Research Article

Proficient Photocatalytic and Sonocatalytic Degradation of Organic Pollutants Using CuO Nanoparticles

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In recent years, due to the advancement in nanotechnology, advanced oxidation processes (AOPs), especially sonocatalysis and photocatalysis, have become a topic of interest for the elimination of pollutants from contaminated water. In the research work reported here, an attempt has been made to study and establish a physicochemical mechanism for the catalytic activity of copper oxide nanoparticles (CuO NPs) in AOPs using the degradation of dyes as model contaminants. CuO NPs exhibited brilliant sonocatalytic and photocatalytic activities for the degradation of a cationic dye (Victoria Blue) as well as an anionic dye (Direct Red 81). The degradation efficiency of CuO NPs was calculated by analysing the variation in the absorbance of dye under a UV-Vis spectrophotometer. The influence of different operating parameters on the catalytic activity of CuO NPs, such as the amount of catalysts dose, pH of the solution, and the initial dye concentration, was thoroughly investigated. In addition, the kinetic process for the degradation was also examined. It was observed that both dyes exhibited and followed the pseudo-first-order kinetics relation. The rate constant for sonocatalysis was high as compared to photocatalysis. The rate constant for both sonocatalysis and photocatalysis was successfully established, and reusability tests were done to ensure the stability of the used catalysts. To get an insight into the degradation mechanism, experiments were performed by using $\cdot\text{OH}$ radical scavengers. The efficacy of CuO NPs for dye decolorization was found to be superior for the sonocatalyst than the photocatalyst.

1. Introduction

Although awareness of the need to avoid contamination of the environment has increased, large amounts of synthetic or natural pollutants, such as dyes, heavy metals, pharmaceutical waste, and agrotoxic waste, like pesticides, continue to be discharged in the environment by different industries [1]. Among these, synthetic organic dyes are one of the leading contributors to environmental pollution since dyes are used by various industries, such as plastic, paper, textile, leather, cosmetic, and food industries [2, 3]. As dyes have a complex aromatic structure and are difficult to degrade, their presence in the aquatic environment can cause problems,

such as color change, odor alteration, eutrophication, under-oxygenation, and bioaccumulation [4]. Therefore, their removal from industrial wastewater is highly desirable to achieve concentrations below environmentally accepted levels for safe disposal.

At present, several techniques have been developed for the removal of pollutants from wastewater, such as adsorption, chemical coagulation, filtration, sedimentation, and advance oxidation process (AOPs) [5–8]. Recently, AOPs are gaining significant importance due to their ability to generate a sufficient number of highly reactive radicals for effective water decontamination. Among numerous AOPs, photocatalysis and sonocatalysis with metal oxide nanoparticles (NPs) have

attracted more attention as efficient techniques for the degradation of toxic organic contaminants [9–18].

In the case of photocatalytic degradation, irradiation with photon energy greater than the band gap of NPs leads to the formation of electron and hole pairs, which further helps in the generation of highly reactive oxygen species (ROS) that eventually participate in the degradation of toxic compounds [19–23]. It is evident that the limiting factor for catalytic degradation depends upon the ability to form greater numbers of ROS [24]. On the other hand, sonocatalytic degradation of toxic compounds is caused by a chemical effect of ultrasonic (US) waves which arises from acoustic cavitation, i.e., formation, growth, and collapse of bubbles in a liquid [25]. The transient bubble collapse generates a localized hot spot with a very high temperature (near about 5000 K) and pressure (~500 bars). Under such extreme conditions, thermal decomposition of water takes place, resulting in the formation of highly reactive radical species such as $\cdot\text{OH}$, $\cdot\text{H}$, and $\cdot\text{O}$, which can oxidize and degrade organic contaminants in water [26].

In keeping with environmental concerns, there is a significant shift towards the use of nanoparticles in developing green and environmentally friendly approaches in synthetic chemistry [27]. In our previous work, we have reported the synthesis of CuO NPs and further investigated their catalytic activity in the synthesis of xanthenes [28]. The synthesis of CuO NPs was carried out with microwaves, using a greener approach, which has achieved many advantages in the synthesis of xanthenes, such as low energy, cost effectiveness, shorter processing time, less pollution, utilization of a green solvent, and a lower reaction temperature with high yield as compared to other methods [28]. As determined through X-ray diffraction studies, the as-synthesized NPs were composed of a pure CuO phase with a monoclinic structure without any peaks of impurity (Figure S1, supplementary data). Particle size, as calculated from FWHM of reflection (111/200) of monoclinic CuO structure using the Debye Scherrer formula, was found to be 18 nm. For determining the morphology, the TEM micrograph of CuO NPs was taken and NPs were observed to be almost spherical in shape, well dispersed, and within the narrow range of size distribution (17–22 nm) (Figure S2, S3, supplementary data) [28].

In the present work, we have explored CuO NPs as a catalyst for degradation of Victoria Blue (VB) and Direct Red 81 (DR) dyes as model organic contaminants. To find out which energy source is better in terms of the synergistic effect with CuO NPs for the degradation of dyes, we have used UV-visible light and US waves as sources of energy. The effect of pH, catalyst dosage, and initial dye concentration with respect to contact time has been particularly evaluated. An attempt has also been made to recover the CuO NPs from the reaction mixture in both cases and to reuse them in subsequent processes. The kinetics rate constant of dyes under both energy sources has been evaluated and found to have significant efficiency.

2. Experimental Details

2.1. Materials and Techniques. Victoria Blue (VB) and Direct Red 81 (DR) dyes were obtained from Sigma-Aldrich.

Dimethyl sulfoxide and sodium bicarbonate were purchased from Qualigens, and absolute ethanol (purity 99.9%) was purchased from Changshu Yangyuan Chemicals, China. All of the chemicals were used as received, and double distilled water was used for the preparation of different solutions. Characterization of recycled nanoparticles was done by transmission electron microscope (TEM) (TEM; Hitachi-H-7500) operating at 80 kV. The crystallinity and X-ray diffraction pattern of the samples were performed at room temperature utilizing X-ray diffraction (XRD; PANalytical X'Pert Pro) equipped with Cu- α radiation ($\lambda = 1.54178 \text{ \AA}$) with a scanning speed of 8 min^{-1} , in the 2θ range of $0\text{--}90^\circ$. The zeta potential of the CuO NPs was examined at different pH ranges with a Malvern Zetasizer (ZS 90) at room temperature.

2.2. Synthesis and Characterization of CuO NPs. CuO NPs have been synthesized via a cost-effective and greener approach by using microwave and DI water as the medium. Within 4 minutes of reaction time, very high yields of CuO NPs were achieved. Detailed procedure and characterization have been reported earlier [5]. To study the photocatalytic and sonocatalytic efficiency of the NPs, surface area of the nanoparticles should be known. BET (Branauer-Emmett-Teller) surface area of CuO NPs was studied using Quanta-chrome Instrument (version 3.01).

2.3. Sonocatalytic and Photocatalytic Degradation Reaction Procedures. To evaluate the catalytic (photocatalytic and sonocatalytic) activity of CuO NPs and to further understand the degradation mechanism of both the dyes, batch experiments were performed at room temperature. Before exposing to ultrasonic waves or UV-visible light, the suspensions (dye+NPs) were kept in dark conditions and stirred for 10 minutes to get the adsorption-desorption equilibrium of the dye on the CuO NPs. Therefore, the effect of adsorption during sonocatalysis or photocatalysis could be calculated accurately.

In case of sonocatalysis, these suspensions were placed in an ultrasonic bath apparatus (PCI Analytics) for a definite interval of time. After ultrasonic irradiation, CuO NPs were separated from the suspension by centrifugation and percent degradation was calculated by measuring the change in the absorbance of dye using UV-Vis spectrophotometer. In the case of photocatalysis, the experiment was carried out by placing the suspended solution in a UV-visible photoreactor (125 W , 198.4 mWS^{-2}) for a definite time interval. After exposure to UV-visible radiations for a desired time interval, samples were withdrawn from the chamber and CuO NPs were separated from the suspension by centrifugation. The degradation rates of the dyes at given time intervals were calculated by measuring the changes in the absorption profile at their maximum absorbance wavelength (λ_{max}) using a UV-vis spectrophotometer (UV 2100, Shimadzu). The degradation observations were performed under ambient conditions and the temperature was kept at $25\text{--}30^\circ\text{C}$. Typically, 20 ml of $10 \times 10^{-5} \text{ M}$ solutions of both dyes with initial solution pH 10 for VR dye and 4.0 for DR dye were taken, and 25 mg of catalyst dose was taken in general throughout the whole investigation. For sonocatalysis, ultrasonic irradiation of 50 kHz frequency and 50 W power were used, and for photocatalysis,

FIGURE 1: (a) N₂ adsorption-desorption BET isotherms and (b) BJH pore size distributions (from the adsorption branch of the isotherms) of synthesized CuO NPs.

at UV-visible irradiation frequency 198.4 mWS^{-2} and 125 W power. In addition, the pH of the dye solutions was adjusted to required pH by adding 0.1 M HCl or NaOH solution. The pH value of solutions was measured by a CyberScan 510 digital pH meter.

The following equation (equation (1)) was used for calculating the degradation efficiency (percent degradation) of dyes:

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

where C_0 is the initial concentration of the dye before irradiation and C_t is the concentration of the dye at a certain reaction time t (min) after irradiation. The sonocatalytic activity of CuO NPs, in terms of the degradation of VB and DR, was compared with that of the photocatalytic activity of CuO NPs under UV-visible irradiation. Multiple factors are responsible for the sonocatalytic efficiency of CuO NPs which are difficult to quantify individually. Moreover, sonocatalysis and photocatalysis are two completely different phenomenon; therefore it is hard to find a correlation factor between the US and UV-Vis energy sources.

3. Results and Discussion

3.1. Characterization of CuO NPs. The BET isotherms and their relative Barret–Joyner–Halender (BJH) pore size distributions obtained from the adsorption branch of the isotherms of the CuO NPs are displayed in Figure 1(a). It was observed that the prepared CuO NPs possess a mesoporous surface as the isotherms are of type IV. The multipoint BET-specific surface area for CuO NPs was found to be $49.33 \text{ m}^2\text{g}^{-1}$. The CuO NPs were found to have an average pore radius of 1.1764 nm (Figure 1(b)).

3.2. Percentage Degradation of VB and DR under Different Processes. The degradation efficiency of VB (pH 10) and DR (pH 4) was investigated by exposing the dye solution to UV-visible irradiation or ultrasonication in the absence and in the presence of CuO NPs (25 mg). Both dyes undergo negligible decomposition under direct UV-visible irradiation or US radiation in the absence of CuO NPs. On the other hand, the presence of CuO NPs showed excellent results as a photocatalyst and sonocatalyst in the degradation of both dyes (Figure 2).

3.3. Effect of pH. The pH of the solution is an important parameter that plays a significant role in the sonocatalytic and photocatalytic degradation of various target pollutants [13, 29]. The zeta potential of the CuO NP dispersions was measured over pH values ranging from 2 to 10, and the corresponding pHzpc was found to be ~ 8.5 (Figure S4 supplementary data). The effect of pH on the photocatalytic activity of CuO was tested using acidic, neutral, and basic media, and the results are shown in Figures 3 and 4, respectively. It was observed that CuO NPs in both degradation processes follow a pseudo-first-order kinetics at different pH [30]. The equation used is as follows:

$$\ln \frac{C_0}{C_t} = kt, \quad (2)$$

where k is the pseudo-first-order rate constant (min^{-1}), C_0 is the initial concentration (at time $t = 0$) of the dye, and C_t is the concentration of the dye at reaction time t . As can be seen in Table 1, rate constant k value increases for the VB dye from pH 4 to pH 10, and for the DR dye, the k value decreases from pH 10 to pH 4. Thus, the increase in pH leads to an enhanced degradation rate of VB dye and it reached maximum at pH 10. However, in the case of the DR dye,

FIGURE 2: Degradation of VB and DR dye treated with different process 10×10^{-5} M dye solution, CuO NP is 25 mg. (a) US irradiation. (b) UV-visible irradiation.

FIGURE 3: Effect of pH on degradation of VB under (a) UV-visible irradiation and (b) US irradiation.

FIGURE 4: Effect of pH on degradation of DR under (a) UV-visible irradiation and (b) under US irradiation.

TABLE 1: Pseudo-first-order kinetics rate constants for the degradation of VB and DR under both sources of energy and for different pH.

Dyes	pH	Sonocatalysis k (min^{-1})	Photocatalysis k (min^{-1})	R sonocatalysis	R photocatalysis
Victoria Blue (VB)	4	0.182	0.04067	0.99986	0.99991
	6	0.29153	0.06185	0.99955	0.99944
	8	0.35388	0.07903	0.9999	0.99959
	10	0.43209	0.09861	0.99992	0.99954
Direct Red (DR)	4	0.3656	0.10587	0.9985	0.99888
	6	0.29098	0.08525	0.99983	0.99982
	8	0.27584	0.08144	0.99901	0.99996
	10	0.20578	0.06428	0.99825	0.99998

the results indicated that the sonodegradation and photodegradation of the dye were maximally efficient in acidic conditions and the optimal pH was observed at about 4.0.

For VB, higher degradation efficiency in the basic medium must be ascribed to the surface charge properties of CuO NPs (zero-point charge (zpc) ~ 8.5). The surface charge is positive at pH values lower than pH_{zpc} , neutral at pH_{zpc} and negative at higher pH_{zpc} value. At higher pH, the CuO NP surface is negatively charged, so it enhances its interaction with the cationic dye (VB) through electrostatic force of attraction [31] (Scheme 1). Whereas in the case of DR, at lower pH, the surface of CuO NPs is positively charged so there is an enhancement of electrostatic force of attraction with the anionic dye (DR). Therefore, there is more degradation of DR dye at pH 4 [32] (Scheme 1).

3.4. Effect of Catalyst Dose. The effect of the catalyst dose on the degradation of VB and DR was studied by varying the

SCHEME 1: Role of zero-point charge of NPs on the adsorption of cationic and anionic dyes.

amount of the catalyst from 3 mg to 30 mg in 20 ml of 10×10^{-5} M dye solution at initial pH of 10 (VB) and 4 (DR) for reaction time, i.e., 7 minutes for sonocatalysis and

FIGURE 5: Effect of catalyst dose on degradation of VB and DR for (a) UV-visible irradiation and (b) under US irradiation.

12 minutes for photocatalysis. Figure 5 revealed that increasing the catalyst dose from 3 to 25 mg resulted in an increase in the degradation efficiency, while further increase in the amount of the catalyst dose to 30 mg caused an insignificant increase in the (%) degradation efficiency (Table S1–S4 supplementary data). Enhanced catalytic activity with increasing CuO NP content could be interpreted by two speculations: (1) there will be more availability of active sites and (2) deactivation of activated dye molecules by collision with molecules in the ground state [13]. $\cdot\text{OH}$ radicals were the actual oxidants for the decomposition of the VB and DR dyes, whose concentration increases with an increase in catalyst dosage [13].

3.5. Effect of Initial Dye Concentration. From an application point of view, it is important to study the effect of initial VB and DR concentration on its sonocatalytic or photocatalytic degradation efficiency (%). It was studied by varying initial dye concentration in the range among 10×10^{-5} , 12×10^{-5} , and 15×10^{-5} M using an NP dosage of 25 mg in 20 ml of dye solution and at a suitable pH. The results showed that the degradation efficiency (%) of dyes is inversely proportional to its initial concentration. As a result, increasing the initial dye concentration led to a decrease in the degradation (%) of dyes (Figures 6 and 7). This negative effect may be caused by the following: (i) The number of dye molecules that was adsorbed on the surface of the catalyst increases with the increasing dye concentration. In addition, at a high dye concentration, a significant amount of UV light or ultrasonic

irradiation may be absorbed by the dye molecules rather than by the catalyst, thereby reducing the efficiency of the catalytic reaction. (ii) The generation of $\cdot\text{OH}$ radicals on the surface of the catalyst is likely to be reduced since active sites on the surface of the catalyst are occupied by the dye ions. (iii) With the increasing dye concentration, the number of hydroxyl radicals required for the degradation of dye molecules increases, although the formation of hydroxyl radicals remains constant for a given catalyst dosage, irradiation time, and intensity [13].

3.6. Mechanism. In the case of photocatalysis, as UV-visible irradiation falls on semiconducting CuO NPs, it induces the formation of electron-hole pairs through the photoexcitation of electrons from the valence band to the conduction band (equation (3)) [33].

Photogenerated electrons react with dissolved molecular oxygen, forming a superoxide ion $\text{O}_2^{\cdot-}$ (equation (4)), which further react with a proton to form a hydroperoxide radical ($\text{HO}_2\cdot$) (equation (5)).

FIGURE 6: Effect of initial concentration VB dye on degradation under (a) UV-visible irradiation and (b) US irradiation.

FIGURE 7: Effect of initial concentration DR dye on degradation under (a) UV-visible irradiation and (b) US irradiation.

SCHEME 2: Schematic diagram representing the photocatalytic and sonocatalytic degradation mechanisms.

FIGURE 8: Influence of adding different scavengers (DMSO and carbonate ion). Experimental conditions: scavenger concentration 1 M, catalyst weights 30 mg, pH 8 (VB), and 4 (DR) (a) under US irradiation and (b) under UV-visible irradiation.

Simultaneously, photogenerated holes can react with water molecules (equation (6)) and the hydroxide anions (OH^-) to form highly active hydroxyl radicals ($\cdot OH$) (equation (7)).

The superoxide and hydroxyl radicals have strong oxidation performance, which can completely oxidize the

VB/DR dye molecules into the final products CO_2 and H_2O (equations (8) and (9)).

On the other hand, the chemical effects of ultrasound are due to the phenomenon of cavitation which is the nucleation, growth, and collapse of bubbles in a liquid

FIGURE 9: Recyclability of CuO NPs (25 mg) for the degradation of VB (pH 10) and DR (pH 4) dyes, time 12 minutes under (a) US irradiation and (b) UV-visible irradiations.

FIGURE 10: TEM of CuO NPs (a) first time synthesized, (b) recycled after sonocatalytic degradation, and (c) recycled after photocatalytic degradation.

[34]. The collapse of the bubbles induces high-energy phenomena, i.e., high temperature and pressure (~ 5000 K and 500 bars), electrical discharges, and plasma effects. The consequences of these extreme conditions are the direct thermal dissociation (sonolysis) of dissolved dioxygen and water molecules into highly reactive radical species such as $\cdot\text{OH}$, hydrogen ($\text{H}\cdot$), and oxygen ($\text{O}\cdot$).

These oxygen radicals react with water to form hydroxyl radicals ($\cdot\text{OH}$)

Moreover, it has been reported that during the transient collapse of cavitation bubbles, emission of light called “sonoluminescence” also takes place. The spectrum of this emission ranges from the ultraviolet region to well beyond the red end of the visible wavelength range, with a peak at 310 nm. This sonoluminescent spectrum of water is associated with the formation of high-energy species (e.g., excited hydroxyl radicals) from molecular fragmentation of compressed gases, rather than with black body radiation [35, 36].

Hence, sonochemistry also involves the emission of light energy for a short period of time, although molecular excitation is thermal, unlike the electronic excitation felt by molecules in photochemical processes. The radiation may lead to the photoexcitation of electrons from the valence band to the conduction band, thus leading to the formation of electron-hole pairs in a similar manner as described above for the photocatalysis (Scheme 2).

FIGURE 11: XRD of CuO NPs (a) first time synthesized, (b) recycled after sonocatalytic degradation, and (c) recycled after photocatalytic degradation.

3.7. Effect of Hydroxyl Radical Scavengers on Degradation of Dyes. To gain insight into the degradation mechanism, experiments were conducted using $\cdot\text{OH}$ radical scavengers. As depicted in earlier research, $\cdot\text{OH}$ free radical oxidation is a key mechanism in all AOPs [32, 37]. To measure the quantitative effect of $\cdot\text{OH}$ radicals on VB and DR degradation, studies were carried out in the presence of DMSO and carbonate ions, which have a hydroxyl radical-scavenging property [13, 38]. To analyse the effect of scavengers on sonocatalytic degradation and UV-visible photocatalytic degradation of both dyes, experiments were done using 20 ml of 10×10^{-5} M dye concentration and CuO NP dosage of 25 mg in the presence of radical scavengers. The solution

was irradiated with US (50 W) for 10 minutes and UV-visible irradiation for 20 minutes. It was observed that the degradation efficiency of both the dyes decreased in the presence of radical scavengers (Figure 8). The plausible mechanism in the presence of DMSO and carbonate ion is shown below

The major decline of degradation efficiency demonstrated that $\cdot\text{OH}$ radical plays a vital role in both the

FIGURE 12: Pseudo-first-order kinetics plot of VB at different concentrations under (a) UV-visible irradiation and (b) US irradiation.

degradation processes and confirms that free radical attack is the dominant controlling mechanism in the degradation of both the DR and VB dyes.

3.8. Reusability of Catalyst. An examination of the sonocatalytic and photocatalytic activities of the recycled CuO NPs was investigated by collecting the NPs from a sample solution after centrifugation. The separated NPs were thoroughly washed with water and ethanol. The reusability test of CuO NPs under UV-visible and ultrasonic irradiation on the same organic dyes show the stability of the catalyst. As shown in Figure 9, the reused catalyst showed very little change in the degradation efficiency in both cases, i.e., sonocatalysis and photocatalysis. This emphasizes the excellent chemical stability of the catalyst, making it beneficial for practical wastewater remediation applications. A slight decrease in the photocatalytic activity in each successive cycle can be attributed to several reasons like a degradation of the photocatalyst (CuO NPs) itself, unavoidable loss of photocatalyst during the recycling processes, and slight aggregation of NPs after the photocatalytic process. To find out why there is a decrease in the activity of used CuO NPs after 4 cycles, the recycled CuO NPs have been characterized by TEM and XRD [Figures 10 and 11]. The characteristic XRD diffraction peaks of CuO NPs are clearly visible and show no notable differences before and after recycling the NPs, indicating that CuO NPs are chemically stable. In contrast, TEM images of CuO NPs before and after photocatalytic reaction (4 cycles) (Figure 11) shows the slight aggregation of CuO NPs, possi-

bly by the interactions between CuO NPs and intermediates formed during the degradation process, thus decreasing the electrostatic energy barrier between NPs and increasing the aggregation behaviour. As these recycled CuO NPs form clusters, hence, the surface to volume ratio of NPs decreases and their catalytic activity also decreases.

3.9. Comparison of Efficiency of Photocatalysis and Sonocatalysis of CuO NPs. Competitive analysis of CuO NPs as sonocatalysts and photocatalysts as shown in Figure 2 reveals that % decomposition is far better in the case of sonocatalysis. In the presence of CuO NPs and under different sources of energy, both dyes demonstrated enhanced degradation than without NPs. This is due to an increase in the generation of hydroxyl radicals by enhancing the electron-hole pair formation rate due to the excitation of the catalyst surface by energy source [5, 13]. To further quantify, kinetics of sonocatalytic and photocatalytic degradation of the VB and DR dyes was studied by conducting reactions at an initial concentration (10×10^{-5} , 12×10^{-5} , and 15×10^{-5}) with a catalyst dose of 25 mg. The graph is plotted for $\ln(C_0/C_t)$ vs. the time for photocatalytic and sonocatalytic degradation which resulted in approximately straight lines, as shown in Figures 12 and 13. The kinetic studies were performed on the basis of disappearance of the dye.

The photocatalyst and sonocatalyst with as-prepared samples could be expressed by Langmuir-Hinshelwood mode, Figures 12 and 13. These figures imply that the degradation of VB and DR in both cases follows a pseudo-first-order kinetics.

FIGURE 13: Pseudo-first-order kinetics plot of DR at different concentrations under (a) UV-visible irradiation and (b) US irradiation.

TABLE 2: Pseudo-first-order kinetics rate constants for the degradation of VB and DR under both sources of energy and for different concentration.

Dyes	Dye concentration	Sonocatalysis k (min^{-1})	Photocatalysis k (min^{-1})	R sonocatalysis	R photocatalysis
Victoria Blue (VB)	10×10^{-5} M	0.43209	0.09861	0.99992	0.99952
	12×10^{-5} M	0.36536	0.07314	0.99975	0.99965
	15×10^{-5} M	0.28177	.05255	0.99988	0.99933
Direct Red (DR)	10×10^{-5} M	0.3656	0.10587	0.9985	0.99888
	12×10^{-5} M	0.27036	0.09159	0.99925	0.99962
	15×10^{-5} M	0.24064	0.08172	0.99915	0.99811

TABLE 3: Comparison of efficiency of photocatalysis and sonocatalysis of CuO NPs.

Dyes	NPs	Photocatalysis k (min^{-1})	Sonocatalysis k (min^{-1})
Victoria Blue (VB) 10×10^{-5} M	CuO	0.09861	0.43209
Direct Red (DR) 10×10^{-5} M	CuO	0.10587	0.3656

The rate constants are determined by fitting the experimental data in equation (2). The pseudo-first-order reaction rate constant k and regression R calculated from Figures 12 and 13 are given in Table 2. On comparing the kinetic constant (k) of sonocatalysis with k of photocatalysis for both dyes, it was found that the obtained value of k for the sonocatalyst is much higher than for the photocatalyst. Hence, proving that US irradiations are a better source than UV-visible irradiation for the degradation of dyes in the presence of CuO NPs. CuO NPs have

a lower band gap (2.3 eV (Figure S5 supplementary data)) so electron-hole recombination is faster and easier. Therefore, the formation of hydroxyl radicals is difficult, which results in lower degradation of dyes in the case of photocatalysis. In the presence of CuO NPs, the sonocatalytic efficiency to decompose organic pollutants was enhanced. This is due to synergistic effects of ultrasound and solid catalyst, namely [39], (i) added powders could provide additional nuclei for cavitation bubble formation, (ii) US irradiation enhances the

mass transfer of organic pollutants between the liquid phase and the catalyst surface, (iii) US irradiation increases the active surface area due to ultrasound deaggregating, and (iv) the catalyst can be excited by ultrasound-induced luminescence which has a wide wavelength and increased production of $\cdot\text{OH}$ in the reaction mixture (Ghosh et al., 2013). Thus, sonocatalysis seems to enhance the degradation ratio of organic pollutants due to the increase in the generation of $\cdot\text{OH}$.

3.10. Comparison of Efficiency of Photocatalysis and Sonocatalysis of CuO NPs. On comparing the photocatalytic and sonocatalytic activities CuO NPs, it was found that the CuO NPs are superior as sonocatalysts than the photocatalysts (Table 3). This may be attributed to the presence of a smaller band gap of CuO NPs (2.3 eV in the present case) which enables the electron-hole recombination to be less or slower, so there is more formation of ROS for the degradation of dyes. Additionally, the CuO NPs being better as sonocatalysts is because of the higher surface area calculated by BET of CuO NPs ($49.33 \text{ m}^2 \text{ g}^{-1}$). Higher surface area leads to the formation of more cavitation bubbles, which, in turn, produces more local temperature and pressure effects and eventually creates more ROS for the degradation of dyes.

4. Conclusion

In summary, we have demonstrated the comparison of the catalytic effect of CuO NPs on the degradation of the cationic (VB) and anionic (DR) dyes under different energy sources, i.e., UV-visible irradiation and US radiations. The synergistic effect of CuO NPs and sonocatalysis has been demonstrated to be more effective in degrading both dyes as compared to CuO NPs and photocatalysis. High catalyst dosage and low initial dye concentration were favoured for the sonocatalytic or photocatalytic degradation of both dyes. Degradation follows the formation of a free radical mechanism, which is further verified by the addition of radical scavengers which reduced the sonocatalytic or photocatalytic degradation. Comparison of the efficiency of photocatalysis and sonocatalysis of CuO NPs was examined and reported. Overall, the application of CuO NPs can be a promising and efficient approach for the sonocatalysis of both the cationic and anionic dyes with high reusability potential.

Data Availability

Data of all by measurements can be available with the authors and shared upon request. Data are stored in secured devices at the author's institutions. Data can be used to reproduce the results and also generate new sets of results. The authors have full access to these data and full permissions to make it available public for greater use to the scientific community.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Figure S1 represents the X-ray diffraction pattern of the as-synthesized nanoparticles, where it is composed of a pure CuO phase with a monoclinic structure without any peaks of impurity. The particle size, as calculated from FWHM of reflection (111/200) of a monoclinic CuO structure using the Debye Scherrer formula was found to be 18 nm. For determining the morphology, TEM micrograph of CuO NPs was taken and the NPs were observed to be almost spherical in shape, well dispersed, and within a narrow range of size distribution (17–22 nm) as demonstrated in Figures S2 and S3 below [28]. The zeta potential of the CuO NP dispersions was measured over pH values ranging from 2 to 10, and the corresponding pHzpc was found to be ~ 8.5 as shown in Figure S4. The lower band gap of CuO NPs ($\sim 2.3 \text{ eV}$) as obtained from the Tauc plot is depicted in Figure S5, and it leads for faster and easier electron-hole recombination processes during the sonocatalytic and photocatalytic processes. Supplementary Table S1–S4. Tables S1–S4 are the statistical analysis data (P value) obtained via the ANOVA for the effect of catalyst dose on the degradation of DR and VB dyes under UV-Vis and US irradiations. (*Supplementary Materials*)

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