

Photocatalytic Degradation of Azo and Rhodamine Dyes Using Copper (II) Oxide Nanoparticles

Etchu E. Mbu, David Dodoo-Arhin, Seteno K. Ntwampe, Edward Malenga and Elvis Fosso-Kankeu

Abstract— Fresh water pollution by dyes from various industries is raising a lot of concern lately. Despite their well-known toxicity to humans, azo dyes make up over half of the used dye population. Rhodamines are also a well-used class of dyes in industry. This study employed a cost effective, energy efficient, environmentally benign method to degrade Methyl Orange (MeO), Methylene Blue (MB) and Rhodamine B (RhB) dyes. The photocatalyst used was copper (II) oxide (CuO) nano-sized particles synthesised from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and NaOH via a simple solution route with neither a catalyst, template nor a surfactant. The nanoparticles were characterised and used for the photocatalytic degradation of the above dyes in the presence of H_2O_2 . The CuO nanoparticles synthesised from both copper precursors were found to degrade all dyes effectively over the same degradation time interval, recording an overall minimum degradation efficiency of 85 % and maximum of 99 %.

Keywords—Azo dye, CuO, Nanoparticles, Photocatalysis, Rhodamine dye.

I. INTRODUCTION

Wastewater pollution is a major problem in most parts of the world today. One of the recalcitrant pollutants in wastewaters are dyes. They are used in a variety of industries, and have been found to be carcinogenic in man. Of over 3000 known organic dyes, half the number belong to the class of Azo dyes[1][2]. Well-known by their characteristic $-\text{N}=\text{N}-$ (azo) group, these compounds are often preferred due to the relative ease with

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which they can be synthesised, the wide variety of colours which they offer, their relatively good adherence and long lasting aesthetics[1]. However, they have also been found to comprise mutagenic and carcinogenic compounds when incompletely broken down[3], [4]. Another well know class of dyes are the Rhodamines. Mostly used in the paper, pharmaceutical and cosmetic industries, the extent of their toxicity to man is yet to be clearly defined[5]. With these dyes often released into the environment in wastewater, it is essential to find appropriate ways of rendering the wastewater harmless prior to its release into the environment. This will involve the degradation of any dyes found in the wastewater.

In recent years, Transition Metal Oxides (TMOs) have been investigated for use in the degradation of organic pollutants such as these dyes. Photocatalysis has been found to be one of the effective mechanisms involving the use of these transition metals in the degradation of dyes in solution. Its low energy requirements, easy usability with catalysts in all three phases of matter and eco-compatibility have made it stand out for this application[6]–[8]. It is based on the principle of the photoelectric effect whereby when an electron absorbs a photon (packet) of light energy which is at least equal to its work-function (bandgap energy), it is promoted from the valence to the conduction band. This electron then goes into solution and interacts with the bonding electrons within the molecules in the system. This interaction results in the formation of free radical species which are unstable and very reactive, thereby resulting in further breakdown of any organic molecules present in the system[9].

TiO_2 nanoparticles are one of the most widely studied TMOs for the dye-degradation process[3], [7], [9]. Other TMOs that have been studied for this application include SnO [10], [11], ZnO and Cu_2O [12] with others like CuO which are gaining more attention in recent times.

This study compared the efficiency of degradation of azo (Methyl Orange (MeO) and Methylene Blue (MB)) and rhodamine (Rhodamine B (RhB)) dyes using CuO nanoparticles synthesised from two different precursor salts and precipitated at three different temperatures. Though other studies have worked with CuO, to the best of our knowledge, it is the first time that CuO nanoparticles arising from this route of synthesis have been tested in photocatalytic applications. The study sought to assess the extent of degradation of each dye using the

synthesised CuO nanoparticles. The overall photocatalytic efficiency of the synthesised nanoparticles was accounted for based on some of the properties observed during characterisation.

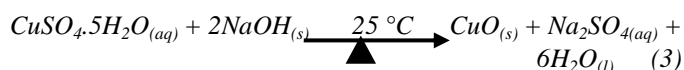
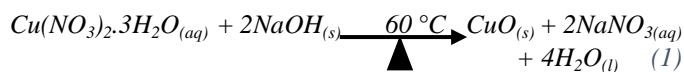
II. MATERIALS AND METHODS

A. Reagents

Analytic grade reagents were used during the entire study. They were, hydrated copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) (Sigma-Aldrich Co., Germany), hydrated copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (Breckland Sc. Supplies, UK), sodium hydroxide (NaOH) (Qualikems Fine Cem Pvt Ltd, India), methyl orange (Fizmerk India Chemicals, India), methylene blue (KEM Light Laboratories Pvt Ltd, Mumbai-India), rhodamine B (Paskem Finechemicals Industry, India), 30 % hydrogen peroxide (Merck, Germany) and ethanol (Fisher Scientific, UK). To reduce interference, during this study, the water used was deionised.

B. Synthesis

Three CuO samples (N60, S60 and S25)¹ were precipitated from 0.02 M copper precursor solutions at 60 °C and 25 °C using 1.6 g/L of NaOH. Equations 1, 2 and 3 summarise the synthesis process for all three CuO samples.



After synthesis, the precipitate was centrifuged, washed with 1:1 ethanol and deionised water. The precipitate was dried in an oven at 70°C, after which a black CuO powder was obtained.

C. Characterisation

X-Ray Diffraction (XRD) (X'Pert PRO X-Ray Diffractometer (PanAnalytical, the Netherlands) operating with Cu K- α radiation (wavelength of 1.544 Å) at 45 kV and 40 mA with a 20° to 70° 2 θ range, a 0.2° step width scanning 1.2 deg/min on a 2 g sample) studies were employed to study crystal properties. UV-Vis spectrophotometer (Thermo Fisher Scientific, China) operating within a scanning range of 200 to 900 nm with a 5 nm scan step on a 3 mL sample) for absorbance. A Scanning Electron Microscope (SEM) – TESCAN with EDX analysis

¹ The letter N and S denote the precursor salt (nitrate or sulphate) from which the nanoparticles were synthesised while the numbers 60 and 25 denote the temperatures in degrees Celsius at which the nanoparticles were precipitated from solution.

software (Performance in Nanospace, Czech Republic) operating at within 0.2 to 30 kV and 2×10^{-5} ms to 10 ms per pixel scanning speed on a 0.5 g sample, was used to study surface morphology. Fourier Transform Infra-Red Spectroscopy was performed using a PerkinElmer Spectrum Two spectrometer (PerkinElmer Inc., UK) with a 4000 to 400 cm^{-1} scanning range and 4 cm^{-1} resolution on a 0.1 g sample. Brunauer–Emmett–Teller (BET) surface area and porosity analysis were carried out using (i) An ASAP 2020 V4.01 for CO_2 adsorptive analysis (Micrometrics, USA) and (ii) A Tristar II 3020 version 2 (Micrometrics, USA) for N_2 adsorptive analysis, on 0.4 g samples.

D. Photodegradation

A 10 mg/L solution was prepared for each dye (MeO, MB, RhB). To 50 mL of each dye solution, 1.5 mL of 30 % H_2O_2 and 50 mg of CuO powder were added and the mixture was stirred in the dark for 15 minutes to establish an equilibrium. The mixture was then exposed to a 400 W white light source, samples were taken at 25 minute intervals for up to 100 minutes and their absorbance recorded to assess the extent and progress of degradation. The suggested mechanism for the degradation for the dye is illustrated in Fig. 1.

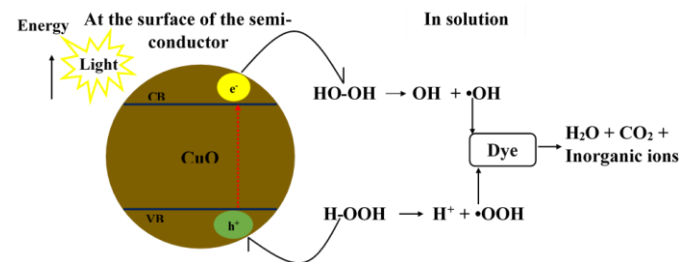


Fig. 1. Simple Representation of the electron-hole pair formation on the surface of CuO in the presence of H_2O_2 and their use in the formation of free radicals for the breakdown of the dye (CB and VB stand for Covalent Band and Valence Band respectively).

III. RESULTS AND DISCUSSION

A summary of the results from characterisation are shown in Table I. The particle sizes were determined using Scherrer's equation and the bandgaps were extrapolated from the Tauc plots for the respective samples. For all three samples after exposure for 100 mins, a minimum of 85 % and a maximum 97 % degradation were recorded. The degradation summary is shown in Fig. 2 from which it was observed that the photocatalyst generally performed considerably well with the highest percentages recorded for RhB. It was also observed that N60 degraded all dyes by at least 90 %. This could be associated with the fact that it had the highest surface area and largest pore volume (Table I). The degradation arises from the attack of the TMO electron on the peroxide molecule in solution (Fig. 1). The amount of dye left was calculated following (4) and (5) and expressed as a percentage of the initial dye concentration.

$$\% \text{ Dye left after } t \text{ mins} = (A_t / A_0) \times 100\% \quad (4)$$

$$(A_0 - A_t) / A_0 = (C_0 - C_t) / C_0 \quad (5)$$

Where, A_0 = Absorbance after 0 minutes of degradation

A_t = Absorbance after t minutes of degradation

C_0 = Concentration after 0 minutes of degradation

C_t = Concentration after t minutes of degradation

The results for each dye over 100 mins are shown in Fig. 3 (a), (b) and (c).

TABLE I: SUMMARY OF CHARACTERIZATION RESULTS

Sample Name	Particle Size (nm)	Band Gap (eV)	BET Surface Area (m ² /g)	Micropore Surface Area (m ² /g)	Pore Size (nm)	Pore Volume (cm ³ /g)
S60	13.5	2.12	28.4	110.9	1.2	0.0083
S25	13	2.11	26.8	91.7	1.3	0.0087
N60	12	2.4	49.3	206.9	0.9	0.0105

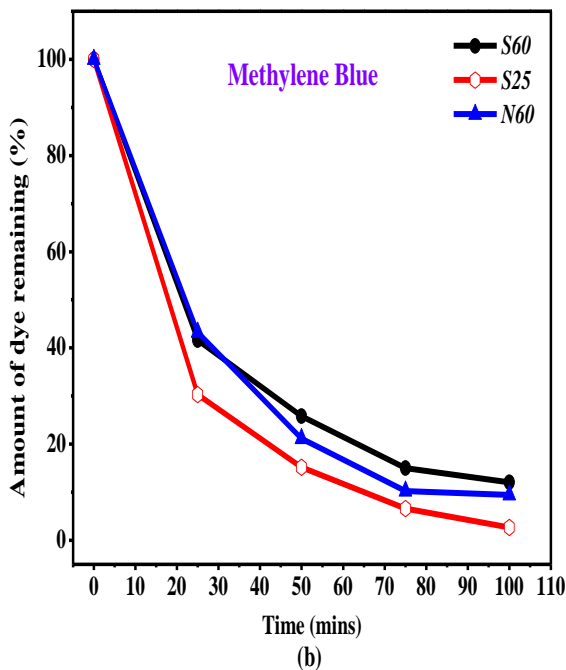
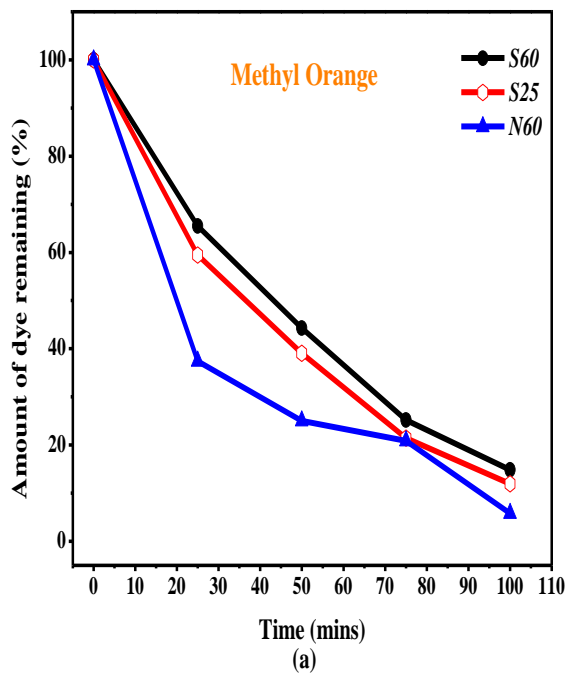
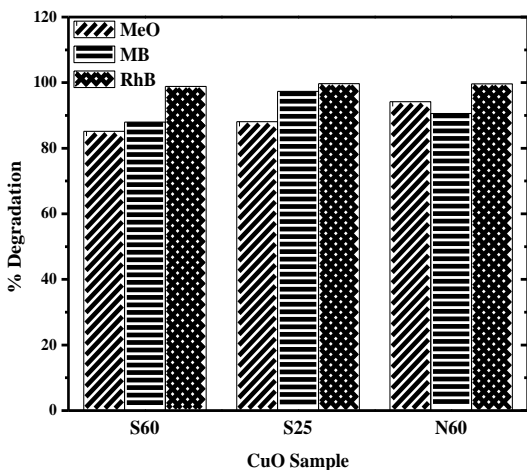


Fig. 2. Summary of degradation results.

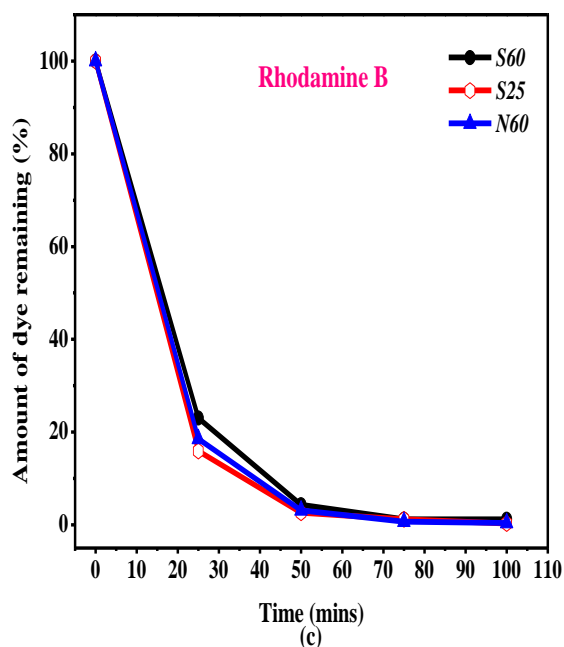


Fig. 3 (a), (b) and (c). Plots showing changes in concentration of the various dyes (expressed as a percentage of the initial amount) with time.

IV. CONCLUSION

CuO nanoparticles of different sizes were successfully synthesised from two copper precursor salts using a simple solution method which excludes the use of surfactant. The synthesised nanoparticles were used with success in the photodegradation of MeO, MB and RhB dyes where all three samples performed appreciably well with a minimum of 85 % and maximum of 99 % degradation recorded on average. However, it was observed that though the efficiency for S60 and S25 dropped to below 90 %, the degradation efficiency for N60 was consistently equivalent to or higher than 90 % for all three dye solutions. This could be associated with the fact that it showed the highest BET surface area.

However, from the overall result, it is feasible to conclude that the synthesised nanoparticles can be suitable for application in dye photodegradation for wastewater treatment.

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