydrogen peroxide solution was added to a test-tube. A measuring cylinder was filled with water and the top was sealed with finger and inverted into the water trough. Bung was loosely connected into the test tube and the delivery tube was also connected to the inverted measuring cylinder, 0.1 g of Co_3O_4 catalyst was added to the test tube and the bung was put back into the test tube, the time was recorded using stopwatch. The volume of gas given off was recorded at regular time interval until no more oxygen was given off. The procedure was repeated for 0.2 g 0.3 g 0.4 g 0.5 g and 0.6 g of catalyst (Hakimeh and Dawood, 2023).

RESULT AND DISCUSSION

The formation of Co_3O_4 nanoparticles was first noticed by the change of color from orange to light purple after addition of sodium carbonate and to black powder after calcinations for 3 hours at 500 °C (Ramzan and Saeed, 2019)

FTIR Analysis

The IR spectra of the synthesized samples were obtained using Fourier Transform Infrared Spectroscopy of model (Perkin elmer specstrum). FTIR spectroscopy was carried out in order to ascertain the purity and nature of metal or metal oxide nanoparticles. FT-IR spectrum of Co_3O_4 nanoparticles showed significant absorption peaks at 564.96 and 662.83 cm^{-1}. The absorption band at 564.96 cm^{-1} was assigned to Co-O stretching vibration mode and 662.83 $cm^{-1}$was assigned to the bridging vibration of O-Co-O bond. The absorption peak at 2923.98 cm^{-1} may be due to $–CH_3$ stretching vibrations. The absorption peaks at ~3532 cm^{-1} and ~3413.61 cm^{-1} was assigned to –OH stretching and bending modes of water respectively absorbed by the sample. The two strong bands at ~564.96 cm^{-1} and ~662.83 cm^{-1} due to υ(Co-O) modes which indicates the presence of crystalline Co_3O_4. This was fairly the same with the result obtained by (Hongyan *et al*., 2014) using sol-gel method of nanoparticle synthesis. FTIR spectroscopy was carried out in order to ascertain the purity and nature of metal or metal oxide nanoparticles. FT-IR spectrum of Co_3O_4 nanoparticles showed significant absorption peaks at 567 and 661 cm^{-1}. The absorption band at 567 cm^{-1} was assigned to Co-O stretching vibration mode and 661 cm^{-1} was assigned to the bridging vibration of O-Co-O bond. The absorption peak at 2926.01 cm^{-1} may be due to $–CH_3$ stretching vibrations. (Kumar *et al.,* 2019)

UV- Visible of Co_3O_4 nanoparticles

UV-Visible Spectroscopy of the prepared sample was carried out between 200-1000 nm. The Co_3O_4 sample was deposited on clean glass substrate using screen printing technique. From UV-Visible spectra of Co_3O_4 sample in table 1. and fig. 1. it reveals that the optical absorbance of Co_3O_4 nanoparticles gradually decreases with an increasing wavelength within region of 200-1000 nm. The absorption optical characterization of the sample was recorded on UV-Visible Spectro-photometer. The surface Plasmon absorption in the metal nanoparticles was due to the collective oscillation of the free conduction band electrons which was excited by the incident electromagnetic radiation, (Igwe and Ekebo, 2018). The UV-Visible absorption spectroscopy of Co_3O_4 nanoparticles showed an absorption peak at about 300 nm due to the excitation and d-d transition ability of cobalt and this is in agreement with the result obtained by (Wadekar *et al*., 2017)

Table 1: UV-visible Result for Co_3O_4 NPs

Wavelength (nm)	Absorbance
200	0.033
300	0.875
400	0.775
500	0.740
600	0.590
700	0.556
800	0.520
900	0.338
1000	0.260

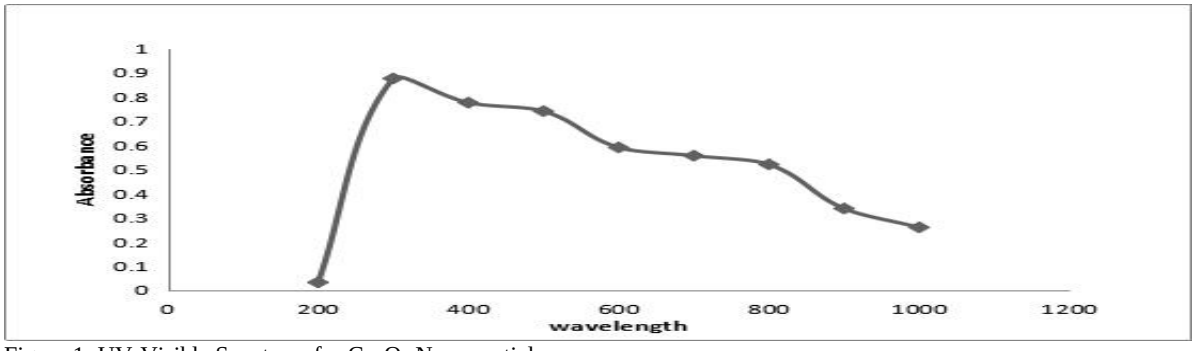

Figure 1: UV-Visible Spectrum for Co_3O_4 Nano particles

XRD result for CO_3O_4Nanoparticles

XRD patterns of the prepared Co_3O_4 nanoparticles from fig. 2 showed that it was amorphous. The samples were calcined at 500 °C for 3hr. The XRD of the calcined Co_3O_4 nanoparticles as shown in figure 2. below showed that cobalt oxide has cubic phase structure. The peak positions (2θ = 18.89°, 31.21°, 36.81° 38.40, 44.79, 49.10 and 55.65° which are associated with the plane 111, 220 ,311, 222 400, 330 and 422. The average crystallite size of Co_3O_4 is determined using Debye-Scherer relation

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

where, β is the full width half maximum in radian, θ is the scattering angle, λ is the X-ray wavelength of radiation with 1.54 Å, K is the correction factor and D is the crystal-lite size of material in nm. Then substituting the values in Debye-Scherer equation, the crystallite size of Co_3O_4 was found to be around 37.1 nm which is in agreement with the result obtained by (Wadekar *et al.,* 2017).

Analysis date	2021-06-30 13:38:25	Measurement start time	2021-06-30 12:35:54
Analyst	Administrator	Operator	Administrator
Sample name	Co3O4 NPs	Comment	
Measured data name	C:\WallPaper\30-06-2021\Co3O4 NPs_20210630_122829_G0...	Memo	

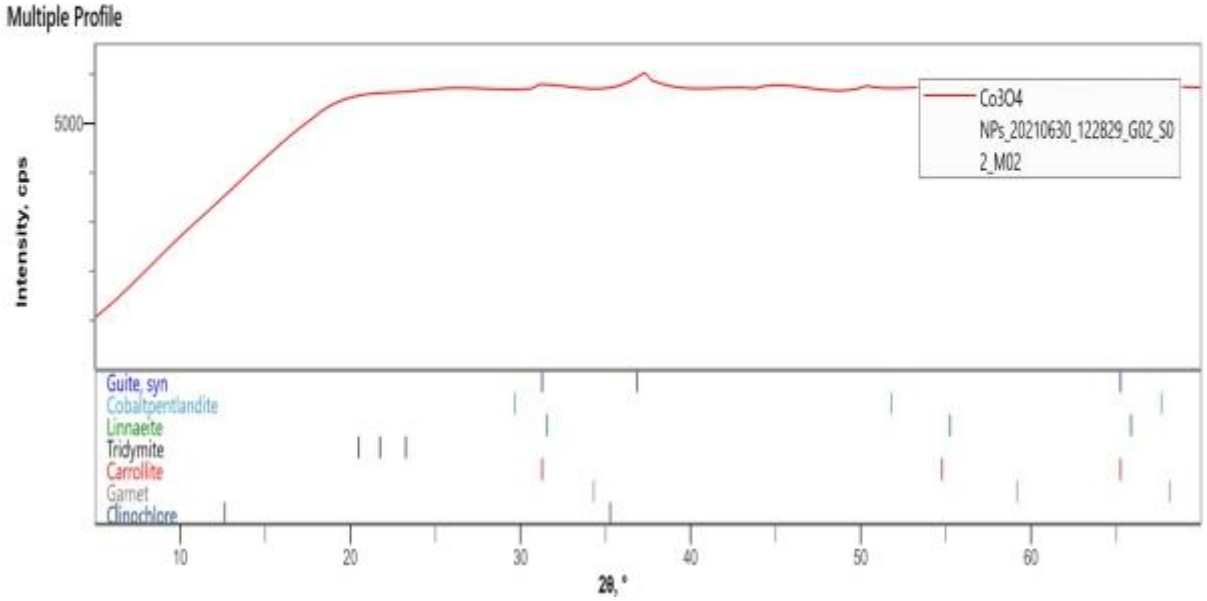

Figure 2. XRD Spectrum for magnetic cobalt nanoparticles

Catalytic decomposition of Co_3O_4 Calcined at 500 °C

Hydrogen peroxide undergoes exothermic reaction to form O_2 and water. The decomposition of hydrogen peroxide was studied using Co_3O_4 catalyst at room temperature catalytic measurement were carried out by gasometric technique, about 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g and 0.6 g of the catalyst was added to 6 test tubes containing 3 ml each of hydrogen peroxide. The volume of oxygen evolved was measured at a regular time interval. Table 2. and fig. 3 below showed that an increase in the concentration of the catalyst accelerated the rate of the reaction and led to the decrease in time taken for the decomposition of hydrogen peroxide hence as the concentration of catalyst increase more oxygen gas was generated during the reaction.

Table 2: Result for catalytic decomposition of H_2O_2 using magnetic cobalt nanoparticles

Co_3O_4NPs	Time (sec)	Volume of O_2 (ml)
0.1	36	260
0.2	18	280
0.3	9	250
0.4	8	200
0.5	6	300
0.6	4	310

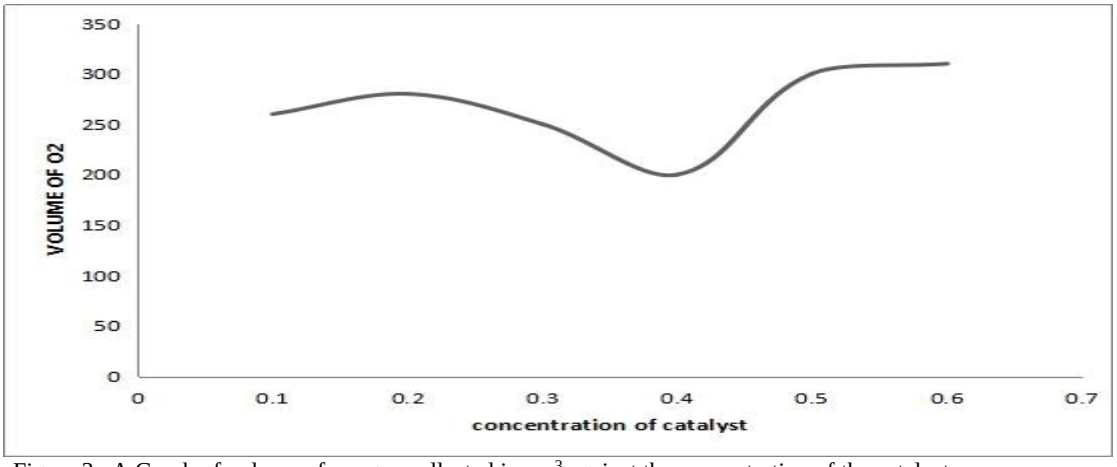

Figure 3. A Graph of volume of oxygen collected in cm^3 against the concentration of the catalyst.

Table 3: Results for the Determination of Partial Order with respect to magnetic cobalt Nano-particle Co_3O_4

S/N	Mass (g)	Concentration ($Moldm^{-3}$)	Time (s)	Rate	Log (conc)	Log (Rate)
1	0.1	0.000415	36	1.1528×10^{-5}	-3.3819	-4.9382
2	0.2	0.000831	18	4.6167×10^{-5}	-3.0803	-4.3357
3	0.3	0.001246	9	1.3844×10^{-4}	-2.9044	-3.8587
4	0.4	0.001662	8	2.0775×10^{-4}	-2.7793	-3.6825
5	0.5	0.002077	6	3.4617×10^{-4}	-2.6825	-3.4607
6	0.6	0.002493	4	6.2325×10^{-4}	-2.6032	-3.2053

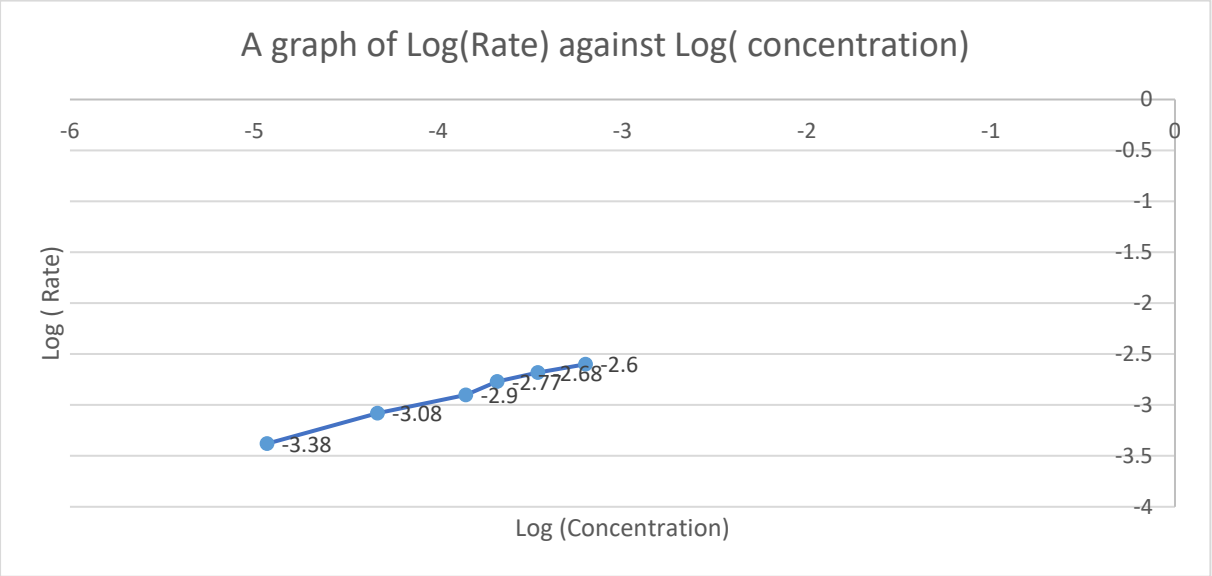

Figure 4: A graph of log (Rate) versus Log(concentration)

From the graph in fig. 4 and table 3. the slope was approximately 2 which is therefore second order with respect to magnetic cobalt nano-particle concentration.

$R=K[Co_3O_4]^2[H_2O_2]^x$

CONCLUSION

The co-precipitation approach of producing nanoparticles is said to be the best due to its affordability, non-toxic nature, and chemicals that are environmentally acceptable, in contrast to earlier methods that were unable to do so. Magnetic cobalt nanoparticles were synthesized, using co-precipitation method then characterized using FTIR, UV-vis and XRD, particle size was calculated using XRD characterization by Debye-Scherrer method. Catalytic properties of the synthesized magnetic cobalt nanoparticles were studied in which the reaction followed second order with respect to the concentration of catalyst synthesized. Therefore, as the concentration of the catalyst increases rate of reaction increases. Finally, the synthesized catalyst can be used in various industries and research institutions.

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