

## Application of Copper Nanoparticles in the Degradation of Methyl Orange in aqueous medium

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### ABSTRACT

The study was primarily focused on novel, simple and environmentally benign technique for the synthesis of copper nanoparticles (CuNPs) and find out catalytic activity in CuNPs/ Peroxomonosulfate (PMS) system for degradation of Methyl Orange (MO). Green synthesized CuNPs were characterized by different instrumental techniques and results indicate synthesized NPs are in crystalline nature and cubical shape with 48 nm size. The increasing concentration of nanocatalyst, peroxomonosulfate, Dye, initial pH and high temperature rapidly promoted the degradation kinetics of MO. The degradation of MO in CuNPs/Peroxomonosulfate system is modeled as pseudo-first order kinetics and activation parameters were also determined. The maximum degradation efficiency of MO reached 98% in 30 min for CuNPs/PMS system at optimum reaction condition. Sulfate radicals (SRs) ( $SO_4^{\cdot-}$ ) were identified as oxidative species using specific alcohols. Employing CuNPs to enhance oxidation capacity of peroxomonosulfate for degradation of MO is a novel, efficient, promising and environmental-friendly method.

**Keywords:** Copper nanoparticle, Methyl Orange degradation, Peroxomonosulfate, Reaction parameters, Kinetic study.

### I. INTRODUCTION

Azo dyes are difficult degraded by conventional treatment methods, because of their complex structure and the stability. The treatment processes like adsorption and flocculation are not efficient methods because they result in solid waste, thus creating other environmental problems requires further treatment [1]. Sulfate radicals ( $SO_4^{\cdot-}$ ) based advanced oxidation process have recently gaining attention due to their high efficiency and selectivity towards degradation of organic pollutants [2]. Here, we have developed a rapid, eco-friendly and convenient green route for the synthesis of CuNPs from copper chloride using leaf broth of Indian medicinal plant namely *A. indica* (Neem). *A. indica* belongs to Meliaceae family and found abundantly in India and in nearby subcontinents. *A. indica* leaf extracts often contain flavonoids, proteins, terpenoids, polyphenols etc. These biomolecules act as reducing as well as capping agents to minimize the coagulation of NPs. A textile azo dye, Methyl Orange (MO) was chosen as the model compound because it is a widely used dye and resistant to degradation by conventional methods [3, 4].

## II. EXPERIMENTAL

### 2.1. Chemicals and Materials

Copper chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) (E. Merck), Peroxomonosulfate ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$  95%) (Sigma-Aldrich), Methyl Orange (MO) and other reagents were of analytical grade. Neem (*Azadirachta Indica*) leaves were collected from Kota (Rajasthan) India, fresh and healthy 30 g leaves with 150 ml  $\text{H}_2\text{O}$  stirred on a magnetic stirrer at 80 °C for 20 min. The prepared extract was filtered two times through Whatman paper and stored at 4 °C temperature further experiments. Deionized water was used throughout the study.

### 2.2. SYNTHESIS OF COPPER NANOPARTICLES

The aqueous solution of copper chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) ( $7.5 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) was prepared in round bottom flask, heated at 85 °C in the oil bath with magnetic stirring and 20% leaf broth added dropwise in this solution. The resulting dark brown dispersion is CuNPs.

### 2.3. Kinetic Measurements

The other reactants and desired concentration of MO placed in stoppered Erlenmeyer flask at 30 °C temperature and degradation of MO was initiated by mixing a known concentration of PMS solution. The rate of decolorization was obtained in terms of decrease in intensity at the characteristic peak 465 nm wavelength in regular time interval studied by UV-Vis Spectrophotometer attached with Peltier accessory (Temperature-controlled). A plot of  $\log(C/C_0)$  versus time was found liner which indicates pseudo first order kinetics.

## III. RESULTS AND DISCUSSION

### 2.4. CHARACTERIZATION OF COPPER NANOPARTICLES

Synthesis of CuNPs was confirmed by the UV-visible spectroscopy (Fig. 1). Owing to the continued reduction of copper ions into CuNPs and finally, SPR band characteristic of CuNPs was detected around 560 nm "Fig. 1". The size and shape of synthesized CuNPs was confirmed by TEM analysis and results shows that particle shape is cubical with the average size in 48 nm. XRD spectrum describe a sharp peak at  $2\theta = 43.5^\circ$ ,  $49.9^\circ$  and  $74.01^\circ$  corresponding to (111), (200) and (220) showed the face-centered cubic structure of copper nanoparticles.

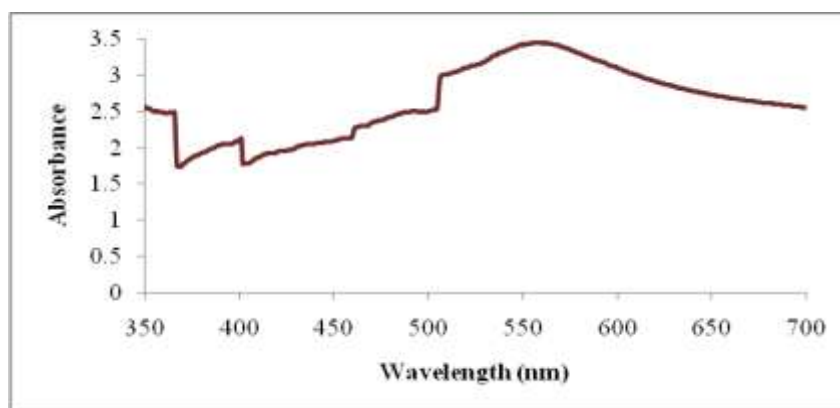


Fig. 1: UV-visible spectra of the synthesis process.



The effect of temperature on the reduction of copper ion is another important parameter for the synthesis of nanoparticles. It was detected that below 65 °C of reaction temperature the reduction of copper ions was not completed. The reduction rate increases by increasing reaction temperature from 65 to 85 °C but at high temperature (90°C) the synthesis rate is very high to control particle size so NPs formed with higher average size were agglomerated.

## 2.5. EFFECT OF EXPERIMENTAL CONDITIONS

### 2.5.1. DYE DEPENDENCE

The initial concentration of MO was varying from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> at 30 °C temperature and other reactant concentrations were constant. Oxidation rate was found to increase with increasing concentration of MO CuNPs/PMS system and after the certain concentration of dye  $5 \times 10^{-5}$  mol dm<sup>-3</sup>, the oxidation rate was decreased.

### 2.5.2. PEROXOMONOSULFATE DEPENDENCE

The degradation experiment was performed in the presence of CuNPs at different concentration ( $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>) of PMS. The rate of degradation initially increases with increase in the concentration of oxidant. Furthermore, the PMS degradation rate increases up to the  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup> concentration of PMS after that rate was constant at higher concentration of PMS.

### 2.5.3. EFFECT OF INITIAL pH

As pH increased from 2.5 to 6.5 the degradation rate dramatically increased further increase in pH shows the degradation rate dropped.

### 2.5.4. COPPER NANOPARTICLES AND TEMPERATURE DEPENDENCE

The catalytic activity of CuNPs was evaluated degradation of MO in PMS system at various concentration  $0.25 \times 10^{-7}$  to  $2.0 \times 10^{-7}$  mol dm<sup>-3</sup> at three temperature viz. 25 °C, 30 °C, and 35 °C respectively. In order to show the catalytic activity, a graph is plotted between the concentration of CuNPs and rate constant obtained at different three temperatures. The plot gives straight lines indicating the direct dependence of reaction rate on CuNPs concentration. The value of activation energy (13.19 kJ mol<sup>-1</sup>) in CuNPs/PMS system shows that the rate of degradation of MO is fast. The values of thermodynamic parameters like the change in enthalpy ( $\Delta H$ ) is 11.39 kJ mol<sup>-1</sup> and change in entropy activation ( $\Delta S$ ) is -258.48 J mol<sup>-1</sup> K<sup>-1</sup> and free energy ( $\Delta G$ ) is 89.69 kJ mol<sup>-1</sup> [5, 6, 7].

### 2.5.5. EFFECT OF ALCOHOL AND T-BUTYL ALCOHOL (TBA)

Ethanol is capable of quenching both sulfate and hydroxyl radicals whereas TBA is effective quenching agent for hydroxyl radicals [5, 8]. The results illustrate that quenching effect of EtOH is greater than TBA in CuNPs/PMS system. Therefore, sulfate radicals are active species in the oxidative degradation of dye in presence of CuNPs.



#### IV. CONCLUSION

From the above experimental results, we conclude that different size of CuNPs produced through bio-reduction of copper salt was strongly dependent on the process parameter of synthesis temperature. These synthesized CuNPs were used for activation of peroxomonosulfate for degradation of hazardous dye in a cost-effective manner. Cu<sup>0</sup> was the source of Cu<sup>+2</sup>, which was verified to be the efficient activating agent for peroxosulfates to produce sulfate radicals. More importantly, these nanoparticles showed a significantly longer lifespan with sustained reactivity, making them the potential application in dye degradation.

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