Degradation of 4-amino pyridine onto cuprous oxide nanoparticles synthesized from *Tabernaemontana divaricate* extract

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In the present study, Cu_2O nanoparticles has been synthesized from *Tabernaemontana divaricate* leaves extract and were analyzed using various characterization techniques UV-Vis, FT-IR and AFM. FT-IR spectra displayed the presence of protein/enzymes along with the aromatics in the spectra of Cu_2O NPs that revealed the formation of Cu_2O NPs from plant mediated biosynthesis. The catalytic activity of Cu_2O nanoparticles was further investigated in a batch photocatalytic reactor for the degradation of 4-amino pyridine using an artificial light source. Under an optimum conditions of initial solution pH: 3, catalyst dose: 0.8 g/L and initial 4-amino pyridine concentration: 5 mg/L, the Cu_2O NPs showed 80% degradation and 82% mineralization of 4-amino pyridine.

Keywords: Cu_2O NPs, FT-IR, AFM, 4-amino pyridine, degradation.

Introduction

4-Amino pyridine now a days have been used as raw material for organic solvents, production of agrochemicals, medicine and active surfactants[1]. 4-Amino pyridines are soluble in polar and nonpolar solvents, due to which these most toxic. 4-Amino pyridine, commercially available as (Ampyra), has been used for many years, prescribed for people with multiple sclerosis. United States Food and Drug Administration (FDA) have approved Dalfampridine a potassium channel blocker, when used correctly improve walking and other activities. A case study have shown that overdose with (4-amino pyridine) can lead to common side effect like kidney or bladder infection, headache, nausea, weakness, back pain etc.[2,3]. Therefore discharge containing 4-amino pyridine is a necessary topic now a days and endless effort has been made by the researchers for the removal it from waste water. Several methods like thermal desorption, flocculation, various advance oxidation processes (AOPs) such as Fenton reagent, UV/H_2O_2, UV/Fenton and biodegradation have been adopted by researchers for the treatment of these pollutants from waste water. But still these processes have limitations such as formation of sludge and time consuming microbial degradation.

Among the various treatment methods for the removal of 4-amino pyridine cuprous oxide nanoparticles (Cu_2O) recently attracted special attention due to its numerous properties such as photocatalytic activity, super conductivity and antibacterial activity. Cuprous oxide is a *p*-type semi-conductor and can be used as photo catalyst under visible light. But in aqueous solution Cu_2O nanoparticles easily undergo oxidation to CuO and can be deactivated by photo-corossion[4]. The stability of Cu_2O nanoparticles could be improved by using capping stabilizing agents such as natural surfactant, conductive polymer layer and lignin[4,5]. Various stabilizing agents are available, but natural surfactants from plants extract were used because of their rich biological activity and physiochemical properties[6].

Present work reported a new technique for the bio-mediated synthesis of Cu_2O nanoparticles using plant extract of *Tabernaemontana divaricate (T. divaricate)* leaves. The synthesized catalysts were characterized to study structural, morphological. Cu_2O nanoparticles was tested for the photocatalytic decomposition of 4-amino pyridine under the visible light.

Experimental

Materials:

4-Amino pyridine (98% (w/w), 94.12 g/mol^{-1}) was acquired from Mumbai, India (S. D. Fine Chemical Limited). L-Ascorbic acid (99%, (w/w), 176.13 g/mol^{-1}), ethanol (99.9%), copper(II) nitrate, trihydrate (241.6 g/mol^{-1}, 99.3% (w/w)), sulphuric acid (98% (v/v)) were purchased from Loba Chemie Pvt. Ltd. (Mumbai, India). Sodium hydroxide, silver sulphate, mercuric sulphate, Ferroin indicator solution (0.025 M), potassium dichromate and ferrous ammonium sulphate were purchased from Hi Media Laboratories Pvt. Ltd. (Mumbai, India). High Pressure Mercury lamp (Philips, 125 W) which emits visible light in the range λ_{max} 436 nm, was used as artificial source of sun light. Reagent grade chemicals were used for all the experiment. The structure of 4-amino pyridine and physico-chemical properties is shown in Fig. 1 and Table 1.
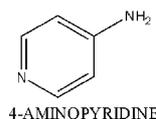
Fig. 1. Structure of 4-amino pyridine.

Table 1. Physicochemical properties of 4-amino pyridine a model pollutant

Chemical formula	$C_5H_6N_2$
Molecular weight (g/mol)	94.1146
Appearance	Colorless solid
Boiling point (°C)	273
Melting point (°C)	155 to 158
Solubility in water (mg/mL)	50, clear, colorless

Methods:

Preparation of aqueous leaf extracts:

T. divaricate leaves were collected from Dr. B. R. Ambedkar National Institute of Technology Jalandhar, Punjab, India. Fresh leaves of *T. divaricate* were washed with distilled water to remove wreckages and contaminants and then dried in hot air oven at 60°C till constant weight. Dried leaves were grounded into powder and used for further experimentation. 100 g of powdered leaves were boiled with 500 mL of distilled water for 10 min to obtain plant extract mixture. After that the mixture was passed through a filter paper of 11 μm pore size to remove the solid particles and stored at 4°C in a refrigerator.

Biosynthesis of cuprous oxide nanoparticles:

The cuprous oxide nanoparticles (Cu$_2$O NPs) were synthesized by the co-precipitation of Cu$^+$ and Cu^{2+} ions under alkaline medium with value pH 9 at 80°C. 15 mL of 1 M NaOH were added to 400 ml of Cu(NO$_3$)$_2$.3H$_2$O (50 mM) solution at 80°C with continuous stirring. After 10 min, 1 mL ascorbic acid (1 M) and then Cu(OH)$_2$ were complete converted to Cu$_2$O NPs by adding plant extract to the mixture. The ethanol was added to the final solution to decompose the plant extract into flavonoids for capping of Cu$_2$O NPs. Finally the orange color obtained was due to the development of Cu$_2$O NPs.

Characterization of Cu$_2$O NPs:

UV/Vis spectrophotometer:

The adsorption band edge and band gap energy of Cu$_2$O NPs was studied by using ultraviolet-visible spectroscopy double beam spectrophotometer (Model: UV 2600, Japan) with a spectrometric quartz cell (1 cm path length). The UV-Vis diffuse reflectance absorption spectra (UV/DRS) of Cu$_2$O NPs were recorded from 200 to 800 nm equipped with an integrating sphere accessory in diffuse reflectance mode using barium sulfate as a reference material.

Fourier Transform Infrared Spectroscopy (FT-IR) spectra of plant extract and Cu$_2$O NPs were done with FT-IR instrument scan range of 400 to 40000 cm^{-1} (Perkin-Elmer, Model: RXI, Tokyo, Japan) at resolution of 1 cm^{-1} using a KBr pellet.

Atomic force microscopy (AFM) was done used to obtain the surface topography and the average particle size of the Cu$_2$O NPs using the microscopy (AGILENT-N9410A series 5500).

Catalytic performance of Cu$_2$O NPs for degradation of 4-amino pyridine:

For the degradation study of 4-amino pyridine onto Cu$_2$O NPs, 100 mL of 4-amino pyridine (5 mg/L) and Cu$_2$O NPs (800 mg/L) was taken and the mixture was stirred for 90 min under dark condition to obtain the adsorption at 3 pH. After that mixture was exposed to the artificial light source (Mercury lamp of 125 W) for 235 min to attain the complete mineralization. Samples were taken from the reaction mixture at fixed interval of 30 min and the reaction was performed for

235 min. The Cu$_2$O NPs were filtered using filter paper 0.2 µm of pore size from the mixture, and the left over solution was examined. The experimental procedure was repeated for various parameter Cu$_2$O NPs dose, pH and concentration were varied from 5 ppm to 9 ppm, 3 to 5 pH and 0.6 g/L to 1.4 g/L respectively by keeping one constant at time while varying the others.

The concentration of 4-amino pyridine was investigated using ultraviolet-visible spectroscopy (Model: UV2600, Shimadzu, Japan) double beam spectrophotometer at λ_{max} 281 nm. COD analysis were done as per APHA method to estimates the mineralization of 4-amino pyridine during degradation. COD measurement were done using a MAC COD digester (Model COD-439, Karnal, India).

Results and discussion

UV-Vis spectra:

Fig. 2 shows the electronic absorption spectra of Cu$_2$O NPs. In the absorption spectra Cu$_2$O showed the broad band at 436 nm in the visible region and no other peak was observed which suggested that bio-surfactant helped in formation of only Cu$_2$O phase only by acting as a good surface capping agent. Broad absorption band in the region 400 to 500 nm, attributed to band-to-band transition, revealed formation of Cu$_2$O NPs[7].
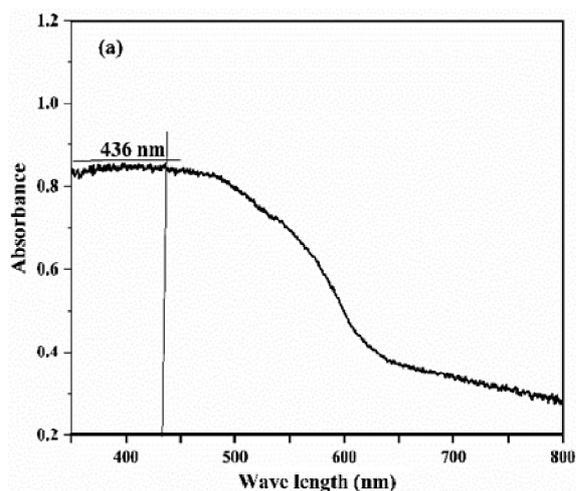
Fig. 2. DRS absorption spectra of Cu$_2$O NPs.

Fourier Transform Infra-Red spectroscopy:

The FT-IR study of *T. divaricate* extract and Cu$_2$O NPs has been done and the results obtained are shown in the

Fig. 3. The FT-IR spectrum of aqueous crude extract of depicted in Fig. 3(a) have distinct peaks at 3310 cm^{-1} which was due to O-H band primary amine and O-H group polyphenolic. A sharp band at 1637 cm^{-1} was attributed to the amide I vibrations. The band 1408 cm^{-1} and 1079 cm^{-1} corresponding to C-C stretching aromatic ring and C-N stretching vibrations of aliphatic amines of proteins respectively[8]. The above peaks observed in the FT-IR spectra confined that flavonoid and other phenolic groups were present in the extract can reduce the metal ions[9].
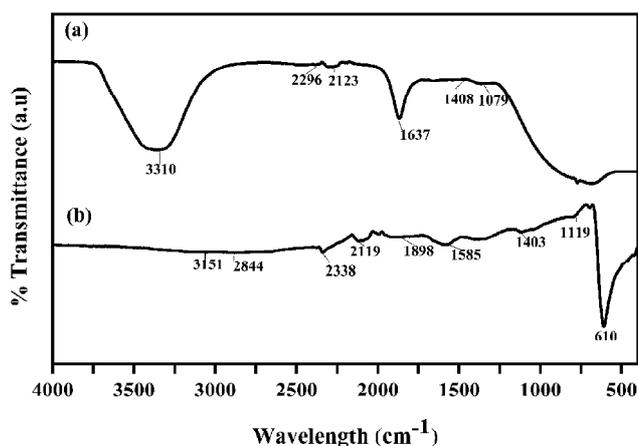
Fig. 3. Fourier transformation infrared spectroscopy spectra of (a) plant extract and (b) Cu$_2$O NPs.

The infrared spectra of Cu$_2$O NPs showed the absorption peak at 610 cm^{-1} attributed to vibration mode Cu-O in Cu$_2$O phase. The peak at 3151 cm^{-1} represent OH functional group and the peaks at 2338 cm^{-1} and 2119 cm^{-1} represented proteins/enzymes were responsible for the reduction of metal ions[9]. The peaks at 1585 cm^{-1} and 1403 cm^{-1} is generally attributed to the binding vibration of aromatic compounds[10,11].

Atomic force microscopy analysis:

AFM has been proven to be very helpful in the determination and verification of various morphological features and parameters. Fig. 4 shows the lateral and 3D AFM images of bio-mediated Cu$_2$O NPs. The topographical images of the NPs showed average size of Cu$_2$O in the range of 51 nm.

Effect of various parameters on the degradation of 4-amino pyridine onto Cu$_2$O NPs:

The effects of initial concentration of 4-amino pyridine, Cu$_2$O NPs dose, and pH on the degradation efficiency of 4-
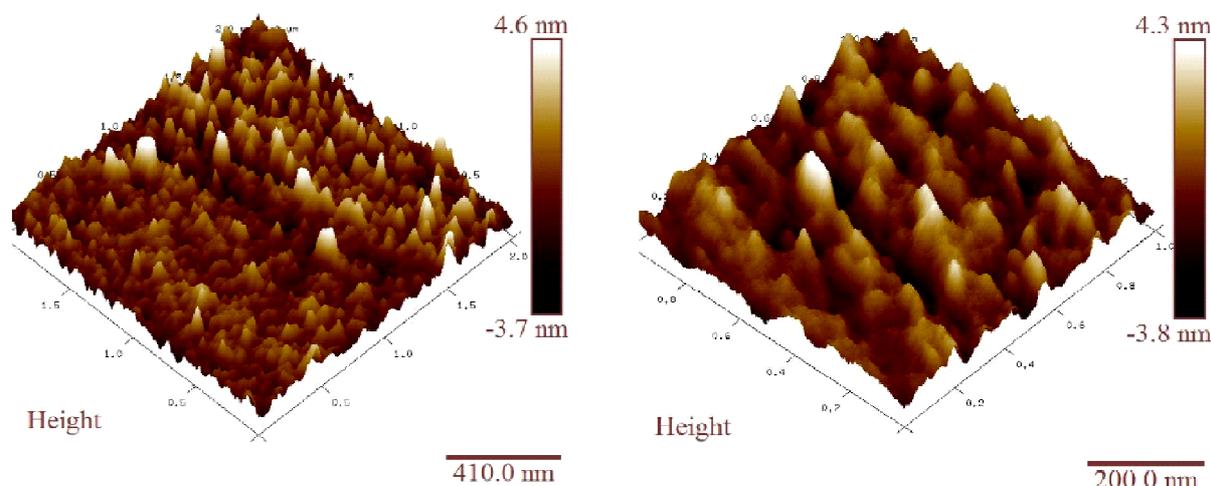
Fig. 4. Atomic force microscopy of Cu_2O NPs.

amino pyridine onto Cu_2O NPs and COD removal were evaluated.

Effect of 4-amino pyridine concentration:

The effect of increase in initial concentration on the degradation of 4-amino pyridine on to Cu_2O NPs was studied and results are shown in the Fig. 5(a). At 5 mg/L concentration of 4-amino pyridine (Dose of Cu_2O NPs: 0.6 g/L, pH 3) it was seen that the degradation efficiency as well as percentage COD removal of 4-amino pyridine improved with time.

After 235 min of the reaction time the degradation efficiency of 4-amino pyridine (5 mg/L) onto Cu_2O NPs was 75% and COD removal was 78%. But 4-amino pyridine from 5 mg/L to 9 mg/L the degradation efficiency reduced by 43%. The degradation efficiency of 4-amino pyridine onto Cu_2O NPs increased with time due the formation of OH radical, but decreased at higher concentration because of overloading of pollutant onto the surface of nanoparticles which caused the reduction in photo-degradation of reactive oxygen species[12,13].
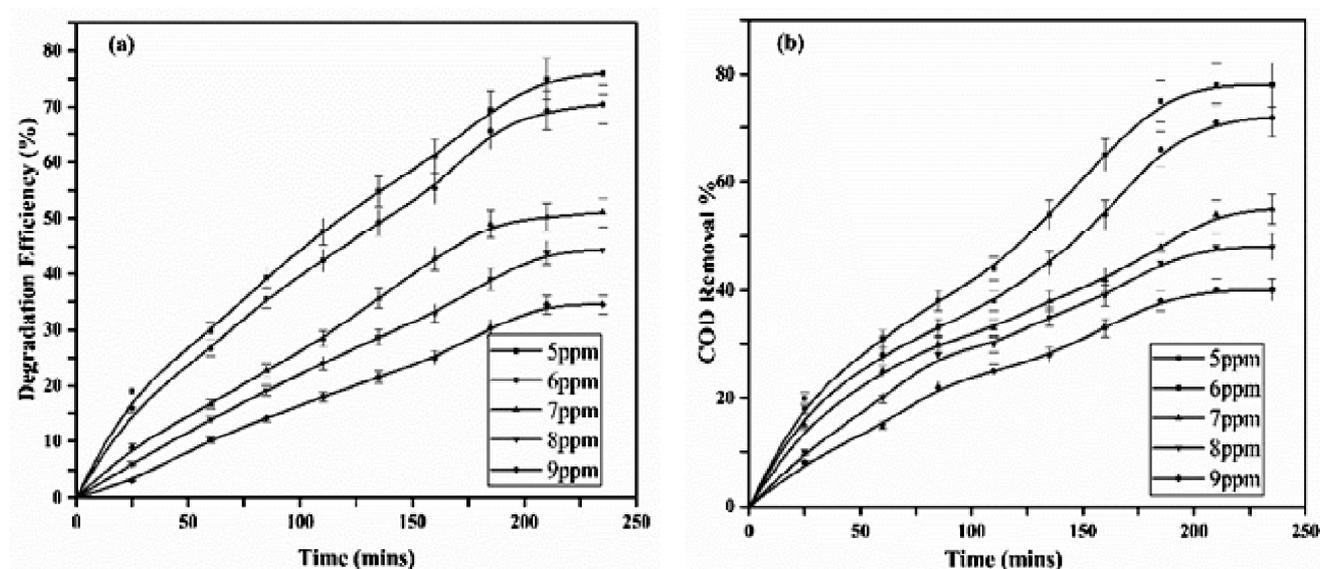
Fig. 5. Effect of initial 4-amino pyridine concentration on (a) degradation efficiency (%) and (b) COD removal (%) of 4-amino pyridine at pH 3 onto 0.6 g/L Cu_2O NPs.

Effect of dosage of Cu_2O NPs catalyst:

The effect of catalyst dose (Cu_2O NPs) was evaluated on the degradation efficiency of 4-amino pyridine (5 mg/L, 3 pH, 235 min) by varying the dose from 0.6 g/L to 1.4 g/L (Fig. 6). With the increase in dose of catalyst from 0.6 g/L to 0.8 g/L the degradation efficiency increased from 75% to 79% and COD removal (%) increased from 45% to 82%. However, further increase in dose of Cu_2O NPs catalyst from 0.8 g/L to 1.4 g/L, the degradation and mineralization efficiency removal percentage of 4-amino pyridine reduced.

Initially the degradation efficiency increased with the dose of catalyst, the increase was due to increase in surface area of Cu_2O NPs and enhancement of number of light photons absorbed.

Effect of pH:

The change in pH value of mixture on the degradation of 4-amino pyridine using Cu_2O NPs was studied in the pH range of 3 to 5 at 5 mg/L of 4-amino pyridine concentration and 0.8 g/L dose of Cu_2O NPs (Fig. 7). The degradation rate of 5 mg/
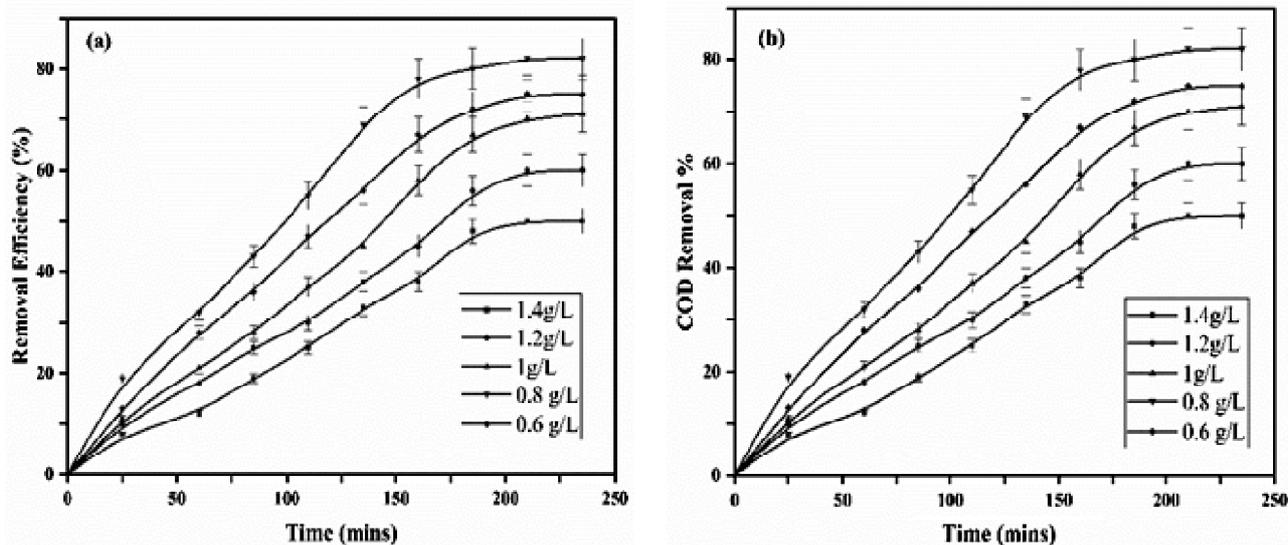
Fig. 6. Effect of dosage of Cu_2O NPs catalyst (a) degradation efficiency (%) and (b) COD removal (%) of 4-amino pyridine at pH 3 for 5 mg/L of 4-amino pyridine.
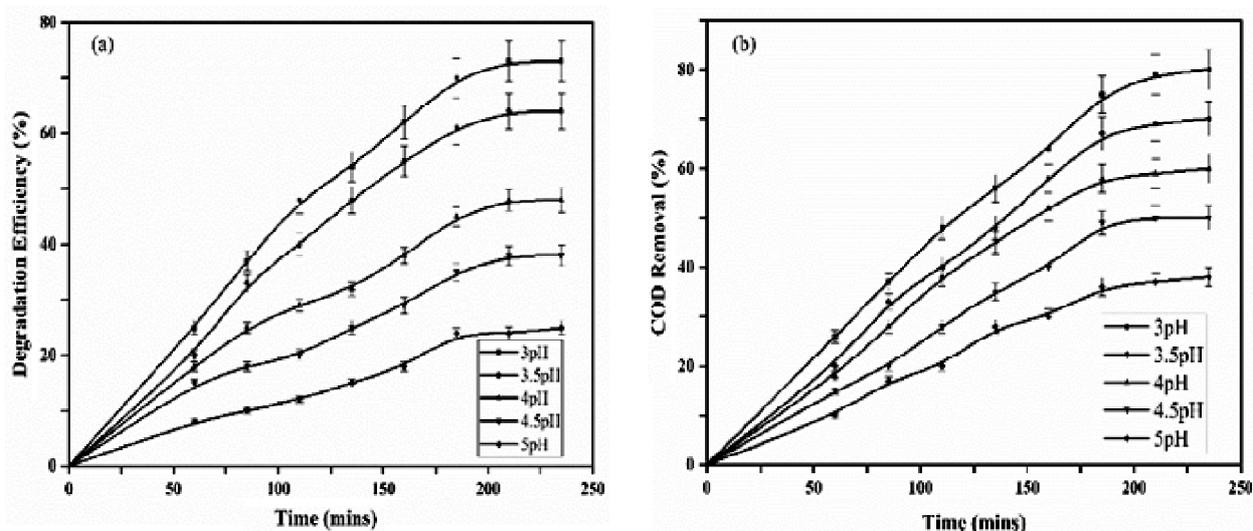
Fig. 7. Effect of pH on (a) degradation efficiency (%) and (b) COD removal (%) of 4-amino pyridine at 5 mg/L of 4-amino pyridine and 0.8 g/L of Cu_2O.

L 4-amino pyridine after 235 min irradiation, showing that the highest activity of Cu_2O NPs in photo degradation of 4-amino pyridine was obtained at pH 3. The 4-amino pyridine degradation is more efficient in acidic media than that in an alkaline one. With increase in pH 5, the degradation efficiency of 4-amino pyridine in 235 min decreased and can be due to the surface charge properties of the nanoparticles.

Conclusion

Cu_2O NPs were successfully synthesized from *Tabernaemontana divaricate* plant extract and the used extract acted as reducing agent along with coating in the production of Cu_2O NPs. The absorption spectra Cu_2O suggested that bio-surfactant present in plant extract helped in formation of Cu_2O NPs and *Tabernaemontana divaricate* leaves extract is a good surface capping agent. The presence of flavonoid and other phenolic groups in the extract showed by FT-IR analysis can reduce the metal ions. The FT-IR spectra of Cu_2O NPs showed sharp peak at 610 cm^{-1}, which correspond to vibration mode Cu-O in Cu_2O phase.

The degradation and mineralization of 4-amino pyridine onto Cu_2O NPs was also examined in the existence of an artificial source of light. The 4-amino pyridine showed highest degradation under the visible light and the degradation of 4-amino pyridine improved with rise in catalyst dose from 0.6 g/L to 0.8 g/L. The degradation behavior of Cu_2O NPs towards 4-amino pyridine showed that the Cu_2O NPs can be effectively used as a favorable photo-catalyst for the treatment of harmful organic pollutant.

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