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Catalytic Reduction of Hazardous Compound (Triethylphosphate) Using Ni Doped CuO Nanoparticles

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ABSTRACT

Nickel doped Copper oxide nanoparticles were prepared by hydrothermal method for catalytic reduction of Triethylphosphate (TEP). It is a well known toxicant from organophosphorous compounds. The nanoparticles were characterized by DLS, UV, FTIR, XRD, SEM and EDAX. FTIR and UV results reveals that the functional properties and the absorbance of NPs. DLS and SEM results reveals that the size and surface morphology of NPs. XRD and EDAX results confirms the structural purity of Ni dopants were substituted into the cubic CuO NPs and the elemental composition. Ni doped CuO is an efficient catalyst for catalytic reduction of TEP using sunlight irradiation and it was monitored by UV VIS spectrophotometer.

Keywords: Ni doped CuO NPs; Hydrothermal method; Decontamination; TEP; Sunlight irradiation

1. INTRODUCTION

Synthesis of bimetal oxide nanoparticles is a field of great interest among researchers due to its catalytic activity and synthesis of transition metal doped with metal oxide nanoparticles gets much more attention in current research[1-3]. Addition of nickel to copper oxides enhances its strength, durability and also resistance to corrosion. The catalytic activity of Nickel doped copper oxide nanoparticles (Ni doped CuO NPs) is determined by many factors such as temperature, time and preparation of catalyst[4-6]. The catalytic activity of the material was evaluated by reduction of Triethylphosphate (TEP). This compound is the surrogate of organophosphorous compounds and chemical warfare agents. This compound is an intermediate product for manufacturing of pesticides[7, 8]. This chemical is a hazard for human health and the environment and also is irritating to the skin and eyes. Hence ecofriendly method for effective decontamination of triethylphosphate has to be explored. Semiconductor metal oxides gives excellent adsorption of organophosphonates. The interactions of chemical warfare agent simulants with metal oxide surfaces needs to be studied to understand the destruction of organophosphates using bimetal oxide nanoparticles[9-12]. Bimetaloxide NPs have been synthesized using various methods like Sol-gel method, Chemical vapour deposition, Chemical reduction method and Wet chemical method[14-17].

In this research paper, Nickel doped copper oxide has been synthesized by environmentally safe hydrothermal method under controlled reaction temperature and pressure. The authors were able to achieve a variety of morphologies and particle sizes of NPs. Decontamination of triethylphosphate by the ecofriendly sunlight irradiation technique was attempted.

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2. EXPERIMENTAL METHOD

2.1 Raw Materials

All the chemicals used in the research work were of AR grade. Copper chloride hexahydrate ($CuCl_2.2H_2O$) was purchased from Himedia laboratories and Nickel chloride hexahydrate ($NiCl_2.6\ H_2O$) was purchased from Merck laboratories Pvt. Ltd. Both were used as metal source. NaOH, triethylamine and potassium dihydrogen phosphate were purchased from Merck laboratories Pvt. Ltd.

2.2 Preparation

Equal amounts of $CuCl_2.H_2O$ and $NiCl_2.6H_2O$ were dissolved in 60 mL of 2 M NaOH solution and after 30 minutes, 3mL of triethyl amine was added to the mixture. Subsequently, appropriate amount of Potassium dihydrogen phosphate was introduced into the reaction mixture. The mixture was then transferred into a Teflon-lined autoclave, sealed and heated at 140°C for 20 hrs and then cooled to room temperature. The resultant products were washed and filtered off with absolute ethanol and distilled water and then dried at 60°C for 12 hrs[14].

3. PHYSICOCHEMICAL CHARACTERISATION

The synthesised nanoparticles were subjected to characterisation studies like conformational changes, functional group, surface morphology, elemental composition and optical behaviour using instruments like X ray diffraction

spectroscopy (XRD), FT-IR Spectroscopy, Scanning electron Microscopy (SEM), EDAX and UV-Visible Spectroscopy.

Ni doped CuO nanoparticles were subjected to UV Visible spectroscopic studies and found to have λ_{max} at 227 nm as shown in Fig. 1.

DLS data for particle size measurement showed that the synthesized nanoparticles were in the range of 734.9 nm as shown in the Fig. 2.

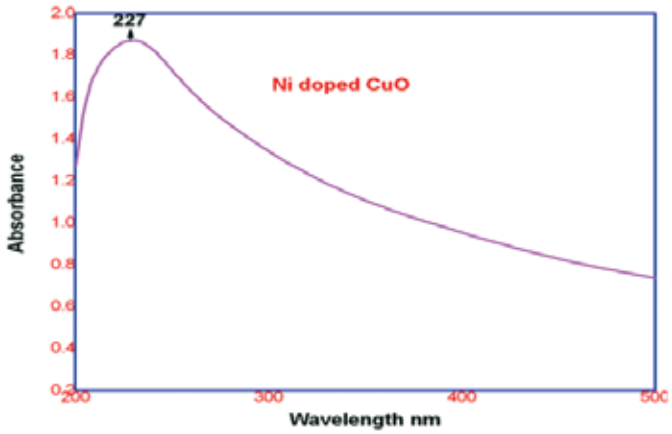

Figure 1. UV Visible spectroscopic studies.

Figure 2. Particle size measurement.

Figure 3 shows the FTIR spectrum of Nickel doped Copper oxide nanoparticles. The absorption peak at 773.46 cm^{-1} is from the vibration of Cu-O-Cu. The broad band at 3628.10 cm^{1} is ascribed to stretching vibration of hydroxyl groups. The band at 2846.03 cm^{-1} is attributed to the C-H stretching vibration[15, 17, 18].

The crystallinity of Ni doped CuO NPs were examined by XRD as shown in Fig. 4. This reveals the face centered cubic structure of bimetal oxide NPs. The X-ray diffraction patterns for pure CuO and Ni doped nanoparticles were indexed as (001), (110), (111), (111), (200), (202), (113) and (220) planes at 2Θ values of 19˚, 32˚, 35˚, 39˚, 51˚, 59˚, 62˚and 72˚respectively that corresponds to JCPDS card Nos. 89-8397, 80-1916, 04-0836. From these observations, it is confirmed that the material was of high crystalline nature[14, 15].

The size and morphology were observed by SEM (Figs. 5(a) and 5(b) at different magnification) and it was observed that Ni doped CuO nanoparticles are having leaf like structure.

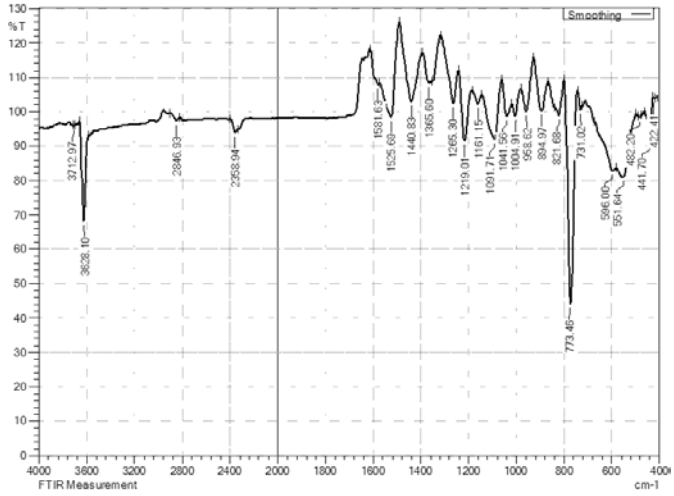

Figure 3. FTIR-Functional group identification of Nickel doped Copper oxide NPs.

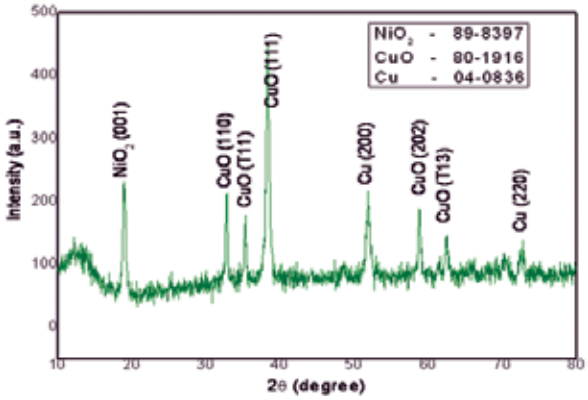

Figure 4. XRD spectra of Ni doped CuO NPs.

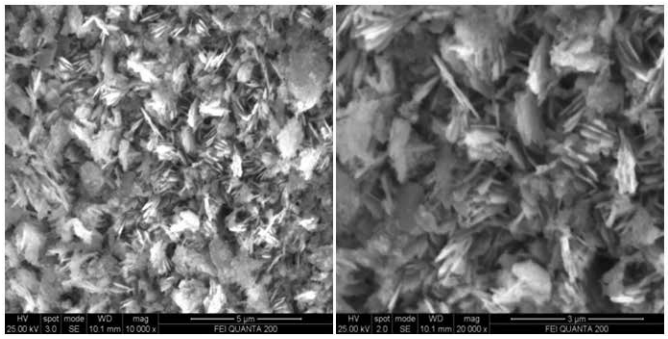

Figure 5. (a) Ni doped CuO NPs at different magnifications.

From the Fig. 6 showing the EDAX profile of Ni doped CuO, it is evident that no other elemental peaks other than Ni, Cu and O were present. The atomic weight composition of elements were Cu 42 per cent, Ni 11 per cent and O 47 per cent. These results confirm the effective doping of Ni into CuO nanoparticles[14].

4. CATALYTIC REDUCTION OF TEP:

The catalytic activity of Ni doped CuO was investigated by reduction of TEP by sunlight irradiation method. Initially the concentration of catalyst was varied as 10 mg, 25 mg and 50

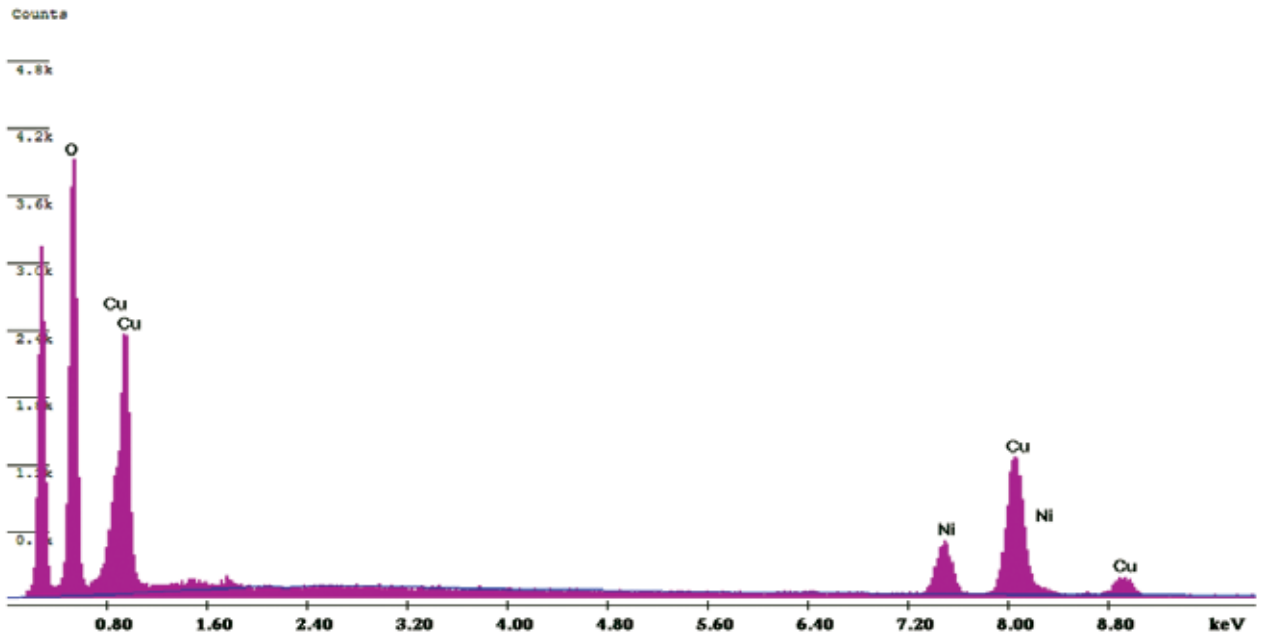

Figure 6. EDS spectrum of Ni doped CuO NPs.

mg. Catalytic reduction of TEP was also evaluated in different pH and found that pH 5.0 showed complete reduction. The catalytic reduction conditions were optimised to be 50 ml of TEP (50 mM) and 10mg of catalyst at pH 5.0. Time dependent absorption spectra were recorded at room temperature with a time interval of 1h to 5hr. Reduction of TEP was recorded using UV-Vis spectrophotometer (Shimadzhu UV 3600). Absorption peak of TEP was obtained at 254 nm as shown in Fig 7(a). Although no change was observed in the control, samples with catalyst showed decrease in the intensity of the TEP peak as shown in Fig 7(b). From these observations, it is proved that Ni doped CuO NPs exhibit significant catalytic activity towards the toxin and the reduction percentage of TEP was calculated as 79 per cent.

5. CONCLUSIONS

- Leaf like crystalline nanoparticles of Ni doped CuO have been successfully synthesized by hydrothermal technique and characterised.
- Catalytic activity of the nanoparticles was proved by complete reduction of the toxin TEP.
- Further studies on confirmation of degraded metabolites using HPLC and GC-MS and scale up for real time applications are under process.

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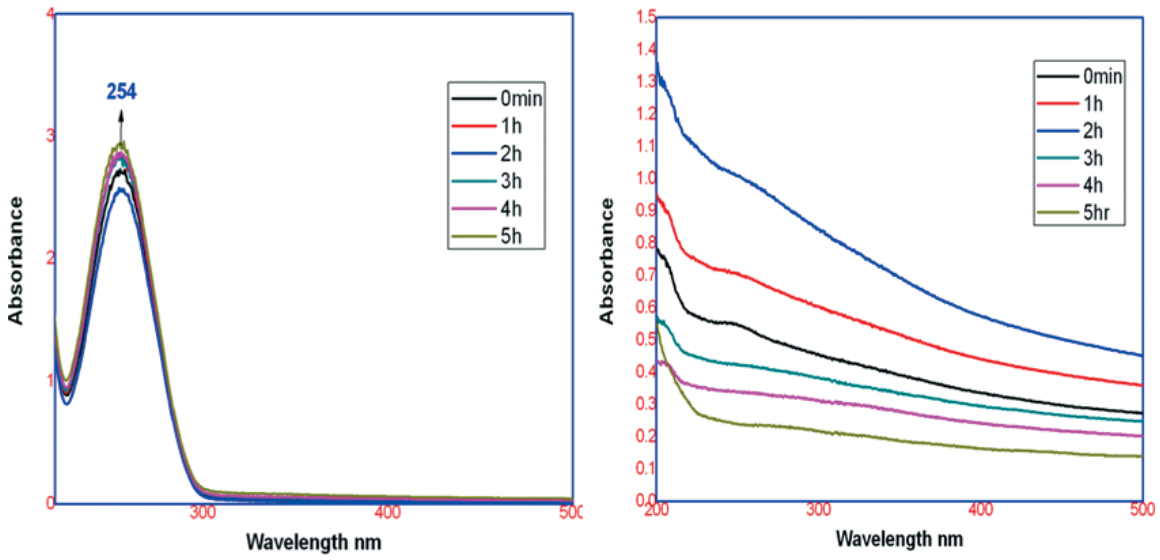

(a) **(b)**

Figure 7. (a) Control-TEP (b) At pH 5.0, catalyst 10 mg.

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