POLYSACCHARIDE-MEDIATED SYNTHESIS OF COPPER OXIDE NANOPARTICLES FOR ENHANCED PHOTODEGRADATION OF METHYL ORANGE AND METHYLENE BLUE

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Copper oxide nanoparticles (CuO NPs) were synthesized using mucilage from the seeds of *Mimosa pudica*. Fully characterized CuO NPs using different spectroscopic techniques, such as UV-Vis, XRD, SEM, and FTIR, were evaluated as catalysts for the photodegradation of methyl orange and methylene blue. The UV-Vis analysis displayed an intense surface plasmon resonance at 273 nm, indicating the formation of CuO NPs. The functional groups in the mucilage and synthesized CuO NPs were examined by FTIR spectroscopy, and a peak at 475 cm^{-1} established the successful synthesis of CuO NPs. The morphology of the CuO NPs was observed by SEM analysis, revealing spherical CuO NPs embedded in the mucilage. The crystalline nature of CuO NPs was confirmed by XRD analysis, which showed a mean crystallite size of 29 nm. Furthermore, following pseudo-first-order kinetics, CuO NPs degraded methylene blue (89.47%) more effectively than methyl orange (79.25%) under sunlight. The reusability of CuO NPs was studied, and, after 4 cycles, CuO NPs indicated excellent photocatalytic performance with minor decrease in efficiency.

Keywords: copper oxide nanoparticles, methyl orange, methylene blue, *Mimosa pudica*, photocatalytic activity, mucilage

INTRODUCTION

The most plenteous natural resource on the planet is water, which is essential for maintaining public health and can be used for domestic purposes, drinking, and industrial applications. A significant proportion of the global population lacks access to clean water. According to the World Health Organization (WHO 2018), 844 million people do not have access to clean drinking water, and half of the world's population will live in water-deprived areas by 2025. The report highlighted the critical need for effective wastewater treatment and water management to meet the world's water needs.[1] Among water pollutants, organic dyes used in the textile industry are one of the biggest threats to human health, causing cancer, jaundice, heart attacks, *etc*.[2-4] As most of the dyes are not biodegradable, they must be eliminated from wastewater before it is released into the environment.[5,6] A few inefficient, costly, and slow methods for removing pollutants from water include adsorption,[7,8] coagulation,[9,10] ozonation,[11] reverse and forward osmosis,[12,13] chemical precipitation and flocculation.[14,15] An economical and environmentally safe process of bioremediation, which employs hydrogels,[16] algae, fungi, bacteria and plants, focuses on the transformation of dissolved pollutants into particles that the organisms can easily remove.[17]

One of the most widely used dyes, methylene blue (MB) is primarily used to colour cotton, silk, paper, wool, and leather.[18] Despite that, it is poisonous, difficult to break down, mutagenic, and cytotoxic to living things.[19] Exposure to high concentrations of MB can result in a variety of health problems, including eyeburn, nausea, diarrhoea, gastrointestinal tract irritation, and irregular heartbeat.[20] Another well-known dye,

methyl orange (MO), emitted by the pharmaceutical, printing, textile sectors, and chemical laboratories has been investigated in significant amounts in wastewater.[21] Research has indicated that MO raises the possibility of risks to human health, decreased food productivity, and soil fertility.[22,23] The detrimental effects of MO and MB on the environment and human health highlight how important it is to have efficient remediation plans before industrial effluent discharge.

Metal oxide NPs, particularly CuO NPs, have been successfully utilized during the past few years to remove organic dyes from wastewater [24-26] due to their high catalytic efficiency, small bandgap, and inexpensiveness. Different chemical and physical techniques are used to synthesize NPs, with the disadvantage of using hazardous chemicals and producing toxic by-products. The synthesis of NPs by green methods is inexpensive and eco-friendly.[25] Recently, problems associated with the chemical production of NPs have been addressed using plant extracts, such as *Euphorbia tirucalli*,[26] *lemon grass*,[27] *Emblica officinalis*,[28] neem,[29] *Cinnamomum camphora*,[30] *Cydonia oblonga*, [31] and tamarind.[32] Polysaccharides, such as glucuronoxylan, [33] arabinoxylan, [34] carboxymethyl-xanthan,[35] *M. pudica* mucilage (MPM),[36] and modified chitosan,[37] have been reported to synthesize nanomaterials.

M. pudica, also known as sleepy plant, lajwanti, chui mui, shy plant, and touch me not, belonging to the *Mimosaceae* family, is found in Asia, Tanzania, America, Brazil, Nigeria, and the Pacific islands.[38] The plant is rich in phytochemicals, such as flavonoids, terpenoids, sterols, and tannins,[39] responsible for treating pyrexia, dysentery, depression, respiratory trouble, ulcers, smallpox, constipation, piles, snake bites, and inflammations.[40] After being cleaned and soaked in H_2O for 12 h, *M. pudica* seeds were heated for 30 minutes at 50 °C to extract mucilage using a cotton cloth.[38] The seeds of the plant extrude polysaccharidal mucilage consisting of *D*-xylose and *D*-glucuronic acid.[41] The MPM has several applications such as water purification [35], drug release, and tablet binder [42]. The MPM is biocompatible and non-toxic.[43] In the present study, we used the mucilage extracted from the seeds to synthesize CuO NPs. CuO NPs were characterized using analytical techniques, such as SEM, XRD, UV-Vis, and FTIR. CuO NPs were further assessed for the photocatalytic degradation of organic dyes, methyl orange (MO), and methylene blue (MB), under sunlight.

EXPERIMENTAL
Materials
MP seeds were acquired from the indigenous market Anarkali, Lahore (Punjab, Pakistan). Copper sulphate pentahydrate ($CuSO_4.5H_2O$) was purchased from Merck, Darmstadt, Germany. Methyl orange and methylene blue dye of analytical grade were used. Distilled H_2O was used for experimental work such as synthesis, solution preparation, and dilution.

Methods
Extraction of mucilage
For the extraction of mucilage, *M. pudica* seeds (50 g) were drenched in distilled water (500 mL) at ambient temperature for 15 min before heating at 60 °C for 2-3 h with constant stirring. The seeds extruded mucilage, which was blended in a blender for a few minutes to detach the MPM from the seeds completely. After extracting MPM, lipophilic materials were removed using *n*-hexane. The MPM was dried in an oven before passing through a 60-mesh sieve and stored in a vacuum desiccator.

Synthesis of CuO NPs
For the preparation of CuO NPs, mucilage (0.5 g) was distributed in distilled water (50 mL) and then mixed with $CuSO_4.5H_2O$ solution (100 mmol, 50 mL). The mixture was heated for 2-3 h at 80 °C until the black precipitates were formed. The precipitates were calcined at 500 °C for 2 h to synthesize the fine black powder of mucilage-based CuO NPs (Fig. 1). The mucilage-based synthesized particles were cooled at room temperature for further investigations. The biodegradable and biocompatible polysaccharides in the mucilage played a key role in the synthesizing CuO NPs. The polysaccharides act as reducing and stabilizing agents to form non-covalent bonds with the metallic ions and convert them into nanoparticles.[44] The possible mechanism for the synthesis of CuO NPs is the following:

$$CuSO_4.5H_2O + MPM \rightarrow Cu(OH)_2$$
$$Cu(OH)_2 + calcination \rightarrow CuO + H_2O \qquad (1)$$
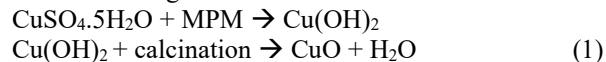
Characterization
The optical properties of the synthesized CuO NPs were examined using an Agilent Cary-60 UV/Vis spectrophotometer. An FTIR spectrophotometer (Nicolet iS5 Spectrophotometer, Thermo Scientific, UK) was used to explore different functionalities in the MPM and CuO NPs. The morphology of the synthesized CuO NPs was obtained from SEM (ZEISS-SEM). The X-ray diffraction technique was used to observe the crystal phase of CuO NPs using a powder X-ray diffractometer (Rigaku Mini Flex 600-C) with Cu anode (λ=1.540 Å).
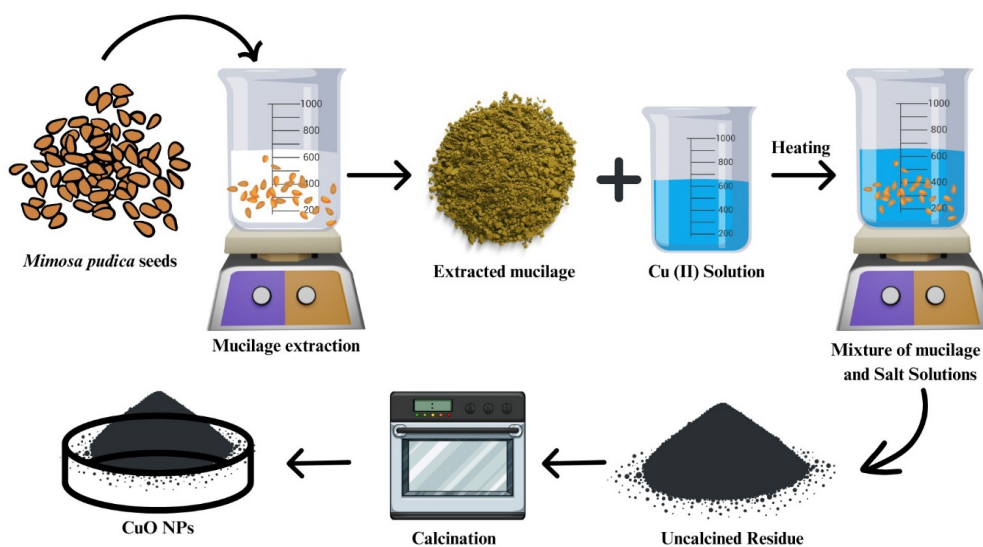
Figure 1: Schematic diagram for polysaccharide-mediated synthesis of CuO NPs

Photocatalytic activity

The photocatalytic potential of CuO NPs was evaluated against the organic dyes methyl orange (MO) and methylene blue (MB). The dye solution (10 ppm) was agitated with CuO NPs (5 mg) for half an hour in the dark for the complete adsorption/desorption of NPs on the dye surface before exposing it to sunlight with constant stirring at 120 rpm. The first sample (5 mL) was taken in a vial immediately after exposing the solution to sunlight and wrapped completely using aluminum foil to protect the sample solution from sunlight. Then, after every 30-minute interval, solutions (5 mL each) were withdrawn and covered with aluminum foil. After this, UV/Vis analysis was performed to check the photocatalytic performance of CuO NPs against methyl orange and methylene blue. The λ_{max} values of MO and MB were at 464 nm and 590 nm, respectively. The absorbance of the dye was measured after the photocatalytic procedure to determine the concentration of the remaining dye (absorbance and concentration are directly proportional to each other). After analysis the %degradation was measured using the formula:

$$\% \text{ degradation} = \frac{A_0 - A_t}{A_0} \times 100 \tag{2}$$

where A_0 and A_t are the maximum absorbance at zero minute and after time (t) of exposure to sunlight.

The Langmuir–Hinshelwood model was used to explore the kinetics of photocatalytic processes as follows:

$$r = -\frac{d_c}{d_t} = \frac{Kkc}{1+KA} \tag{3}$$

where k is rate constant, t – time, r – rate of reaction, K – Langmuir constant, and A is the equilibrium concentration of the reagent. The following pseudo-first-order equation can be used to simplify this equation in cases where the concentration of the reacting reagents is very low.[45]

$$r = -\frac{d_c}{d_t} \text{kapp A} \tag{4}$$

By integrating Equation (4), we get:

$$\ln \frac{A_t}{A_0} = -\text{kapp t} \tag{5}$$

In this equation, the rate constant for the pseudo-first-order reaction is denoted by kapp, while A_0 and A_t indicated the concentration of dye at t=0 and any instant t, respectively, and t is time.[46] After plotting this equation, the order of reaction can be determined.

RESULTS AND DISCUSSION
Synthesis of CuO NPs

The UV/Vis spectrum of CuO NPs is shown in Figure 2. The colloidal solution of NPs (1.0 mg) was prepared in distilled water (10 mL) to determine the absorbance of NPs. The interband transition of the electrons in the copper is responsible for a strong band at 273 nm, confirming the formation of CuO NPs.[47] CuO NPs synthesized from the extracts of *P. guajava*,[48] *G. globose*[49] and *Rheum palmatum* L.,[50] and those from a quince seed hydrogel[51] showed bands at 282, 290.5, 250-300, and 279 nm, respectively. These reported values are close to the value reported in present study.

The XRD technique determined and confirmed the crystal structure of CuO NPs. The XRD pattern of CuO NPs revealed sharp peaks, indicating their crystalline nature (Fig. 3). The crystal planes at 101, 336, 377, 151, 104, 111, and 119 correspond to diffraction angles of 32.51°,

35.50°, 38.1°, 48.7°, 58.2°, 61.5°, and 66.1°, respectively. The mean crystallite size of CuO NPs was 29 nm calculated by the Debye-Scherrer[52] formula (6):

$$D = \frac{K\lambda}{\beta Cos\theta}$$

(6)

Figure 4 depicts comparatively the FTIR spectra of CuO NPs and MPM. Chemical interaction between CuO NPs and MPM was evaluated using FTIR spectroscopy. There is a clear difference between peak intensities and shape, establishing the formation of NPs from the mucilage. The band at 1028 cm^{-1} in the mucilage is due to the bending vibration of the C-O-C group in the polysaccharides. The bands at 1230

and 1646 cm^{-1} are due to the vibration of the CH_2 groups. The peak at 2940 cm^{-1} is due to the C-H stretching of polysaccharides. The peak at 3362 cm^{-1} is due to hydroxyl groups. The FTIR spectrum of CuO indicates the presence of peaks at 3560, 2920, and 1020 cm^{-1}, corresponding to the vibrations of -O-H, C-H, and C-O groups, respectively. The band at 475 cm^{-1} is due to the stretching vibration of the metal (Cu) and oxygen bond. The literature revealed that the region between 400 and 600 cm^{-1} is allotted to the metal-oxygen bond. The value of 475 cm^{-1} in the present study is close to values reported in the literature, specifically for CuO NPs from *C. papaya* [53] (473 cm^{-1}), and *C. japonica* (480 cm^{-1}).[54]
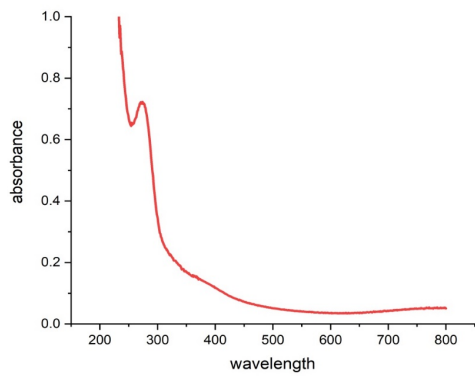

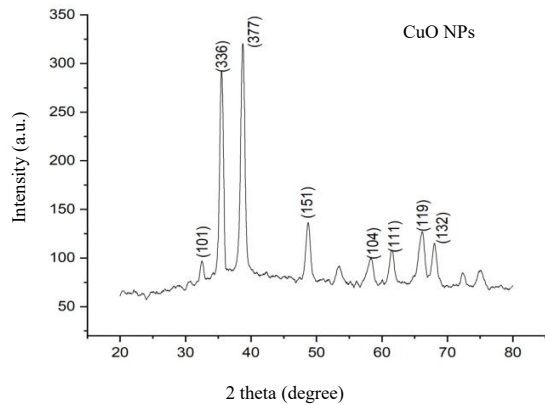Figure 2: UV-Vis analysis of CuO-NPs showing a peak at 273 nm

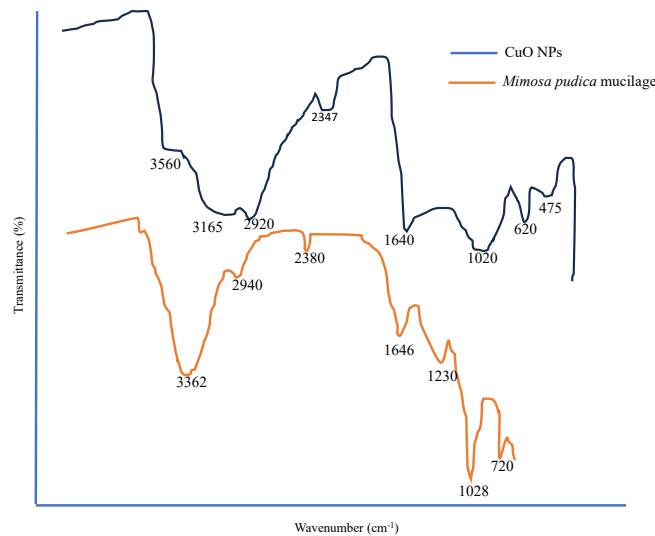Figure 3: XRD pattern of CuO NPs showing diffraction planes

Figure 4: FTIR spectra of mucilage-based CuO NPs and mucilage

SEM analysis was used to observe the structural and morphological properties of CuO NPs (Fig. 5a). SEM images revealed small and large particles due to the agglomeration of small

particles. This agglomeration might be due to the van der Waals forces of attraction between particles. Most NPs are spherical, some are irregularly shaped, and most particles are

embedded in the mucilage. The average size of the particles measured using ImageJ software is 80 nm (Fig. 5b). Previously reported data indicated that the nanocomposite of carboxymethylated starch containing CuO (CMS@CuO) had a diameter of 30-50 nm,[55] and carboxymethyl chitosan-based CuO nanocomposites had a diameter of 20-50 nm.[56]

Photocatalytic activity of CuO NPs

The dye degradation performance of CuO NPs against methyl orange and methylene blue in sunlight was investigated. The absorbance spectra were measured between 200-800 nm using a spectrophotometer. Figure 6 ((a) and (b)) shows the absorption spectra for MO and MB degradation, respectively, using CuO NPs in sunlight. It has been noted that the intensity of the absorption decreases with the increase in irradiation time, and the colour of the dye solutions faded, indicating the degradation of the dyes. After 2.0 h, the percentage degradation of the dye solutions was calculated using the formula (2).

The percentage degradation of MO was 79.25% and MB was 89.47% in sunlight. CuO NPs depicted more photocatalytic activity for MB, as compared to MO. The higher percentage of dye degradation for MB might be due to the creation of more hole-electron pairs and lessening in the recombination of electrons and holes.
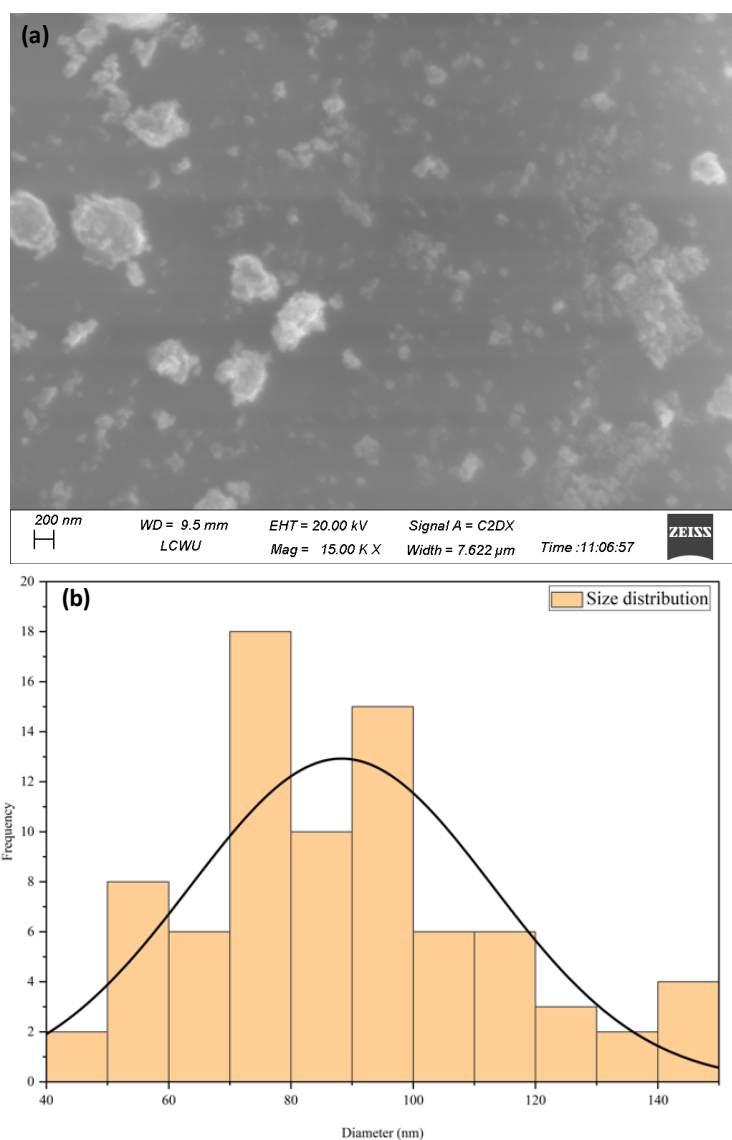

Figure 5: (a) SEM image of mucilage-based CuO NPs, and (b) average size distribution of mucilage-based CuO NPs
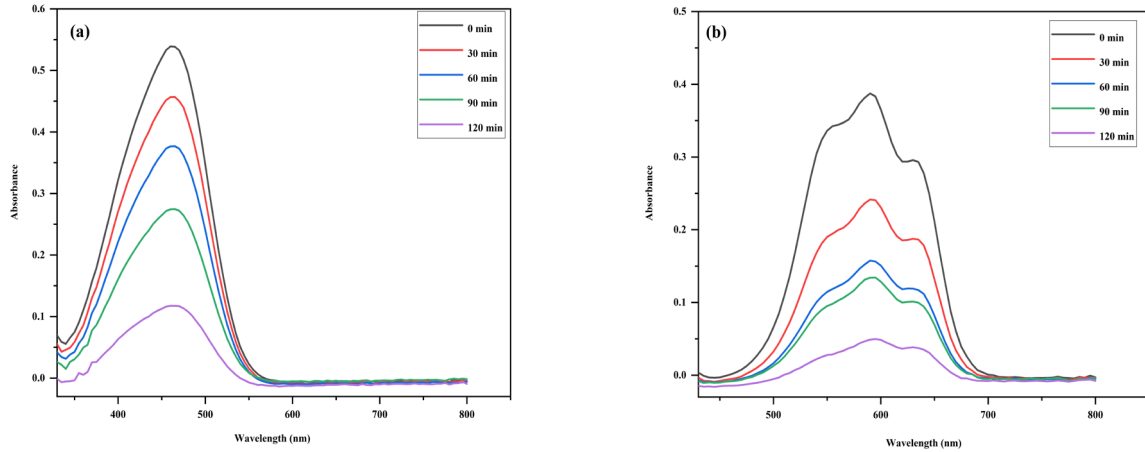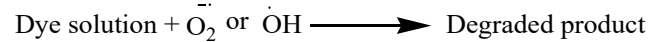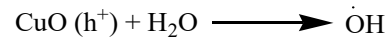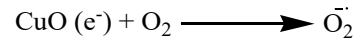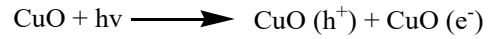
Figure 6: UV-VIS spectra of (a) MO, and (b) MB, using mucilage-based CuO NPs under sunlight

The previous studies revealed that CuO NPs from *Jasmin sambac* extract showed 97% MB degradation after 210 min.[57] Similarly, CuO NPs from the extract of *B. ciliata* rhizome degraded MR (85%) and MB (92%) in 135 min.[58] Another study reported that CuO NPs from *S. oliverianum* leaf extract degraded MG (65.231% ± 0.242) and MO (65.078% ± 0.392) after one hour.[59]

The mechanism for the dye degradation proceeded by a photochemical reaction in which light interacts with CuO NPs and leads to the generation of holes and electrons. The holes are the source of hydroxyl radicals (OH$^\cdot$) produced by the oxidation of water. The electrons in the conduction band interacted with oxygen to produce superoxide anion radicals. Thus, the reactive oxygen species, such as hydroxyl radicals and superoxide anion radicals, degraded dyes. The equations involved in the mechanism are described below:[48]

$$CuO + h\nu \longrightarrow CuO\,(h^+) + CuO\,(e^-)$$

$$CuO\,(e^-) + O_2 \longrightarrow \dot{O}_2^{-}$$

$$CuO\,(h^+) + H_2O \longrightarrow \dot{O}H$$

$$Dye\ solution + \dot{O}_2^{-}\ or\ \dot{O}H \longrightarrow Degraded\ product$$

It has been reported that from hydroxyl radicals and superoxide anions, the more dominant species is hydroxyl radical when we use CuO NPs to degrade dyes.[60] The possible mechanism is shown in Figure 7.
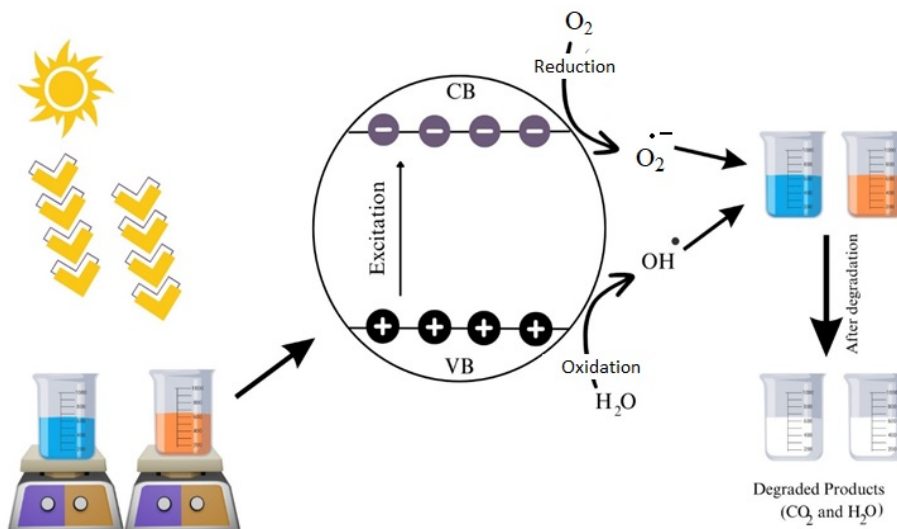

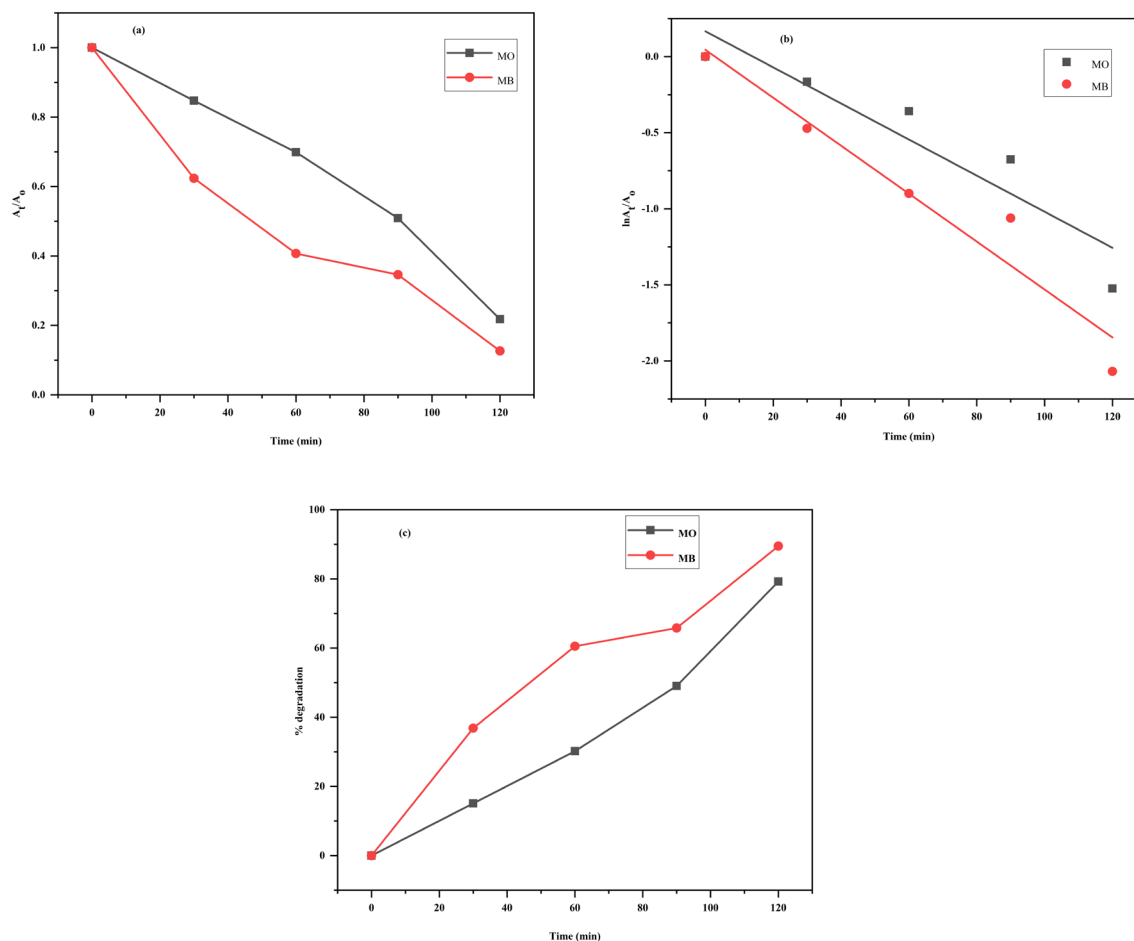Figure 7: Possible mechanism of dye degradation using mucilage-based CuO NPs

Figure 8: Decrease in concentration of dyes over time (a), dye degradation kinetics following the pseudo 1st order model (b), % degradation of dyes as the exposure time increases (c)

The decrease in dye concentration over time was observed after exposure to sunlight (Fig. 8a). The degradation of MO and MB is a pseudo-first-order process, calculated using Equation (5), because there is a linear relationship between time t and $ln\frac{A_t}{A_o}$, and the rate constant values for MO and MB are -0.012/min and -0.016/min, respectively ($R^2 > 0.85$) (Fig. 8b). As time increases, the % degradation of MO and MB in sunlight increases (Fig. 8c).

For practical use, photocatalyst reusability is a significant aspect to remove dyes from wastewater in an efficient and long-lasting manner. In the present study, the reusability of CuO NPs as a photocatalyst was also studied. Once the reaction was completed, the photocatalyst was taken out, rinsed with distilled H_2O, and sonicated with distilled H_2O for 30 min. After air drying the photocatalyst for one day, it was further used in various successive degradation reactions. MO and MB degradation was 79.25 and 89.47% in the 1st cycle, and 78.43 and 88.21% in the 2nd cycle, which declined further to 77.04 and 86.93% in the 3rd and to 73.13 and 82.11% in the 4th cycle (Fig. 9). The results of the reactions indicated that, even after 4 runs, CuO NPs showed good photocatalytic performance against MO and MB dyes, which indicates the stability of the photocatalyst. The loss of NPs during collection and washing may be the cause of the slight decline in photocatalytic activity after 4 cycles. Other reasons for the declining performance of the photocatalyst might be due to the intermediate's formation[61] during degradation reactions, or deterioration of the catalyst's surface after multiple uses.[59]

Several parameters affect the degradation reaction. For better photocatalytic performance, certain aspects like light source, structure and nature of the catalyst, concentration of catalyst and dyes, and irradiation time need to be taken into account.
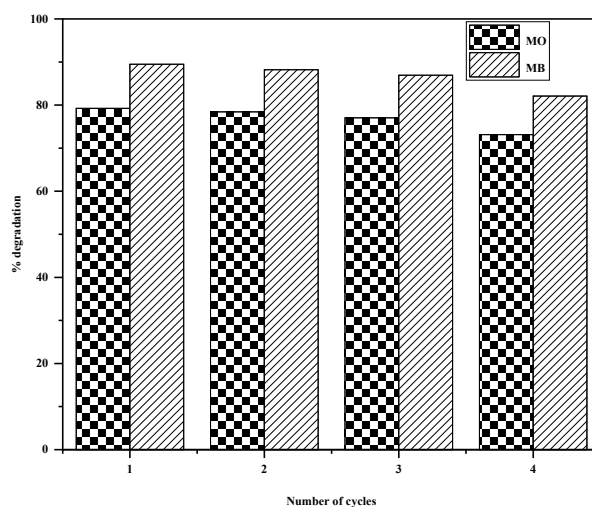
Figure 9: Reusability of CuO NPs for dye degradation

Literature suggests that when dye concentrations are raised, there is no interaction with the catalyst's active sites, resulting in an inhibited reaction. This is because the dyes cannot absorb light at a high concentration and find it difficult for electrons to go to the photocatalyst. As a result, there are not enough hydroxyl radicals to degrade the dye, which leads to inadequate results.[62] As the amount of photocatalyst increases, more interaction sites open up, which boosts the generation of hydroxyl radicals and hole-electron pairs needed for the effective detoxification of organic contaminants. Similarly, particle size also affects the process. With a small particle size, the number of active sites increases for dye adsorption, which enhances the photocatalytic performance.[63] In the present study, optimized conditions, such as amount of photocatalyst (5.0 mg of CuO NPs), dye solution (10 ppm), and sunlight are used to degrade the dyes.

CONCLUSION

The present study reported the eco-friendly synthesis of CuO NPs from the polysaccharide isolated from seeds of *M. pudica*. The polysaccharide acted as a reducing and stabilizing agent. The synthesis of CuO NPs was observed by colour change and maximum absorption at 273 nm. The SEM images and XRD peaks demonstrate the morphology and crystalline nature of the synthesized nanoparticles, respectively. In the FTIR spectrum, the peak at 475 cm^{-1}, due to the metal-oxygen bond, indicates the formation of NPs. The NPs of CuO were used to evaluate their photocatalytic degradation performance against organic dyes, methyl orange and methylene blue under sunlight. CuO NPs synthesized from *M. pudica* mucilage showed more photocatalytic activity for methylene blue, as compared to methyl orange under sunlight. The dye degradation increased over time, and degradation kinetics followed the pseudo-first-order model. The reusability of CuO NPs as a photocatalyst was also investigated, and after 4 cycles CuO NPs showed excellent results, with a slight decrease in efficiency. In future research, mucilage can be considered as a potential candidate for the green synthesis of nanoparticles to degrade dyes and other toxic pollutants from contaminated water.

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