Journal of Advanced Zoology
ISSN: 0253-7214
Volume 45 Issue 1 Year 2024 Page 1044:1051

Removal Efficiency of Synthetic Dyes by Copper Nanoparticles

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Article History

Received:
Revised:
Accepted:

Abstract

Water contaminant and pathogenic microorganism elimination using nanotechnology is a fantastic potential. NaBH4 was used to create copper nanoparticles, and the effectiveness of the dye removal was assessed. Utilising scanning electron microscopy (SEM), DLS, UV-visible spectroscopy, and energy dispersive analysis by X-rays, the synthesised nanoparticles were characterised. This study examined the elimination of COD and BOD utilising (CuNPs) at various (20–100 ppm) levels. Both the chemical oxygen demand (COD) and the biological oxygen demand (BOD) were shown to be effectively removed by CuNPs. Additionally, the synthesised copper nanoparticles are highly effective at removing synthetic dyes like methyl orange (89%), methylene blue (95%), and malachite green (97%).

Key words*: *Copper nano, COD, BOD, textile dye, methyl orange

INTRODUCTION

Water pollution from a variety of contaminants, particularly heavy metals, textile industry dyes and pigments, and other suspended hazardous particles, continues to be a danger to the environment and public health. The discharge of these harmful chemicals into the environment and aquatic bodies should thus be controlled [1]. Many techniques have been used to physically and chemically remove contaminants from wastewater, including ion exchange, flocculation, reverse osmosis, electrodialysis, and neutralisation [2,3]. Nanoparticles are used more frequently, and one of the ways this happens is through sewage treatment systems, which allows nanoparticles to enter the environment. Due to their settling, biosorption, and other activities involving activated sludge microorganisms, there is also rising worry that the liberated nanoparticles have a negative impact on the sewage treatment processes [4-6].
It was discovered that the physicochemical characteristics of activated sludge can be altered by copper nanoparticles. [7]. Extremely tiny copper nanoparticles with a high surface-to-volume ratio can also act as

antifungal and antibacterial agents [8–10]. The biological oxygen demand (BOD), which has precise long estimation periods, is slower than the chemical oxygen demand (COD), which is a key indicator for determining the level of water pollution caused by generic organic compounds [11,12]. By assessing the chemical and biological oxygen demands of waste water at various dosage levels of the synthesised copper nanoparticles, a prospective application of the particles was effectively outlined in this study. Additionally, the effectiveness of synthetic dye removal was demonstrated using synthesized copper nano particles.

MATERIALS AND METHOD

Materials

$CuSO_4.5H_2O$ (AR), EDTA (AR), $NaBH_4$ (LR), KOH (LR), were purchased from Merck, India. The mineral acids (LR) and solvents (LR) were purchased from Fischer scientific company, India. The COD and BOD chemicals (potassium dichromate(LR), silver sulphate(LR), mercuric sulphate(LR),ferrous ammonium sulphate(LR), phenanthroline monohydrate(LR), potassium dihydrogen phosphate(LR) , dipotassium hydrogen phosphate(LR), disodium hydrogen phosphate heptahydrate(LR) , ammonium chloride(LR), magnesium sulphate(LR), calcium chloride(LR), manganese sulphate(LR), sodium azide(LR), and starch(LR)) were purchased from SRL, India.

Characterization

Surface and bulk characterization tests were performed on the produced copper nanoparticles. SEM (ZEISS) scanning electron microscopy was used to evaluate the particular surface textures. Size Distribution Intensity Determination: Dynamic Light Scattering (Nano Plus) measured the dynamic light scattering capacity (DLS). Using EDAX, elemental analysis is determined. Utilizing a UV-Vis spectrophotometer from Perkin Elmer, absorption studies were carried out.

Synthesis of Cu nanoparticles

$CuSO_4$ (12 mmol) and EDTA (12 mmol) were dissolved in distilled water for the synthesis of copper nanoparticles. As a reducing agent, $NaBH_4$ (48 mmol) was added to the aforementioned solution, which was then agitated at room temperature before the aqueous solution was filtered. The final step was drying in a vacuum oven after the product had been rinsed three times with ethanol, water and acetone separately. The production of copper hydroxide precipitate in an alkaline solution is prevented by the addition of EDTA.

$$4CuSO_4.5H_2O + NaBH_4 + 8KOH \longrightarrow 4Cu + 4K_2SO_4 + NaBO_2 + 11H_2O$$

Different molar ratios are employed in the experiment, and the reaction time is fixed at 30 minutes

Waste water treatment experiments

Waste water treatment using Cu nanoparticles that were synthesized. CuNps were added to the waste water (100 ml) in a beaker at various concentrations (between 20 and 100 ppm). After stirring for five minutes, the flocculant-containing effluent was allowed to settle for 20 minutes. Wastewater that contains municipal, industrial, and domestic wastes. It was discussed that the biological oxygen demand (BOD) or chemical oxygen demand (COD) measures the strength of waste water.

Determination of COD

In the presence of Ag_2SO_4 and $HgSO_4$, a known volume of waste water sample is refluxed with a known excess of $K_2Cr_2O_7$ in a diluted H2SO4. The sample's organic material oxidises to produce H_2O, CO_2, and NH_3. A ferrous ammonium sulphate standard solution is used to titrate the excess unreacted $K_2Cr_2O_7$ in the solution. Let V_1 ml represent the FAS volume. Additionally, a blank titration is performed, substituting distilled water for the sewage in the same volume.

Determination of BOD

Distilled water is used to dilute a known volume of waste water sample. Two stopper bottles (bottle 1 and bottle 2) are used to collect the diluted sample of known volume. Bottle-1's dissolved oxygen level is recorded as blank. After five days of incubation at $20^{O}C$, the bottle-2's unused dissolved oxygen is measured. After five days, the BOD is determined by comparing the original oxygen concentration in the unused and blank waste water to that difference.

$$BOD_5 = (D_{ob} – D_{oi}) \text{ x Dilution factor mg/l}$$

where

D_{ob} = Dissolved oxygen present in the blank before incubation (bottle-1)

D_{oi} = Dissolved oxygen present in the sewage after incubation (bottle-2)

Removal Efficiency of Dyes by Copper Nanoparticles

A method as described by Dlamini et al. [13] was adopted to evaluate dye removal efficiency by nanoparticles. Decolorization experiments were performed, where 1 mL of copper nanoparticles was added into a 50 mL dye solution (4 g/L), after which the mixture was shaken for a minute and was left to stand for 10 min at room temperature. Test dyes (g/L) included (methylene blue, malachite green, methyl orange). The supernatant was taken for analysis using UV-VIS Spectrophotometer after the mixture had been stirred for a minute and allowed to settle for 10 min. The absorbance of each sample was measured at the maximum wavelength of each dye. Decolorization efficiency was calculated using the formula below:

A technique as reported by Dlamini et al. [13] was used to assess the effectiveness of nanoparticles in removing dye. In order to undertake decolorization tests, 50 mL of dye solution (4 g/L) was mixed with 1 mL of copper nanoparticles. The mixture was then agitated for a minute before being allowed to stand for 10 minutes at room temperature. Methylene blue, malachite green, and methyl orange were used as test dyes (g/L). The mixture was stirred for a minute and then allowed to settle for 10 minutes before the supernatant was removed for analysis with a UV-VIS Spectrophotometer. Each sample's absorbance was calculated at the dye's maximum wavelength. The following formula was used to determine the efficiency of decolorization:

$$RE\ (\%) = [(C_0 - C)/C_0] \times 100 \qquad (1)$$

where C_0 is the initial value and C is the value after the flocculation treatment.

Based on the initial and final dye concentrations, it is important to measure residual concentration of the dye in the samples after treatment [14].

RESULTS AND DISCUSSION

UV-Visible Absorption Spectroscopy of Copper Nanoparticles

Cu NPs' UV-visible absorbance spectrum revealed a λmax of 432, as illustrated in Figure 1. The primary cause of this absorption band is the surface plasmon resonance of Cu NPs. The earlier study by Jain and Mehata (2017) reported a comparable outcome. [15]. Every researcher reports a different λmax value for NPs synthesized because the surface plasmon absorbance depends on the size of NPs [16].

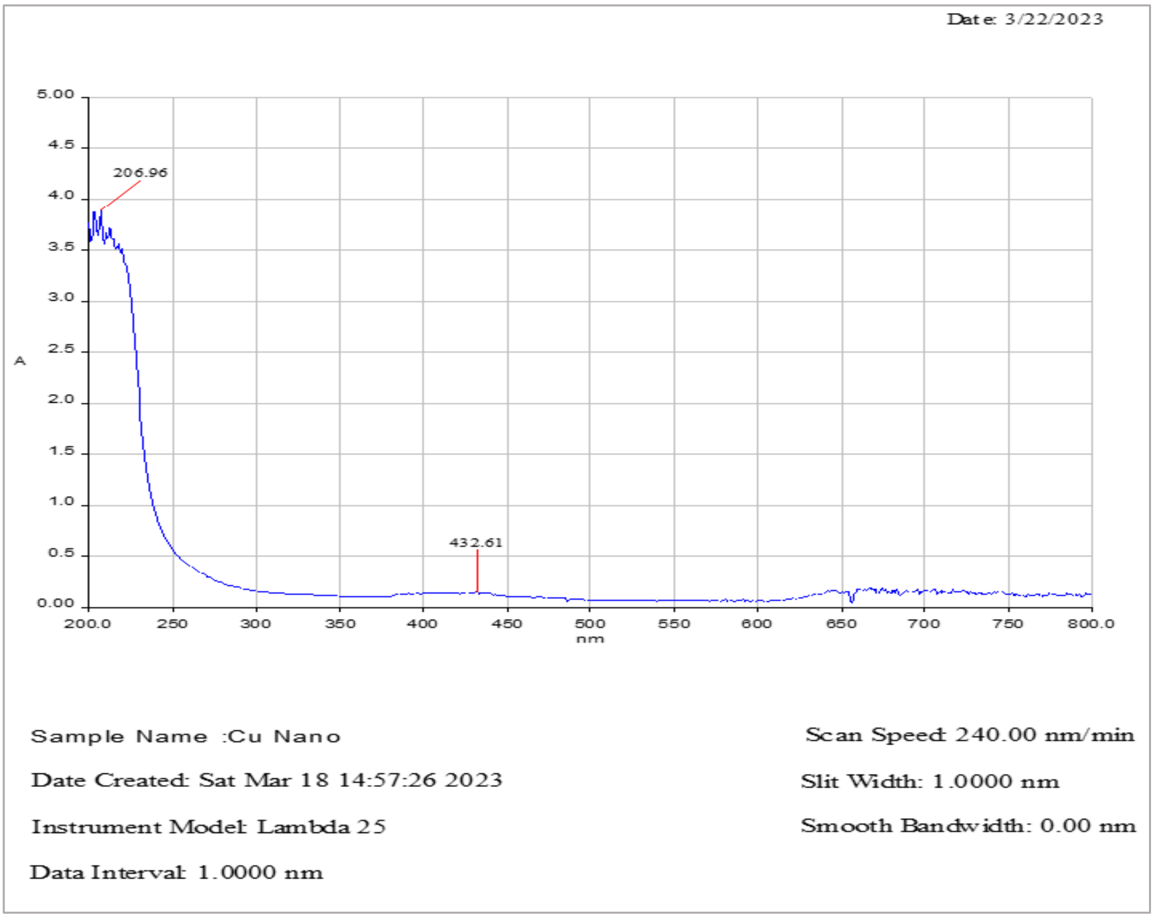


Fig. 1. UV-Visible Absorption Spectrum of Copper Nanoparticles

SEM Analysis of Copper nanoparticles

SEM is used to look at the shape of the Cu nanoparticles (Fig.2). The micrograph revealed that the nanoparticles had aggregated over time as a result of ageing. The particles' distribution is also not uniform, and they have an uneven shape. When sodium borohydride is employed as a reducing agent and a SEM image is taken without the use of any dispersing agents, copper nanoparticles can be obtained.

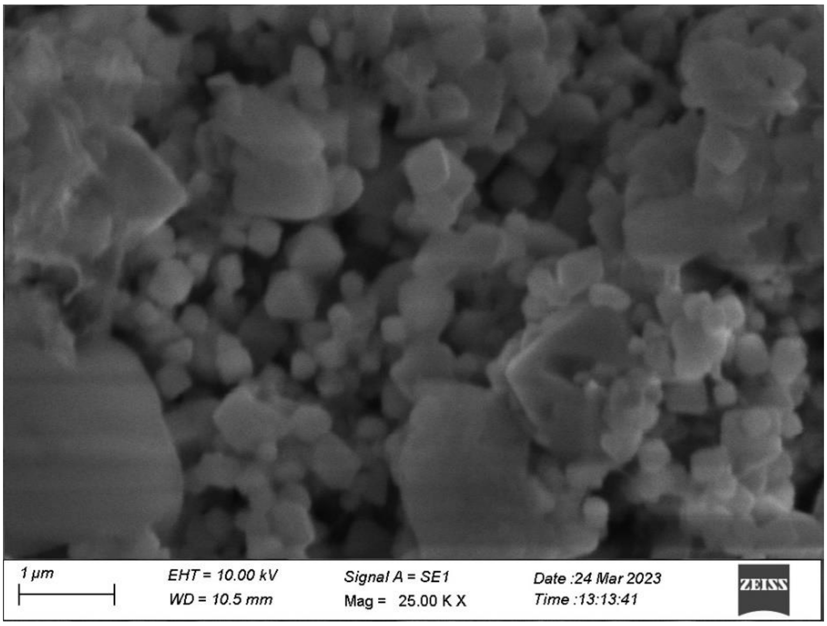


Fig.2: SEM image of Cu nanoparticles

Peak	Diameter (nm)	Std. Dev.
1	172.1	159.1
2	0.0	0.0
3	0.0	0.0
4	0.0	0.0
5	0.0	0.0
Average	172.1	159.1

Residual : 2.378e-003 (O.K)

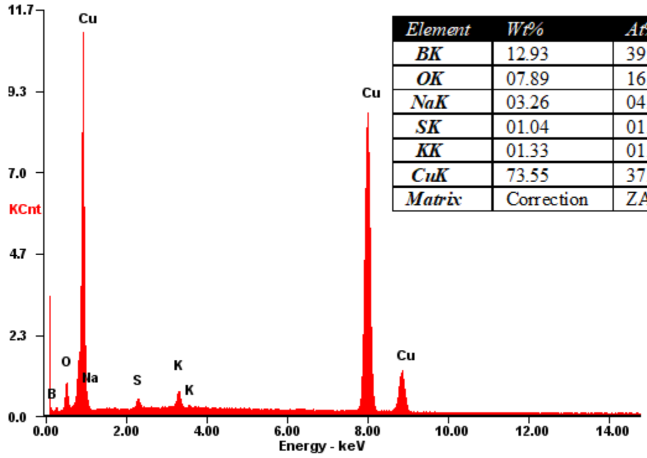
Fig.3. DLS plot for CuNPs

DLS plot CuNPs

One of the most flexible methods for determining the average size of nanoparticles is DLS. DLS was also used to describe the CuNps. Fig.3 displays the average particle size distribution of CuNps.In this scenario, the average particle size distribution will be around 95.2 nm, and 47% of the particles will be within 100 nm. The DLS only measures the diameter of the nanoparticles, not their actual size, hence this study is acceptable. The lone peak shows that the nanoparticles are distributed uniformly.

Elemental analysis

For the samples that were prepared, Energy Dispersive Analysis by X-Rays (EDAX) performed an elemental analysis, and the results are tabulated in Fig. 4. The estimated and synthesised Cu nanoparticles' elemental analyses coincide, and they are as follows: Cu Nps Discovered This artificially created Cu Nps contains 73.55% copper and roughly 13% boron, demonstrating the impure nature of nanoparticles.



Element	Wt%	At%
BK	12.93	39.14
OK	07.89	16.14
NaK	03.26	04.65
SK	01.04	01.06
KK	01.33	01.12
CuK	73.55	37.89
Matrix	Correction	ZAF

Fig. 4. EDAX graph of Cu metallic nano particles.

Chemical Oxygen Demand

Before treatment for metallic copper nanoparticles, the waste water's chemical oxygen demand value was 2988 mg O_2 per litre. After treatment for metallic copper nanoparticles, the chemical oxygen demand value of the waste water is displayed below (Table 1).

Table 1. Observed COD values of waste water at different Cu nano particle dosage levels

S. No.	Cu nano particles dosage (ppm)	COD- Value (mg O_2/L)	Removal Ratio (%)
1	20	2370	21
2	40	1442	52
3	60	1339	55
4	80	1133	62
5	100	824	72

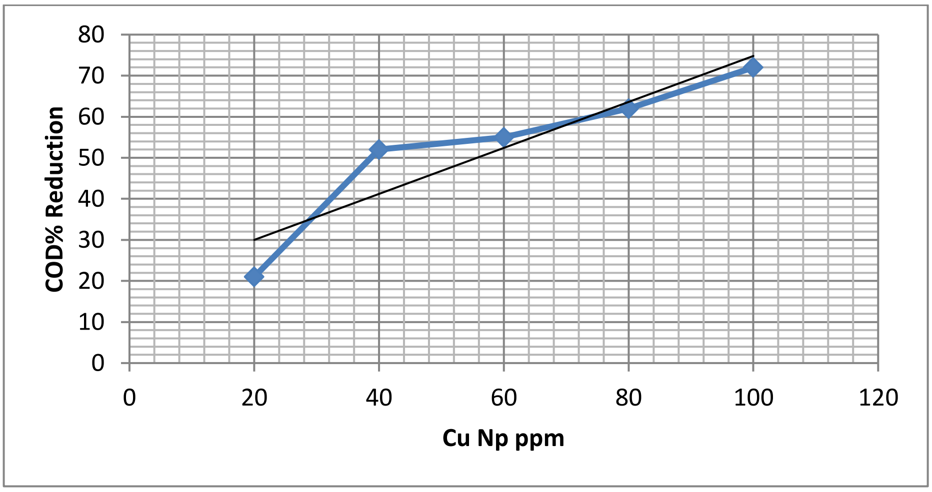


Fig.5. Plot of % COD reduction Vs Cu nano particle dosage

The proportion of COD removed following copper nanoparticle treatment is shown in Fig. 5. The percentage COD reduction is displayed against the copper nanoparticle concentration (ppm). The flocculates that were disseminated in the tannery effluent are being attacked by the copper nanoparticles because they have more surface area. This outcome saw all of the flocculates mixed with the Cu nanoparticles and demonstrating the effects. The floc size was enlarged after that, and it began to settle in the beaker.
According to the graph, the Chemical Oxygen Demand for the industrial effluent treated at 20 ppm exhibits a relatively low reduction percentage, whereas at 100 ppm it exhibits the largest reduction. From 20 to 100 ppm, the reduction percentage gradually increases. The reduction percentage rises from 20 ppm to 80 ppm, the greatest COD reduction percentage in the Cu nanoparticles is 72%.

Biological Oxygen Demand
The Biological Oxygen Demand Value of the waste water after treatment of Metallic Cu Nano particles is given below (Table 2).

Table 2. Observed BOD values of waste water at different Cu nano particle dosage levels

Serial Number	Cu nano particles level (ppm)	BOD- Value (mgO_2/L)	Removal Ratio (%)
1	20	113	61
2	40	92	68
3	60	87	70
4	80	50	83
5	100	36	88

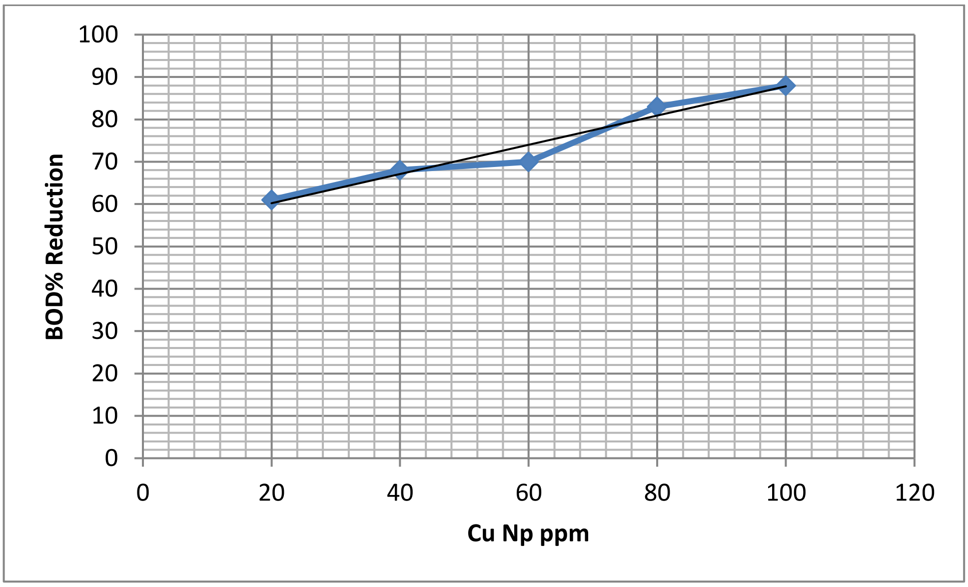


Fig.6. Plot of % BOD reduction Vs Cu nano particle dosage

Fig.6 shows the percentage removal of biological oxygen demand after treatment of copper nanoparticles. The copper nanoparticle ppm level is plotted against percentage reduction of BOD.

From the graph we can conclude that the Biological Oxygen Demand for the industrial effluent treated at 20ppm shows very low reduction percentage, whereas at 100ppm it shows the maximum reduction. The reduction percentage is uniformly increased from 20-100ppm. The BOD of the tannery effluent shows very efficient removal using Cu nano particles.
This Cu nano particle effectively determines the relative oxygen requirements by decomposing the organic materials that was present in waste water. After Cu nanoparticles were treated, the amount of oxygen that was consumed by microorganisms in the tannery effluent was calculated.
At various dosage levels of the synthesized Cu nanoparticles, the chemical oxygen demand and biological oxygen demand decrease of removal ratio in waste water showed the effective flocculation behavior. Cu nanoparticles can reduce BOD by up to 88 percent.

Effect of Copper Nanoparticles on Dye Removal

Effect of copper nanoparticles on dye removal is seen in Fig. 7. All of the dyes that were tested had a strong affinity for the synthesized nanoparticles, and their removal effectiveness is above 89%. When used to remove colors from wastewater from many industries, including the textile industry, these copper nanoparticles are effective.

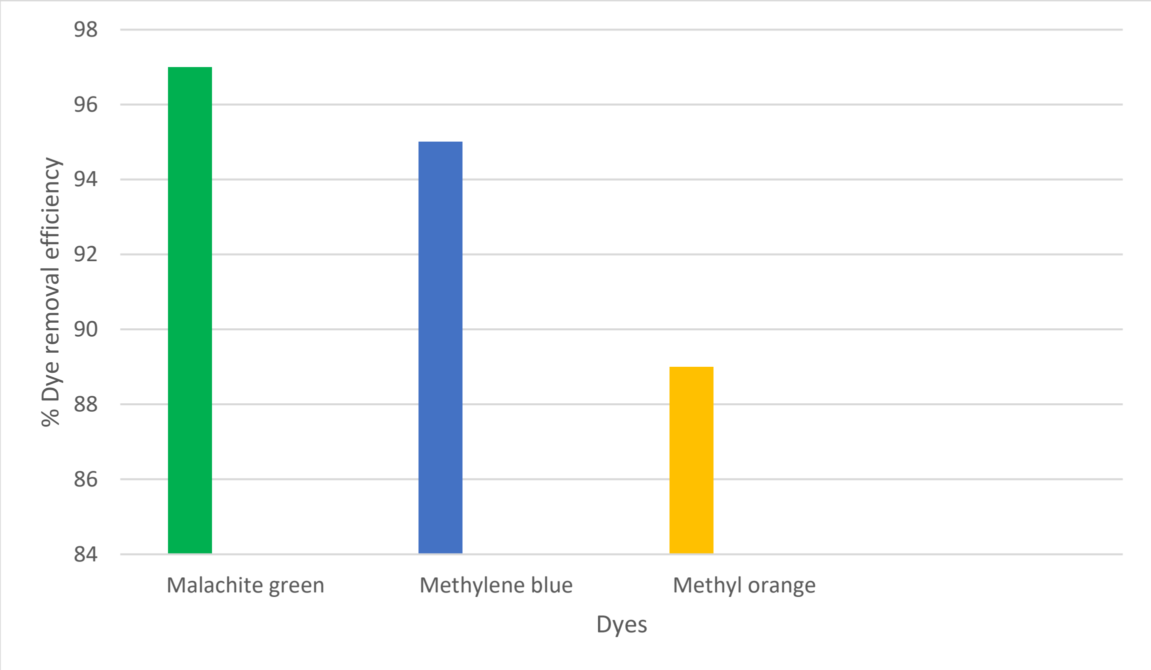


Fig.7. Effect of copper nanoparticles on synthetic dye removal

The ability of synthesized copper nanoparticles to remove dye was studied. All kinds of dyes were able to be eliminated by synthetic nanoparticles. This might be attributable to the particle aggregation brought on by bridging and charge neutralization, as was previously described [17]. Bridging happens when a particle extends into a solution from the surface over a longer distance than the antiparticle repulsion is effective. All of the dyes that were evaluated have a great deal of removal power for the synthesized nanoparticles. Because all dyes had removal efficiencies above 89% without the addition of cations, the nanoparticle concentration remained constant (0.2 mg/mL), demonstrating their efficacy. This was in contrast to the findings published by Deng et al. [18] who found that high bioflocculant concentrations were directly related to the removal effectiveness of dyes.

CONCLUSION

In conclusion, metallic copper nanoparticles were synthesized and examined using scanning electron microscopy (SEM) and UV-visible spectroscopy. The chemical and biological oxygen demands of waste water at various dose levels were successfully measured in order to characterize a potential application of the synthesized copper nanoparticles. At a ppm level of 100, chemical oxygen requirement reveals a maximum removable percentage of 72%. At a ppm level of 100, biological oxygen demand reaches its maximum percentage of 88%. Additionally, at a low concentration of 0.2 mg/mL and a 10-minute contact time, they can remove dyes. The outstanding abilities of the synthesized nanoparticles to remove textile colors raise the possibility of using them to remove dye effluents from wastewater.

Conflict of interest

The authors declared no conflict of interest.

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