Synthesis of flower-like MoS$_2$/CNTs nanocomposite as an efficient catalyst for the sonocatalytic degradation of hydroxychloroquine

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ABSTRACT

Contamination of water resources by pharmaceutical residues, especially during the time of pandemics, has become a serious problem worldwide and concerns have been raised about the efficient elimination of these compounds from aquatic environments. This study has focused on the development and evaluation of the sonocatalytic activity of a flower-like MoS$_2$/CNTs nanocomposite for the targeted degradation of hydroxychloroquine (HCQ). This nanocomposite was prepared using a facile hydrothermal route and characterized with various analytical methods, including X-ray diffraction and electron microscopy, which results confirmed the successful synthesis of the nanocomposite. Moreover, the results of the Brunauer-Emmett-Teller and diffuse reflectance spectroscopy analyses showed an increase in the specific surface area and a decrease in the band gap energy of the nanocomposite when compared with those of MoS$_2$. Nanocomposites with different component mass ratios were then synthesized, and MoS$_2$/CNTs (10:1) was identified to have the best sonocatalytic activity. The results indicated that 70% of HCQ with the initial concentration of 20 mg/L could be degraded using 0.1 g/L of MoS$_2$/CNTs (10:1) nanocomposite within 120 min of sonocatalysis at the pH of 8.7 (natural pH of the HCQ solution). The dominant reactive species in the sonocatalytic degradation process were identified using various scavengers and the intermediates generated during the process were detected using GC–MS analysis, enabling the development of a likely degradation scheme. In addition, the results of consecutive sonocatalytic cycles confirmed the stability and reusability of this nanocomposite for sonocatalytic applications. Thus, our data introduce MoS$_2$/CNTs nanocomposite as a proficient sonocatalyst for the treatment of pharmaceutical contaminants.

1. Introduction

Economic development and fast-increasing health demand due to the emergence of new diseases have led to the rapid industrialization of pharmaceutical companies. The pharmaceutical industry needs sustainable sources of pure water in its various processes such as production, formulation, cooling, and processing of the products. The use of water in these processes leads to the production of effluents in high volumes in the pharmaceutical industry [1]. These effluents often contain high concentrations of toxic organic and inorganic compounds along with pharmaceutical residues [2].

The presence of pharmaceutical residues in the effluents is a matter of concern because these compounds are biologically active and potentially pose significant risks to human and animal health. The discharge of these untreated effluents into nature leads to the entry and persistence of pharmaceuticals in the environment [3]. Although pharmaceuticals are present in small concentrations in aquatic environments, it has been reported that even small amounts of them can upset the ecological balance. Morphological changes in the vital organs of fish are an example of the adverse effects of pharmaceuticals on the environment [4,5]. In the case of anti-viral drugs, the excessive discharge of them into ambient waters may lead to the development of drug-resistant viral strains within the local fauna, which may act as a natural reservoir for these viruses [6,7]. Given the potentially serious effects of such contaminations, it is clear that the effective treatment and mineralization of these pollutants using different techniques is critically important.

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for both environmental and public health. Hydroxychloroquine (HCQ) is a well-known anti-malarial drug that is also used to treat autoimmune rheumatic diseases. It was one of the first antivirals to demonstrate any effect against the latest pandemic, Coronavirus disease 2019 (COVID-19), and was granted emergency use licensing for application in the first waves of this disease [8,9]. However, the use of HCQ for treating COVID-19 remained a matter of debate among healthcare researchers and FDA revoked the emergency use authorization for this drug on June 15, 2020 [10].

Advanced oxidation processes (AOPs) have recently started to attract considerable attention as viable techniques for the removal of chemically stable and non-biodegradable organic pollutants from municipal and industrial effluents [11]. Among the various AOPs, ultrasound-based processes are of great importance owing to their simple operation, low chemical consumption, and efficacy against various pollutants [12]. These processes are considered as one of the developing methods because of their capability in interacting with fluid environments and combining with other methods as well [13]. The acoustic cavitation and sonoluminescence phenomena associated with these processes can be significantly altered via the addition of different materials with semiconducting properties. Employing such materials as sonocatalysts enhances ultrasonic degradation by providing more nucleation sites for cavitation. Moreover, excitation of semiconductors when exposed to sonoluminescence emission improves the generation of reactive oxygen species (ROS) by inducing the formation of electron-hole pairs on their surface [14].

Recent studies have extensively focused on the applications of MoS2 as it demonstrates significant chemical stability and adjustable morphology [15]. MoS2 is a type of 2D transition metal dichalcogenide with outstanding properties and a wide array of applications across several fields including electronics, lithium and sodium batteries, hydrogen evolution reactions, energy storage and conversion, as well as the production of solid lubricants for the aerospace industry [16,17]. MoS2 is composed of several layers with a thickness of three atoms (S-MoS), where the plane of Mo atoms is sandwiched between two planes of S atoms, causing each Mo atom to be surrounded by six S atoms. There are strong covalent bonds between the crystal atoms within each layer, while adjacent layers are held together via weaker van der Waals forces, allowing them to slide beside each other [18]. However, there are relatively few studies examining the sonocatalytic activity of MoS2. This may be ascribed to the low density or poor activity of MoS2 catalytic sites, and the high recombination rate of sono-generated electron-hole pairs. Combining the MoS2 with carbon-based materials is proposed to overcome these shortcomings [15]. These materials are of great importance in modern technologies because of their promising characteristics such as low weight and cost, chemical stability, structural tunability, and good electrical conductivity [19,20]. Among the various available carbon-based materials, carbon nanotubes (CNTs) can be employed to enhance the sonocatalytic activity of the semiconductors owing to their high potential for the physical adsorption of pollutant molecules, decreasing the electron-hole recombination rate, and promoting the production of reactive radicals by increasing the number of cavitation bubbles [21].

Here, we described the synthesis of a flower-like MoS2/CNTs nanocomposite using a simple one-step hydrothermal process and its application for the sonocatalytic degradation of HCQ. The characteristics of the synthesized nanocomposite were investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) spectroscopy, dot-mapping, X-ray diffraction (XRD) analysis, UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), Brunauer–Emmett–Teller (BET) surface area analysis, Fourier-transform infrared (FT-IR) spectroscopy, and photoluminescence (PL) spectroscopy. The effect of various parameters, including the mass ratio of the components in the nanocomposite, initial pH of the solution, initial concentration of the contaminant, sonocatalyst dosage, and the inhibitory effects of various radical and non-radical scavengers on the degradation efficiency (DE%, Eq. (S1)) of HCQ were also investigated. In addition, the reusability of the catalyst was assessed, and a plausible mechanism facilitating the degradation of HCQ was proposed based on the results of gas chromatography-mass spectrometry (GC–MS) analysis. To the best of our knowledge, this is the first paper evaluating the application of MoS2/CNTs nanocomposite as an efficient sonocatalyst for the remediation of pharmaceutical contaminated waters.

2. Materials and methods

2.1. Chemical reagents

CNTs were supplied by Cheap Tubes (USA) and used as received, without further modification. HCQ powder was purchased from Mofid Pharmaceutical Co. (Iran) and all other chemicals, including sodium molybdate dihydrate (Na2MoO4·2H2O), thiourea (CH4N2S), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium nitrate (NaNO3), p-terphenyl (C20H14), t-buty alcohol (C6H13OH), formic acid (COOH), terephthalic acid (C8H6O4), fufuryl alcohol (C5H8O2), L-histidine (C6H9N2O2), diethyl ether (C4H10O), and N,O-bis(trimethylyl) acetamide were procured from Merck (Germany).

2.2. Synthesis of MoS2/CNTs nanocomposite

The MoS2/CNTs nanocomposite was synthesized in a high yield (~81%) using a simple hydrothermal method. Firstly, 1.2 g sodium molybdate and 1.5 g thiourea were dissolved in 60 mL deionized water and then 0.08 g of CNTs were added to the prepared solution and exposed to ultrasonic irradiation for 30 min to produce a homogeneous suspension. The resultant mixture was then transferred into a 100 mL hydrothermal reactor and heated at 220 °C for 24 h. After cooling to room temperature, the black precipitated nanocomposite was separated via centrifugation and washed several times with deionized water. Finally, it was dried at 60 °C overnight to produce the nanocomposite powder. This product was specified as MoS2/CNTs (10:1). To prepare other nanocomposites with different MoS2/CNTs mass ratios of 15:1 and 40:1, we changed the CNTs contribution to 0.053 g and 0.02 g, respectively. Pure MoS2 was also synthesized with the aforementioned method without the addition of CNTs.

2.3. Characterisation methods

SEM micrographs, EDX elemental analysis, and dot mapping patterns were all recorded using a Tescan MIRA3 microscope (Czech Republic), operated at 15 kV. TEM images were obtained using a Philips EM 208S microscope (the Netherlands) under an accelerating voltage of 100 kV. The crystallographic characteristics of the samples were investigated using XRD analysis on a Philips PW1730 X-ray diffractometer (the Netherlands) with Cu Kα radiation (λ = 0.154 nm). The N2 adsorption-desorption analysis was performed at 77 K using a Belsorp Mini II (Japan) apparatus. The FT-IR spectra were recorded using the KBr disk technique on a Brucker Tensor 27 spectrometer (Germany). In addition, a PerkinElmer LS45 fluorescence spectrometer (USA) was used to study the photoluminescence properties of the samples and the intermediates generated during the HCQ degradation process were identified via GC–MS analysis on an Agilent 6890N gas chromatograph coupled with an Agilent 5973N mass spectrometer (Canada).

2.4. HCQ removal procedure

We conducted the sonocatalytic evaluations using a 250 mL Erlenmeyer flask firmly fixed within an ultrasonic bath (James Products Limited, Ultra 8060D-H, 150 W, England) as a reactor and investigated the sonocatalytic degradation process by adding a predetermined amount of synthesized catalyst to the reactor flask containing 100 mL of
HCQ solution at a predetermined initial concentration. We also evaluated the effect of pH on these processes by changing the pH of the starting reaction mixture using 0.1 M HCl or NaOH. At regular time intervals during the sonocatalytic process, 3 mL of the reaction mixture was sampled. These samples were then centrifuged at 2500 rpm for 15 min and passed through a 0.22 \( \mu \)m syringe filter to remove the remaining sonocatalyst particles before being exposed to an Analytik Jena Specord 250 spectrophotometer (Germany) to record their UV–Vis absorption spectra. These data were then used to determine the sonocatalytic degradation efficiency (DE%) of the reactions by measuring the absorbance at the maximum wavelength of 220 nm. However, since most of the scavengers used in this study show absorbance under 300 nm, to avoid the potential interference between the scavengers and pollutant, the DE% for the scavenger experiments was determined using the other detection peak of HCQ at the \( \lambda_{\text{max}} \) of 343 nm.

The adsorption tests were also conducted with a similar procedure by continuously stirring the reaction solution in the absence of ultrasonic waves in the dark medium.

3. Results and discussion

3.1. Characterization

Fig. 1a–c show the SEM images of the CNTs, MoS\(_2\), and MoS\(_2\)/CNTs (10:1) samples. These images clearly reveal the expected tubular morphology of the CNTs, with an average diameter of 40 nm (Fig. 1a) and the flower-like arrangement of the MoS\(_2\) nanosheets with a relative thickness of 35 nm (Fig. 1b). These globular flower-like structures have a diameter of about 3–5 \( \mu \)m. The SEM images illustrated in Fig. 1c prove the successful synthesis of the MoS\(_2\)/CNTs (10:1) nanocomposite. As can
be seen, the CNTs are well incorporated into the flower-like microspheres of MoS$_2$ and created a perfectly uniform hybrid structure.

Fig. 1 d shows the elemental composition of the MoS$_2$/CNTs (10:1) nanocomposite from the EDX analysis. The co-appearance of Mo, S, and C peaks in the EDX spectrum indicates the successful synthesis of the MoS$_2$/CNTs nanocomposite and the lower intensity of the C peak reflects the low concentration of the CNTs used for the synthesis of this nanocomposite. In addition, the atomic ratio of Mo and S in the nanocomposite reveals perfect compatibility with MoS$_2$ stoichiometry. The supporting EDX spectra for CNTs and MoS$_2$ are also presented in Figs. S1 a and b. It should be noted that the Au peak observed in all spectra arises from the gold coating used in the SEM protocol applied in this study.

The distribution patterns of Mo, S, and C in the MoS$_2$/CNTs (10:1) nanocomposite were obtained using dot mapping analysis. Fig. 1 e demonstrates the uniform distribution of these three elements across the structure of the MoS$_2$/CNTs (10:1) nanocomposite. These results were further validated by the relatively low abundance of C, reflecting its significantly lower concentration in the nanocomposite.

The morphology of the synthesized samples was then evaluated using TEM analysis, which confirmed the flower-like assembly of the MoS$_2$ nanosheets (Fig. 1 f) and penetration of the CNTs into the interlayer spaces of the MoS$_2$ structure (Fig. 1 g), affirming the successful synthesis of the nanocomposite.

XRD patterns of the CNTs, MoS$_2$ and MoS$_2$/CNTs (10:1) samples are presented in Fig. 2 a. The resultant pattern for the CNTs revealed a broad but intense peak at the 2$\theta$ of 26.1°, which can be attributed to the reflection of the (0 0 2) plane in its graphitic crystalline structure. Moreover, the peaks observed in the 2$\theta$ range of 42–46° can be assigned to the reflection of the (1 0 0) and (1 0 1) planes within the graphenic layers of CNTs [22,23]. The diffraction peaks centered at 2$\theta$ = 14.2°, 33.7°, 39.6°, 49.5°, and 58.9° correspond to the reflection of the (002), (100), (103), (105), and (110) planes in the hexagonal structure of MoS$_2$ (JCPDS card No. 37-1492) [24,25] and the absence of other
additional peaks in this sample indicates the high purity of the MoS$_2$ used in this study. The coexistence of the characteristic peaks of MoS$_2$ and CNTs in the XRD pattern of the MoS$_2$/CNTs (10:1) demonstrates the successful synthesis of the nanocomposite. However, because of the low mass ratio of CNTs, the (1 0 0) and (1 0 1) planes could not be detected in the XRD pattern of the MoS$_2$/CNTs (10:1) nanocomposite while the peak of the (0 0 2) plane appeared at relatively low intensity. The interplanar spacing of MoS$_2$ was calculated using Bragg’s law according to Eq. (1), and it was obtained to be 0.62 nm based on the vibration in the CNTs [27].

\[
2d \sin \theta = n \lambda
\]

where “$d$” is the distance between parallel atomic layers, “$\theta$” is the diffraction angle, “$n$” is the diffraction order, and “$\lambda$” is the wavelength of the X-ray beam, which was 0.154 nm for the Cu lamp.

FT-IR spectroscopy was then carried out to investigate the functional groups on the surface of the nanostructures, and the resultant spectra are shown in Fig. 2b. The broad peak observed for CNTs at 3440 cm$^{-1}$ can be attributed to the stretching vibration of the hydroxyl groups present on the external surface of the CNTs. These hydroxyl groups stem from the partial oxidation of the surface of CNTs during their purification step in the production process [27]. This peak can also be the result of water adsorption on the external surface of the CNTs. These hydroxyl groups are likely to be related to the symmetric and asymmetric stretching vibrations of the C–H bond in the CNTs [25] and the bands detected at 1064 and 1631 cm$^{-1}$ are associated with the stretching vibrations of the C–O and C=O bonds. In addition, the peak at 1385 cm$^{-1}$ is probably the result of the C=C bond vibration in the CNTs [27–29]. The peaks recorded for both MoS$_2$ and the nanocomposite at 457 cm$^{-1}$ are likely to be attributed to the vibration of the Mo–S bond [30]. The peaks observed at 723, 1034, and 1180 cm$^{-1}$ may be due to the formation of sulfate groups following the surface oxidation of MoS$_2$ in response to its contact with air [31]. The broad peak observed around 3450 cm$^{-1}$ for both MoS$_2$ and the nanocomposite may be related to the stretching vibration of adsorbed water molecules [25] and the peaks at 2855 and 2919 cm$^{-1}$ can be attributed to the symmetric and asymmetric stretching of the C–H bond, respectively. The appearance of these two peaks along with the C–C bond peak centered at approximately 1400 cm$^{-1}$ in the MoS$_2$/CNTs (10:1) spectrum confirms the presence of carbonaceous material within the structure of the nanocomposite.

The specific surface area of the samples was evaluated using nitrogen adsorption-desorption analysis and the corresponding isotherms are illustrated in Fig. 2c–e. According to the IUPAC classification system, the nitrogen adsorption-desorption isotherm for CNTs can be of type IV, while those obtained for MoS$_2$ and MoS$_2$/CNTs (10:1) are more likely to be type V. A type H3 hysteresis loop can be observed in the isotherms of MoS$_2$ and nanocomposite, which might be the result of the plate-like structure of these materials [32]. These evaluations also revealed a significant increase in the specific surface area of the MoS$_2$, from 2.0 to 30.6 m$^2$/g, following the introduction of CNTs to its structure. This increased specific surface area of the nanocomposite can improve the sonocatalytic performance of this material by increasing the number of catalytically available active sites [14].

UV–Vis DRS was then used to evaluate the optical properties of the synthesized samples and estimate the band gap energy of these sonocatalysts using Tauc’s equation (Eq. (2)) [33]:

\[
\alpha(h\nu) = K (h\nu - E_g)^n
\]

where “$\alpha$”, “$h\nu$”, “$K$”, and “$E_g$” are the absorption coefficient, photon energy, constant of proportionality, and band gap energy, respectively. The value of “$n$” depends on the type of electronic transitions in the material, which is equal to $\frac{1}{2}$ for direct allowed transitions in MoS$_2$ [34]. The band gap energy was calculated by plotting $(\alpha h\nu)^2$ against $h\nu$ and extrapolating the linear region of the plot to intersect the x-axis. The results of these calculations (presented in Fig. 2f and g) revealed the band gap energies of 1.4 and 1.2 eV for the MoS$_2$ and MoS$_2$/CNTs (10:1) nanocomposite, respectively. This result indicates that the CNTs help reduce the band gap energy of the nanocomposite, which increases its sonocatalytic activity by providing more effective charge transfer. Introducing CNTs into the nanocomposite may result in vacancy defects within the MoS$_2$ structure, which can in turn narrow the band gap [14].

We then went on to investigate the recombination rate of the sonogenerated electron-hole pairs in the synthesized sonocatalysts using PL spectroscopy at the excitation wavelength of 450 nm. As illustrated in Fig. 2h, MoS$_2$ demonstrated a strong emission peak at 670 nm. However, this fluorescence emission intensity significantly decreased for the MoS$_2$/CNTs (10:1) nanocomposite, indicating a reduction in the radiative recombination of electron-hole pairs during the sonocatalytic process [35]. The effective charge transfer from MoS$_2$ to CNTs leads to the suppression of radiative recombination of charge carriers generated on its surface. This reduced recombination rate of charge carriers increases the lifetime of the holes, resulting in the generation of more OH radicals. Thus, these results suggest that CNTs play a key role in the charge separation process, thereby improving the sonocatalytic activity of the MoS$_2$/CNTs (10:1) nanocomposite.

3.2. Comparing HCQ removal methods

To investigate the HCQ remediation using various processes, we

Fig. 3. (a) Removal efficiency of HCQ through various processes and (b) sonocatalytic degradation efficiency of HCQ over various catalysts with different MoS$_2$/CNTs ratio ([HCQ] = 20 mg/L, [MoS$_2$/CNTs (10:1)]$_a = 0.1$ g/L, [catalyst]$_b = 0.5$ g/L and pH = 8.7).
evaluated sonolysis, adsorption, and sonocatalysis. The results given in Fig. 3a revealed that only 20% of HCQ was adsorbed onto the surface of MoS$_2$/CNTs (10:1) within 120 min, while sonolysis was able to remove 28% of this contaminant at the same time. The resultant poor degradation efficiency via the production of hydroxyl radicals and other reactive radical species. The highest degradation efficiency of 70% was achieved via the simultaneous application of both ultrasonic waves and the sonocatalyst, demonstrating their clear synergistic effect during the degradation of HCQ. The increased degradation efficiency of sonocatalysis can be explained based on the sonoluminescence phenomenon. Briefly, the nanocomposite with the band gap of 1.2 eV can be excited under the UV light emitted via sonoluminescence, resulting in the generation of electron-hole pairs on the nanocomposite surface (Eq. (3)) [36], which then initiate secondary reactions to produce homogeneous ROS. Electrons can reduce oxygen molecules to form reactive O$_2^\cdot$ radicals which play a vital role in destroying the target pollutant (Eq. (4)) [37]. The holes can directly attack and destroy the contaminant molecules or oxidize the water molecules to ‘OH radicals and degrade the HCQ indirectly by means of these radicals (Eq. (5)) [36]. The generated O$_2^\cdot$ radicals can also participate in producing O$_2$ (Eqs. (6)-(8)), further supporting the HCQ degradation [38].

\[
\text{MoS}_2/\text{CNTs (10 : 1) } \rightarrow \text{MoS}_2/\text{CNTs (10 : 1)}^+ (e^- + h^+) \tag{3}
\]

\[
e^- + O_2^\cdot \rightarrow O_2 \tag{4}
\]

\[
h^+ + H_2O \rightarrow OH + H^+ \tag{5}
\]

\[
2O_2^\cdot + 2H_2O \rightarrow H_2O_2 + 2OH^- + ^1O_2 \tag{6}
\]

\[
\quad \quad \quad H^+ + O_2^\cdot \rightarrow HO_2 \tag{7}
\]

\[
\quad \quad \quad H + HO_2 \rightarrow H_2 + ^1O_2 \tag{8}
\]

In addition, ultrasonic waves can improve mass transfer processes by increasing the dispersion of MoS$_2$/CNTs (10:1), which in turn enhances the degradation efficiency. Besides, more active sites are provided for cavitation in the presence of sonocatalyst particles. As a result, more reactive radicals are produced for the degradation of HCQ in the presence of a sonocatalyst [37]. Table 1 shows the superior catalytic activity of the prepared MoS$_2$/CNTs nanocomposite as compared to the other MoS$_2$-based nanocomposites reported in the literature.

3.3. Sonocatalytic degradation of HCQ over MoS$_2$/CNTs nanocomposite

3.3.1. Effect of the MoS$_2$/CNTs ratio on sonocatalytic activity of the nanocomposite

The sonocatalytic activities of the MoS$_2$ and MoS$_2$/CNTs nanocomposite at different MoS$_2$/CNTs ratios (10:1, 15:1, and 40:1) were investigated. As shown in Fig. 3b, MoS$_2$ was able to remove 63% of the target contaminant within 120 min of reaction time, while the MoS$_2$/CNTs nanocomposites represented better sonocatalytic performance across all three studied ratios. As can be seen, the degradation efficiency of HCQ increased from 68% for MoS$_2$/CNTs (40:1) to 85% and 97% for MoS$_2$/CNTs (15:1) and MoS$_2$/CNTs (10:1), respectively, suggesting that CNTs loading had a positive effect on overall catalytic activity. Given its superior performance, MoS$_2$/CNTs (10:1) nanocomposite was selected for all further experiments. The improved sonocatalytic activity of the nanocomposites compared with MoS$_2$ can be attributed to the reduced electron-hole recombination rate resulting from the acceleration of electron transfer processes in the presence of CNTs, which was confirmed during PL analysis [44]. In addition, the narrower band gap of these composite materials is also likely to have increased the degradation efficiency via the production of more son-induced electron-hole pairs [45]. Previous studies have shown that the adsorption of pollutant molecules onto the surface of sonocatalysts plays an important role in the degradation process as the adsorbed pollutants can be more easily exposed to sono-generated radicals than their bulk solution counterparts [21,45,46]. These findings agree with our results, suggesting that the addition of CNTs increases the physical adsorption capacity of the nanocomposite, which helps improve the overall degradation efficiency of this catalyst.

3.3.2. Effect of sonocatalyst dosage

Fig. 4a and b show the effect of MoS$_2$/CNTs (10:1) dosage on the adsorption efficiency and sonocatalytic degradation of HCQ, respectively. The results demonstrate that by increasing the sonocatalyst dosage from 0.025 to 0.5 g/L, the sonocatalytic degradation efficiency was enhanced from 60% to 97%, at the same reaction time of 120 min. This is because at high dosages of sonocatalyst, more reactive radicals can be generated owing to the increase in available active sites, which in turn enhances the degradation efficiency. At the same time, the adsorption of the pollutant showed significant enhancement from 18% to 80%, following this increase in the sonocatalyst dosage. It is likely the result of the greater accessible surface area at higher dosages of the sonocatalyst material. These results indicate that the changes in sonocatalyst dosage simultaneously affect both adsorption and sonocatalytic degradation. However, given that the primary aim of this research is not the phase transfer but rather to increase the total degradation of the pollutant molecules, we calculated the synergy effect for these changes over a predefined reaction time to identify the optimum catalyst dosage.
These calculations were conducted using Eq. (9) [47]:

\[
\text{Synergy effect} = \frac{\text{DE (\%)}_{\text{sonocatalysis}}}{\text{DE (\%)}_{\text{sonolysis}} + \text{RE (\%)}_{\text{adsorption}}} \quad (9)
\]

Fig. 4c presents the synergy effect diagrams for different dosages of the catalyst during the sonocatalytic process. The synergy effect greater than one indicates that the overall sonocatalytic process has a greater effect than the sum of the individual processes of adsorption and sonolysis. Close examination of these data shows that the catalyst dosage of 0.1 g/L produces the highest synergy effects over 120 min of reaction time, making it the optimum content of the sonocatalyst for these evaluations.

3.3.3. Effect of pollutant concentration

As the concentration of contaminants plays a crucial role in water treatment processes, the effect of the initial concentration of HCQ on the sonocatalytic degradation efficiency was also evaluated. These assays indicated that increasing the concentration of HCQ from 10 to 25 mg/L reduced its degradation efficiency from 94% to 47% over the same 120 min of reaction time (Fig. 5a). Under the constant operational conditions of the process, including catalyst dosage, ultrasonic power, and initial pH of the solution, a definite amount of reactive radical species can be produced which in turn degrade a certain amount of pollutants. Therefore, in situations where high concentrations of pollutants are expected, the amount of available reactive radicals is insufficient, and this reduces the degradation efficiency of the pollutant [48]. In addition, more active sites of the sonocatalyst can be occupied by HCQ molecules and their degradation by-products at high pollutant concentrations, which reduces the absorption of the energy by the sonocatalyst. As a result, the generation of reactive radical species at the catalyst surface decreases, followed by the reduction of degradation efficiency [12].

3.3.4. Effect of pH

The solution pH is one of the most significant parameters that directly influences the sonocatalytic degradation of organic contaminants as it has a direct effect on the surface charge of catalysts and the nature of contaminants. Given this, we first evaluated the structural stability of HCQ in response to the pH changes, which revealed that the UV–Vis absorption spectra for this contaminant remained stable in the pH range of 3–9 and the pH changes had a negligible effect on the degradation of HCQ molecules (Fig. S2a). Afterward, a series of experiments were carried out to investigate the effect of the initial pH on the sonocatalytic degradation of HCQ. Fig. 5b shows that the degradation efficiency of HCQ increased from 55% to 73% by changing the initial pH of the solution from 3 to 7, but this trend was reversed following a further increase in pH.

These results spurred us to try to predict the surface charge of the sonocatalyst by calculating its point of zero charge (PZC) using the pH drift method [49]. This assay revealed that the pH_{PZC} value for this nanocomposite was approximately 1.77 (Fig. S2b), suggesting that this catalyst will have a positive surface charge at pH values below 1.77, encouraging the preferential adsorption of negatively charged compounds. Conversely, higher pH values will induce a negative surface charge for this catalyst, facilitating better interactions with positively charged species. Thus, it can be concluded that the MoS_2/CNTs (10:1)
Fig. 5. Effect of (a) HCQ concentration, (b) pH and (c) various scavengers on the sonocatalytic degradation efficiency of HCQ; (d) PL spectra changes of the sonocatalytic system; and (e) reusability of MoS$_2$/CNTs (10:1) nanocomposite ([HCQ] = 20 mg/L, [MoS$_2$/CNTs (10:1)] = 0.1 g/L, pH = 8.7).
nen. For this purpose, we examined the sonocatalytic degradation of HCQ. For this purpose, we examined the sonocatalytic degradation of HCQ at a pH of 7, suggesting the better performance of this sonocatalytic system for the remediation of HCQ in contaminated waters with natural pH.

### 3.3.5. Effect of scavengers

Scavengers are reagents that can inactivate or reduce the oxidative activity of radical or non-radical reactive species involved in advanced oxidation processes [36]. The presence of various compounds with such scavenging effects in natural aquatic environments and industrial wastewater is inevitable. Therefore, it is necessary to investigate the effect of these compounds on the degradation efficiency of HCQ. In addition, the role of reactive species participating in the sonocatalytic degradation of target pollutants can be evaluated using diverse scavengers. For this purpose, we examined the sonocatalytic degradation of HCQ in the presence of tert-butyl alcohol, formic acid, and para-benzoquinone acting as \( \cdot \text{OH}, h^+, \) and \( \text{O}_2^- \) scavengers, respectively [51], as well as furfuryl alcohol and L-histidine, which act as \( ^1\text{O}_2 \) scavengers [52]. These evaluations revealed that the degradation efficiency of HCQ decreased from 73% to 48%, 22%, 37%, 35%, and 48% in the presence of tert-butyl alcohol, formic acid, para-benzoquinone, furfuryl alcohol, and L-histidine, respectively (Fig. 5c). This indicates that \( \cdot \text{OH}, h^+, \text{O}_2^- \), and \( ^1\text{O}_2 \) are all involved in the sonocatalytic degradation of the target pollutant. Formic acid exhibited the most inhibitory effect, which demonstrates the critical role of \( h^+ \) in the degradation of HCQ. Sonocatalytic processes take place on the surface of the catalyst material may improve the degradation efficiency via both the direct oxidation of the contaminant molecules and the acceleration of \( \cdot \text{OH} \) radicals production within the sonocatalytic system [36]. The inhibitory mechanisms of tert-butyl alcohol [53], formic acid [54], and para-benzoquinone [55] can be explained by Eqs. (10)–(12), respectively:

\[
\begin{align*}
(\text{CH}_3)_2\text{COH} + \cdot \text{OH} & \rightarrow \text{CH}_3(\text{CH}_3)_2\text{COH} + H_2\text{O} \\
\text{HCOOH} + 2(e^- - h^+) & \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \\
\text{C}_6\text{H}_4\text{O}_2 + \text{O}_2^- & \rightarrow \text{C}_6\text{H}_6\text{O}_2^- + \text{O}_2
\end{align*}
\]

Likewise, the deactivation of \( ^1\text{O}_2 \) using L-histidine [56] and furfuryl alcohol [57] can be explained using Eqs. (13) and (14):

\[
\begin{align*}
\text{O} = \cdot \text{OH} + ^1\text{O}_2 \rightarrow \text{OH}_2^+ + \text{O}_2 \\
\text{OH} + ^1\text{O}_2 \rightarrow \text{HO}_2^- + \text{O}_2
\end{align*}
\]

### 3.3.6. Detection of \( \cdot \text{OH} \) radicals

We further evaluated \( \cdot \text{OH} \) radical production during the sonocatalytic process using terephthalic acid (5 \( \times \) 10^{-4} mol/L) photoluminescence. Terephthalic acid reacts with \( \cdot \text{OH} \) radicals to form 2-hydroxy terephthalic acid, which exhibits an intense fluorescence emission [58]. Thus, we could evaluate radical production via the fluorescence emission intensity of the sonocatalytic system in the presence of terephthalic acid at different points within the reaction (Fig. 5d). These assays revealed that the fluorescence intensity gradually increased over time, confirming the generation of more \( \cdot \text{OH} \) radicals with increasing process time.

### 3.3.7. Stability and reusability of the sonocatalyst

The structural stability and reusability of heterogeneous sonocatalysts are significant factors when evaluating their practical application and economic viability. Here, the catalytic activity of MoS\(_2\)/CNTs (10:1) nanocomposite across four consecutive cycles of the sonocatalytic process under optimum conditions was evaluated (Fig. 5e). The results showed that there is only a slight decrease (about 4%) in the sonocatalytic activity of the nanocomposite over the first three cycles. However, in the fourth cycle, the HCQ degradation efficiency decreased by 11% compared to the first run. Moreover, evaluations including SEM, EDX, dot-mapping, and XRD (Fig. 5f–h) revealed that there were no significant changes in the morphology, elemental distribution, or crystalline structure of the nanocomposite after using it in the sonocatalytic process, demonstrating the high structural stability of this sonocatalyst. Overall, these data suggest that the MoS\(_2\)/CNTs (10:1) nanocomposite exhibits good stability and acceptable reusability when used for sonocatalytic applications.

### 3.3.8. Degradation intermediates

AOPs produce a variety of reactive radical species that lead to the oxidation or breakdown of pollutant molecules, creating various intermediate products. This means that it is important to identify these intermediate molecules to propose a mechanism for the degradation process. Given this, we used GC-MS analysis to identify the
intermediates generated during the sonocatalytic degradation of HCQ and accordingly identified eleven intermediate molecules as summarized in Table S1. We then used these intermediates to propose a probable mechanism underlying the sonocatalytic degradation and mineralization of HCQ (Fig. 6).

4. Conclusion

Herein we describe the hydrothermal synthesis of a flower-like MoS$_2$/CNTs nanocomposite for remediation of pharmaceutical contaminated waters. XRD and FT-IR analyses along with microscopic imaging confirmed the successful synthesis of this high-purity nanocomposite. In addition, the results of BET and DRS analyses demonstrated that the synthesized nanocomposite had a higher specific surface area (30.6 m$^2$/g) and a lower band gap energy (1.2 eV) than pure MoS$_2$. These two factors play an essential role in increasing the sonocatalytic activity of the nanocomposite. Further investigations revealed a decrease in the PL intensity of the nanocomposite compared to that of pure MoS$_2$, confirming the effective role of the CNTs in improving the charge separation process and reducing the recombination rate of sonogenerated electron–hole pairs in this material. The nanocomposite was then used as a catalyst for the sonocatalytic degradation of HCQ to reduce the potential pollution associated with its application as an effective therapeutic agent for COVID-19. These evaluations revealed that the nanocomposite led to a significantly better sonocatalytic degradation of HCQ than the pure MoS$_2$, causing the final degradation efficiency of 70% within 120 min when applied under the optimal operational conditions ([MoS$_2$/CNTs (10:1)] = 0.1 g/L, [HCQ] = 20 mg/L, and pH = 8.7). A further evaluation on the effects of various radical and non-radical scavengers confirmed the roles of ‘OH, O$_2^-$, •O$_2$ and especially h$^+$ in the sonocatalytic degradation of HCQ and the results of reusability tests revealed a good stability for this nanocomposite and its efficiency even in successive sonocatalytic processes. Finally, the intermediate molecules produced during the HCQ degradation process were identified using GC-MS analysis, and the results confirmed the efficiency of this sonocatalytic system for the degradation of HCQ. These findings give a promising future application of MoS$_2$/CNTs nanocomposite for the efficient removal of pharmaceutical pollution from natural water systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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