



Solar Photocatalysis for the Decontamination Of Water from Emerging Pharmaceutical Pollutant Chloroquine Using Nano ZnO as the Catalyst

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Abstract Photo-driven advanced oxidation process (AOP) with pharmaceutical wastewater has been poorly investigated so far. This paper presents the results of an experimental investigation on the photocatalytic degradation of emerging pharmaceutical contaminant chloroquine (CLQ) in water using zinc oxide (ZnO) nanoparticles as the catalyst and solar light (SL) as the source of energy. The catalyst was characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDAX), and transmission electron microscopy (TEM). The effect of various operating parameters such as catalyst loading, the concentration of target substrate, pH, and the effect of oxidants and anions (salts) on the efficiency of degradation was tested. The degradation follows pseudo-first-order kinetics. Surprisingly, contrary to the observation in most photocatalytic studies, the degradation is more efficient under solar radiation, with 77% under solar (SL) irradiation and 65% under UV light in 60 min. The

degradation leads to slow and complete COD removal through several intermediates identified by the liquid chromatography–mass spectrometry (LC-MS) technique. The results suggest the possibility of using inexpensive natural, non-renewable solar energy for the purification of CLQ-contaminated water, thereby enabling the reuse of scarce water resources.

Keywords Photocatalysis · Solar light · Chloroquine · Zinc oxide · Oxidants · Anions

1 Introduction

Pharmaceutical contaminants and endocrine-disrupting compounds (EDCs) have emerged as a new class of environmental pollutants over the last few decades. The rapid growth of the population along with urbanization, industrialization, and economic development, together with pollution-related and lifestyle diseases, raised the demand for the production and consumption of such products. The presence of pharmaceutical compounds in various aquatic systems such as rivers, lakes, oceans, groundwater, and consequently in drinking water has been well documented (Bottoni 2010; Chander et al., 2016; Balakrishna et al., 2017; Lozano et al., 2022). The improper disposal and treatment of municipal and industrial effluents increased their levels in water sources (Miettinen et al., 2022; Dhanalakshmi et al., 2022). Residues of pharmaceuticals in water can affect the food and reproductive

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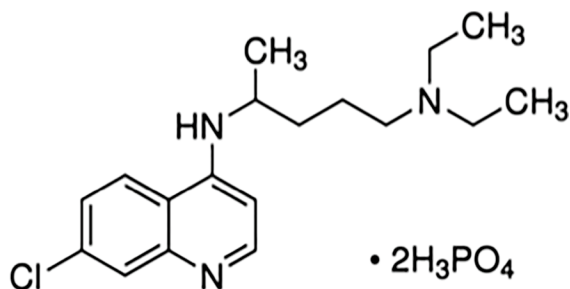
cycle of aquatic organisms and may even lead to their death due to the highly toxic effects of pharmaceuticals on natural fauna and flora. In humans, they can affect the endocrine system's normal functioning, resulting in neurological disorders, reproductive and sexual irregularities, and increased incidents of testicular, prostate, ovarian, and breast cancer. Thus, the presence of these pollutants in water remains a great threat to aquatic as well as human health (Sayadi et al., 2012; Rzymiski et al., 2017; Vaudin et al., 2022; Mohan et al., 2022; Ortuzar et al., 2022).

One of the major pharmaceutical families in use is quinolines. Chloroquine (chloroquine diphosphate), an aminoquinoline derivative, was discovered in 1934 and introduced into medicine in the 1940s as an important class of synthetic drugs for treating malaria. CLQ is a generic medication, advised as the principal antimalarial preventative drug and to treat conditions including rheumatism (lupus erythematosus) and amoebic dysentery. The advantages of this drug are its low cost, long usage history, and easy availability. It is administered orally as chloroquine phosphate and by intramuscular injection as chloroquine hydrochloride. In recent times, CLQ has been proven effective for *in vitro* antiviral activity against SARS-CoV-2 (Khuroo et al., 2020; Rebeaud & Zores, 2020). International and national health organizations recently approved the use of chloroquine to treat certain hospitalized patients who are infected with coronavirus (COVID-19). The role of chloroquine (CLQ) or hydroxychloroquine (HCLQ) alone or in combination with other pharmaceuticals in the management of the emerging coronavirus was studied by many researchers (Gasmi et al., 2021). Initial results show that the drug was effective for treating symptoms of COVID-19. However, preliminary results from large-scale randomized controlled studies did not show any survival advantage of such medication therapy against the COVID-19 virus. Due to its antiviral and antibacterial properties, CLQ has considerable potential for persistence, bioaccumulation, and transfer to live organisms in enhanced hazardous forms. The negative effects of its use included cardiotoxic effects and interaction with a wide range of medications. During the pandemic, the uncontrolled, indiscriminate, and intensive use of CLQ in hospitals occurred and the concentration of CLQ increased drastically in our water bodies. Due to the risk of heart rhythm problems in humans, the use of hydroxychloroquine

or chloroquine for COVID-19 outside of the hospital setting or a clinical trial is discouraged. But its usage continued due to a lack of awareness among the masses resulting in drastic adverse effects on human health and the environment. The high risks of natural water contamination and consequent effects on human health and the environment necessitated more attention on CLQ compared to other pharmaceutical drugs in water bodies.

Advanced oxidation processes (AOP), broadly defined as aqueous phase oxidation methods based on the generation of highly reactive oxygen species (ROS) such as $\bullet\text{OH}$, $\text{HO}_2\bullet$, and $\text{O}_2^{\bullet-}$ are widely investigated in recent years as a potential safe technique for the removal of chemical and bacterial pollutants from water (Glaze et al., 1987(a) and Glaze et al., 1987(b)). Extensive research has been carried out in the area of AOPs for industrial and urban effluent treatment (Pandis et al., 2022). Of these, the most promising technique for industrial applications has been photocatalysis and its variations (Karungamye, 2020; Chen et al., 2022; Saravanan et al., 2022). Most catalysts used in photocatalysis are of the semiconductor oxide type, of which ZnO and its nanocomposites are the most extensively studied (Mahdizadeh et al., 2020; Pham et al., 2020; Cruz et al., 2020; Hosny et al., 2022). This is mainly due to their non-toxicity, wide band structure, spectral overlap with SL emission (about 5%), high catalytic activity, low cost, low toxicity, biological and chemical stability, and easy applicability in ambient and harsh conditions (Raizada et al., 2019). ZnO nanoparticles enabled a higher degradation rate of target pollutants in water than regular ZnO under solar/UV irradiation (Hariharan, 2006; Sanna et al., 2016). The presence of light can excite ZnO resulting in the shifting of electrons from the valence band to the conduction band creating holes in the valence band. The electrons and holes result in the generation of $\bullet\text{OH}$ radicals, though by different mechanisms, which interact with organic pollutants and degrade them. The well-defined crystal structure of ZnO nanoparticles and the high specific surface area provide many positively charged sites for scavenging photo-generated electrons, thereby preventing their recombination with the holes and facilitating the redox reactions.

In the present study, the application of photocatalysis as an AOP for removing CLQ from water is investigated using ZnO nanoparticles as the catalyst and SL as the energy source. The structure of CLQ is as follows:



Chloroquine diphosphate (Aminoquinoline)

Chemical Formula $C_{18}H_{29}ClN_3O_4P$

Molar mass 515.86

Melting Point $193-198^{\circ}C$

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2 Materials and Methods

2.1 Materials

Chloroquine diphosphate salt (98.5–100.0% purity) was purchased from SIGMA-ALDRICH. The ZnO nanoparticles (>99.5% purity, specific surface area of 15–25 m²/g, and particle size of 40–100 nm) were purchased from ALFA-AESAR. Other chemicals used for the study were also of AnalaR grade or equivalent unless indicated otherwise.

2.2 Experimental Setup

The photocatalytic experiments were conducted using simulated wastewater containing CLQ. In a typical experiment, the sample solutions of the required concentrations and catalyst at the required

dosage are taken in a 2500-ml open Pyrex glass reactor. The reaction system is mixed periodically. Solar experiments were performed under natural SL, specifically from 11.00 a.m. to 14.00 p.m. in sunny weather on the rooftop of our laboratory at Kochi, Kerala, India ($9^{\circ}59'28.29''$ N, $76^{\circ}13'57.08''$ E), on sunny days in February–April 2022. The SL intensity was 780 W/m² built on Metravi 207 Solar Power Meter. For UV experiments, the UV source (400W low-pressure mercury arc lamp), was placed in a chamber in the inner compartment of the photo reactor setup. In all the experiments, the samples were placed such that the light radiation directly fell on the sample solutions. The temperature was kept at $34 \pm 2^{\circ}C$, the whole experiments were performed under varying reaction conditions, and optimum parameters for the degradation of the CLQ were identified.

2.3 Analytical Methods

The morphological characterizations and details of the surface of the ZnO nanoparticles were performed using SEM analysis. The determination of the composition and characteristics of the nanocomposite crystalline structure was done by XRD (Model Bruker D8 Advance). The elemental identification and quantitative compositional information were performed using the surface analytical technique SEM-EDAX (Model Jeol 6390LA-OXFORD XMX N). TEM analysis was done to determine the particle size, shape and distribution of the catalyst.

2.3.1 Dark Control Experiments

Preliminary experiments under dark conditions were performed to evaluate the effect of light on the degradation of the target CLQ pollutant in water. Different concentrations of an aqueous solution of CLQ were used. After 60 min of stirring in the dark, the control sample was taken to evaluate the concentration of the contaminant.

2.3.2 Solar/UV Irradiation Experiments

Investigations on the degradation of target pollutant CLQ were conducted under appropriate

reaction conditions in presence of light to evaluate the efficiency of photodegradation of CLQ in water. Further, the effect of semiconductor oxides, which are known as good photocatalysts, on the degradation of CLQ is tested using regular and nano TiO_2 (nTiO_2) and ZnO (nZnO). The effect of the concentration of CLQ on its photocatalytic degradation was investigated using varying concentrations of the substrate (5 to 50 mg/L) and a constant amount (0.10 g/L) of ZnO under SL. All other parameters are kept constant.

The experiments were performed under varying reaction conditions and optimum parameters for the degradation of the pollutants were identified. The reaction volume is maintained at 50 ml unless indicated otherwise. Samples (2 ml) were drawn periodically and filtered through a 0.22- μm filter head in the case of experiments with catalysts to remove the suspended materials and analyzed for the remaining substrate in the solution using ELICO Double Beam SL 210 UV-VIS Spectrophotometer by measuring maximum absorbance (λ_{max}) at 342 nm. Duplicate experiments were conducted for each study and the mean values were used to represent each evaluation. The percentage degradation was calculated using the following Eq. (1):

$$\text{CLQ degradation(\%)} = \frac{(C_0 - C_t)V}{C_0} \times 100 \quad (1)$$

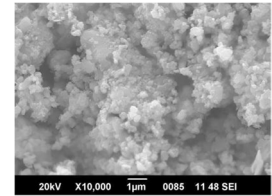
where C_0 and C_t are the concentration of CLQ in the solution before and after the time t of the reaction, respectively.

The mineralization of CLQ in the solar catalytic degradation process was evaluated by measuring the COD of the solution using the standard method (Clesceri et al., 1998). The kinetics of pollutant degradation and mineralization was assessed by the pseudo-first-order kinetic model (Eq. 2) which will be discussed in detail later in this paper.

$$\ln\left(\frac{C_t}{C_0}\right) = k_1 t \quad (2)$$

where C_0 and C_t are the concentration of CLQ in the solution before and after the time t of the reaction, respectively, and k_1 is the pseudo-first-order reaction rate constant.

Fig. 1 SEM image of ZnO particles



LC-MS analysis was used to evaluate the by-products and intermediates generated during the photocatalytic degradation of CLQ. The standard analytical procedure for LC-MS is followed. LC-MS analyzer used for the study was of make SHIMADZU (LCMS-8045 (Mass), Nexera X2 (HPLC)). The mobile phase used was 0.1% formic acid in water (Gradient A) and Methanol (Gradient B), and the column was C18 (2.1 \times 150 mm, 1.9 μm). The flow rate was kept as 0.3 ml/min.

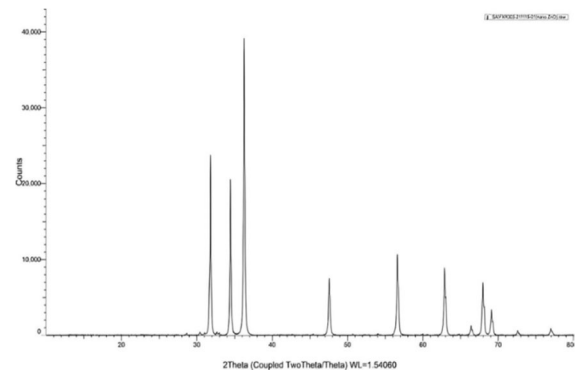


Fig. 2 XRD pattern of ZnO particles

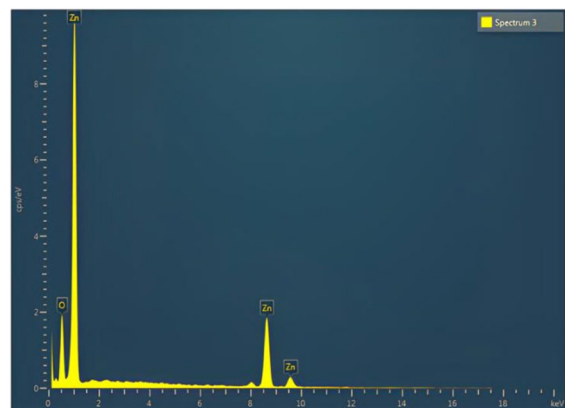


Fig. 3 SEM-EDAX pattern of ZnO particles

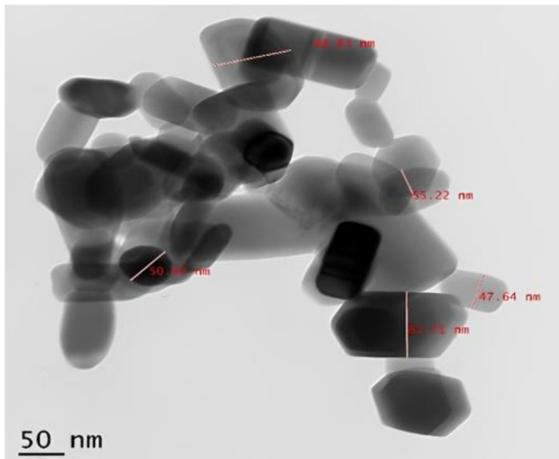


Fig. 4 TEM image of ZnO particles

3 Results and Discussion

3.1 Characterization of the Catalyst ZnO

SEM images revealed that ZnO nanoparticles are uniform in size and have aggregated spherical shapes with homogeneous distribution (Fig. 1). XRD pattern revealed nanoparticles that were validated using SEM micrograph. Using monochromatic x-rays, the x-ray powder diffraction patterns were recorded in the angular range of 20° – 80° (Fig. 2). The XRD peaks at 2θ are sharp indicating a good crystalline hexagonal phase of zincite. The spectra (Fig. 3) obtained from EDAX analysis revealed the purity of nanoparticles by showing the presence of separate peaks for zinc and oxygen. TEM (Model HRTEM: Jeol/JEM 2100) image showed that ZnO nanoparticles are aggregated loosely and nano-rods are combined in a special way by producing hierarchically secondary pores directing the flux of the pollutant solution in photo-catalysis (Fig. 4).

3.2 Dark Control and SL/UV Experiments

The results showed that no degradation occurred in the presence and absence of ZnO catalyst at room temperature under dark conditions. The moderate decrease in the concentration of CLQ was confirmed to be due to adsorption. Subsequently, the effect of light on the degradation of the CLQ molecule is evaluated. The SL/UV

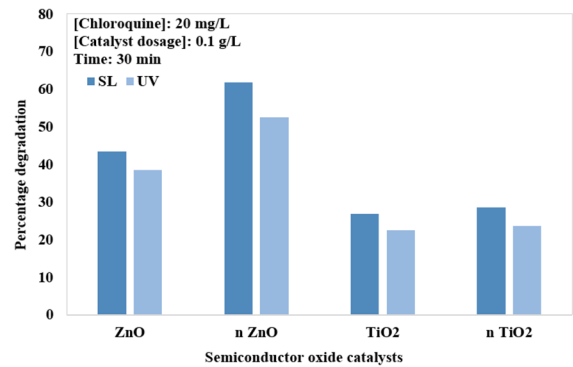


Fig. 5 Screening of ZnO and TiO₂ catalysts for the degradation of CLQ

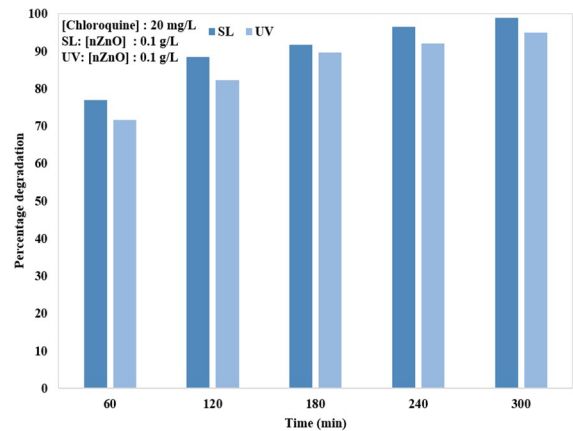


Fig. 6 Comparison of UV and solar photocatalysis for the degradation of CLQ

experimental studies showed that both UV and solar photolysis are potential energy sources for the removal of CLQ. The results show maximum degradation efficiency in the case of ZnO (42% in SL and 38% in UV) and TiO₂ (28% in SL and 22% in UV) in 30 min. ZnO nanoparticles showed an even higher degradation efficiency of 62% in SL and 52% in UV while the efficiency of nanoTiO₂ remained more or less the same as that of regular TiO₂ within 30 minutes. The results are compiled in Fig. 5.

The solar photocatalysis was compared with UV photocatalysis, under identical conditions and the results, are presented in Fig. 6. The degradation of CLQ is fairly identical under SL and UV light. Hence, further studies were made using ZnO nanoparticles

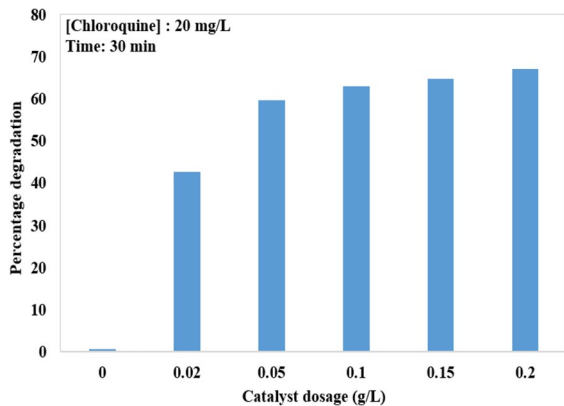


Fig. 7 The effect of catalyst (ZnO) dosage on the degradation of CLQ under SL

as the catalyst and the natural inexpensive SL as the energy source.

3.2.1 The Effect of Catalyst Dosage

The effect of catalyst loading is an important parameter in the heterogeneous photocatalytic process and the results in this respect for CLQ degradation are presented in Fig. 7. The photodegradation efficiency increases with an increase in the catalyst loading possibly due to an increase in light absorption and the higher number of active sites in contact with the target pollutant. A catalyst dosage of 0.1 g/L ZnO nanoparticles is chosen as the optimum dosage for CLQ degradation under solar irradiation.

At higher loadings beyond the optimum, there is stabilization/reduction in the surface area available for light absorption and consequent generation of h^+ / e^- pairs. The aggregation of catalyst particles leads to a decrease in the number of available active surface sites thereby reducing adsorption of the substrate on the surface. Beyond a particular loading, the particles cannot be fully and effectively suspended in a particular reactor leading to higher turbidity which can lead to sub-optimal penetration of radiation. Higher loadings increase the scattering effect of light irradiation (Gayathri et al., 2019). The adsorbed molecules get degraded faster and mostly desorbed from the surface where fresh molecules get adsorbed in presence of light. However, as the reaction progresses the surface will gradually get covered by the relatively more stable intermediates and the optimum will be reached. Since most of the molecules are

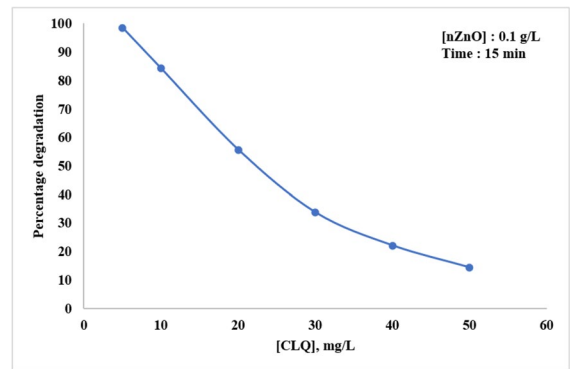


Fig. 8 The effect of concentration of CLQ on its % degradation under SL

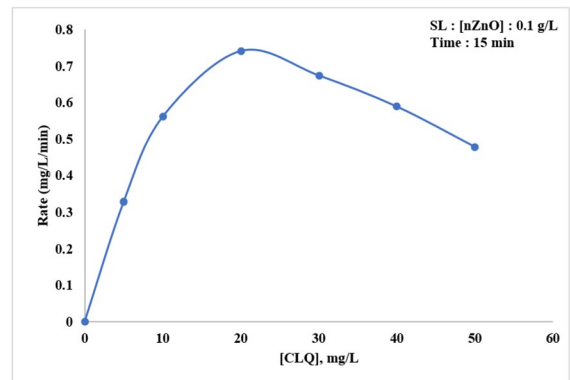


Fig. 9 Rate vs. concentration graph for the degradation of CLQ under SL

degraded at this stage, the rate of degradation also slows down leading to stabilization or decrease. Yet another reason for the decrease in degradation at higher catalyst loading is the deactivation of the activated catalyst particles by interaction with the ground state particles. However, the optimum catalyst loading will also depend on the size, shape, and geometry of the reaction systems. Hence, for each reactor configuration, the optimization has to be made separately.

3.2.2 The Effect of Concentration of Substrate

The percentage removal of CLQ as a function of its initial concentration is given in Fig. 8. Chloroquine showed a decrease in the percentage degradation with an increase in its concentration. This is similar to the observations in most AOP systems (Anju et al.,

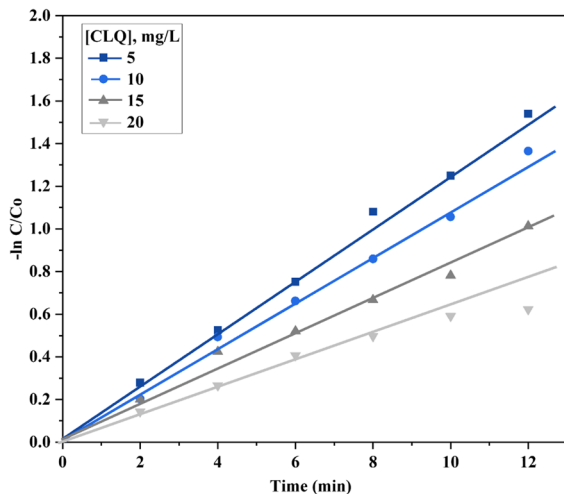


Fig. 10 Logarithmic plot for solar degradation of CLQ

2012; Reza et al., 2017; Mirzaeifard et al., 2020). The photocatalytic degradation showed a downward trend percentage-wise when the pollutant concentration is increased. Since the catalyst dosage is constant, during the reaction, the relative number of active catalytic sites will be reduced upon pollutant adsorption onto the surface of the catalyst resulting in a decreased production of active radicals ($\bullet\text{O}_2^-$, $\bullet\text{OH}$, and $\bullet\text{OH}_2$) resulting in a drop in the degradation efficiency. Furthermore, the turbidity of the reaction mixture will be enhanced when the pollutant concentration is increased. It inhibits the photons to reach the catalyst for activation thereby decreasing the rate of degradation of pollutants. However, the rate of degradation of the pollutants, rather than the percentage degradation, is a more appropriate parameter to evaluate the concentration effect. Hence, the rate at different concentrations is computed and the results are presented in Fig. 9.

3.2.3 Reaction Kinetics

The photodegradation rate in the presence of optimized ZnO nanoparticle dosage is shown in Fig. 9. As seen in the figure, the rate increases initially, stabilizes, and decreases thereafter. This is consistent with the kinetics of degradation of most organic molecules under AOP, according to which at lower concentrations the reaction follows pseudo-first-order kinetics (Anju et al., 2012; Cheng et al., 2015). The order of

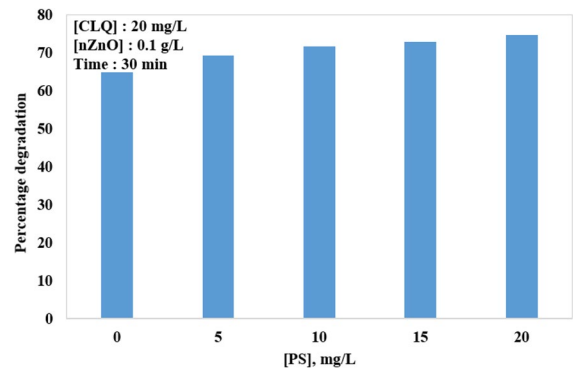


Fig. 11 The effect of PS on the degradation of CLQ under SL

the reaction decreases with an increase in concentration. The kinetics followed zero-order at higher concentrations, and at still higher concentrations followed a negative order.

The zero-order kinetics at higher concentrations is because, at these concentration ranges, there are enough substrate molecules to interact with all of the available catalyst sites, activate them, and then react with the in-situ generated reactive oxygen species. Therefore, as long as the catalyst dosage is kept constant, a subsequent rise in concentration does not result in more interaction or degradation. At a higher concentration, the substrate absorbs more photons thereby decreasing the photons available for ZnO activation. The substrate molecules are in excess in relation to the available active sites at very high concentrations (Zawadzki et al., 2021). They are a lot more compared to the generated ROS as well. These factors can result in a decrease in the relative number of surface-initiated $\bullet\text{OH}$ radicals. Furthermore, the ability of the catalyst surface to activate is diminished as a result of the adsorption of molecules in multiple layers on the surface. Any hindrance to the interaction and activation of the catalyst to produce $\bullet\text{OH}$ radicals will reduce degradation because free radicals are the primary requisite for degradation as mentioned above. As a result, the degradation of the pollutant decreases. The kinetics is in agreement with that reported in the case of AOP degradation of several organic contaminants in water in the presence of heterogeneous catalysts (Anju et al., 2012; Shubin et al., 2015; Feliciano et al., 2020).

Also, the variable kinetics can be explained as follows. In the early stages of the reaction, the substrate

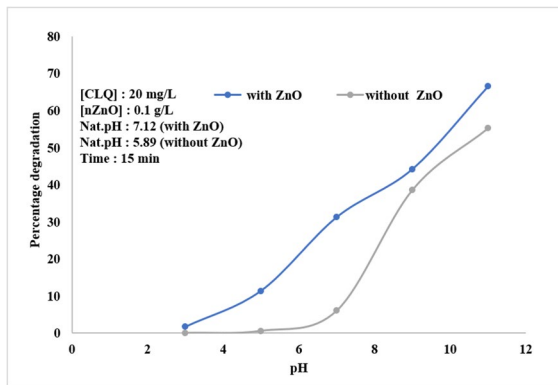


Fig. 12 The effect of pH on the degradation of CLQ under SL

has full access to the entire catalyst surface, resulting in a rapid rate of degradation. As the reaction proceeds, an increasing number of slowly deteriorating intermediates are built up in the solution and compete with the substrate for ROS and the catalyst's active sites (Gayathri et al., 2019). Its competitive power is lowered by the decrease in substrate concentration. With time, the rate of degradation is slowed down by these factors. Any additional increase in substrate concentration cannot produce correspondingly more ROS or other reactive free radicals once it has filled all the active sites on the catalyst and interacted with the available free radicals. The production of surface-initiated reactive free radicals is suppressed by the reactant, intermediaries, and/or products that completely dominate the catalytic surface (Zawadzki et al., 2021). At any point in time, there will be an optimum for the maximum number of substrate molecules to interact with the reactive free radicals formed by the surface. This optimum will be determined by several factors, including the substrate's initial concentration, the mass of the catalyst, and the type and geometry of the reactor. As a result, measurements and calculations cannot be generalized beyond the specific reaction conditions.

The kinetics of photocatalytic degradation of pollutants usually follows pseudo-first-order kinetics and Langmuir-Hinshelwood Mechanism (Khezrianjoo & Revanasiddappa et al., 2012). This is verified in the case of SL/ZnO degradation of CLQ by the logarithmic plot ($-\ln [C/C_0]$ vs with time) at low concentration ranges of 5, 10, 15, and 20 mg/L of CLQ (Fig. 10). The linear plot confirms first order kinetics. A decrease in the rate of photocatalytic degradation

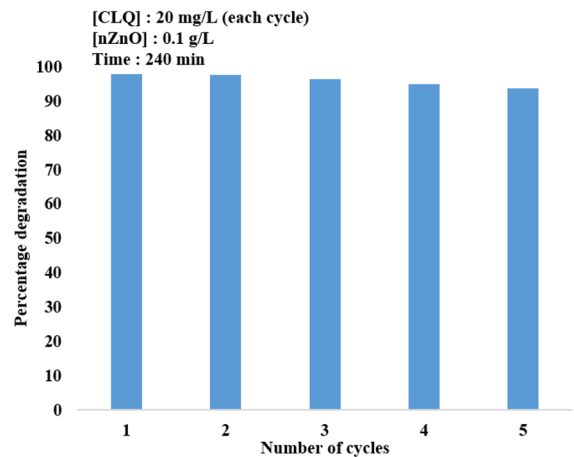


Fig. 13 Recycling of used catalyst under SL

and hence in the order of the reaction at higher concentrations of the reactant has also been reported earlier (Hamza et al., 2013; Gayathri et al., 2017).

Once all the surface sites are occupied, any further increase in the concentration of the substrate cannot result in increased adsorption on the surface and the photocatalytic CLQ removal becomes independent of the concentration. Hence, any increase in the concentration of CLQ can more effectively utilize the otherwise limited $\bullet\text{OH}$ radicals leading to increased degradation only up to an optimum value. This increase in degradation will continue until the CLQ concentration is sufficiently high to interact with an optimum number of $\bullet\text{OH}$ radicals.

3.2.4 The Effect of Oxidants Hydrogen Peroxide and Persulfate on the Degradation of CLQ

The oxidant H_2O_2 (HP) plays an important role in the photocatalytic decomposition of organic contaminants (da Silva-Rackov et al., 2016). But the addition of HP at a higher concentration and dose does not necessarily guarantee better performance of a catalytic system. The effect of HP and PS concentration on the degradation of CLQ is studied in the concentration range of 5 to 20 mg/L. HP showed almost no effect in the concentration ranges studied here. This may be because when the concentration of HP is increased, excess $\bullet\text{OH}$ radicals generated in presence of the catalyst are scavenged due to the interaction with the HP in the system as in Eq. (3).

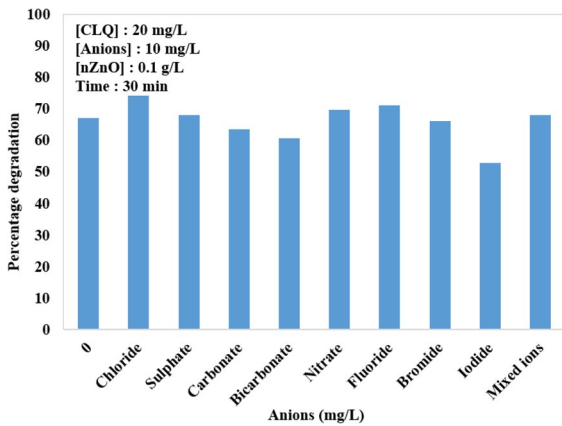


Fig. 14 The effect of the presence of various anions in CLQ solution on its degradation

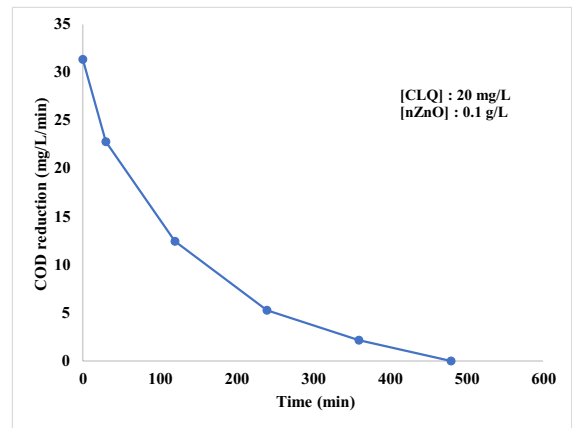
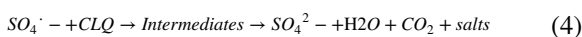


Fig. 15 COD reduction of CLQ-contaminated water under SL/ZnO

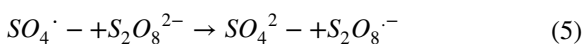


Persulfate-AOPs have gained significant attention nowadays as a viable alternative to traditional $\cdot OH$ -based AOPs (Gayathri et al., 2019; Lee et al., 2020; Kiejza et al., 2021). Persulfate (PS) is proven to be a strong oxidant due to the formation of highly reactive $SO_4^{\cdot -}$ radical anions. The probability of enhancing the efficiency of CLQ degradation under SL by the addition of persulfate is tested at various concentrations at different reaction times. Different concentrations of persulfate from 5 to 20 mg/L are used for the study. The results are plotted in Fig. 11.

Persulfate has a positive effect on the degradation of CLQ, probably due to the efficient generation of reactive radicals $SO_4^{\cdot -}$ under solar radiation. With the increase in the concentration of PS, more reactive $SO_4^{\cdot -}$ radicals may be formed under the oxidizing environment. These radicals can interact with the substrate CLQ present in water and result in its enhanced degradation/mineralization (Eq. 4).

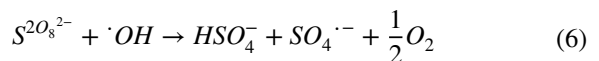


At higher concentrations of PS, $SO_4^{\cdot -}$ can interact with the former and transform the same to less reactive $S_2O_8^{\cdot -}$ in Eq. 5.



In presence of ZnO, the higher concentration of $\cdot OH$ radicals generated may not be useful in presence of PS because they ($\cdot OH$) may be interacting

more with the $SO_4^{\cdot -}$ resulting in the destruction of both by chain termination. This leads to fluctuation in the concentration of $\cdot OH$ and $SO_4^{\cdot -}$ with time resulting in a net decrease or stabilization in the degradation of the substrate. The $\cdot OH$ radicals can also interact with $S_2O_8^{2-}$ as follows (Eqs. (6) and (7)):



3.2.5 The Effect of pH on the Degradation of CLQ

The effect of pH on the degradation of CLQ under SL irradiation is tested under optimized conditions. The results are presented in Fig. 12. The degradation increases with an increase in pH. The rate of degradation varies depending on the solution pH, zero-point charges (ZPC) of the catalyst, and the component molecular structure. The CLQ is a cationic amphiphilic drug. The interaction of a photocatalyst with cationic compounds would be favored at pH greater than the photocatalyst ZPC, while anionic compounds would interact more favorably at pH less than the catalyst PZC. Since the ZPC of ZnO is ~ 9.07 , its surface is negatively charged above $pH \sim 9$. A higher pH value could provide a higher concentration of hydroxyl ions to react with holes to

Table 1 Major intermediates formed during the solar photocatalytic degradation of CLQ

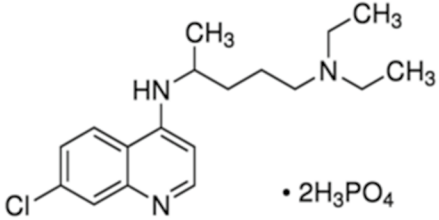
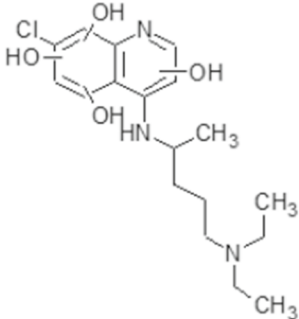
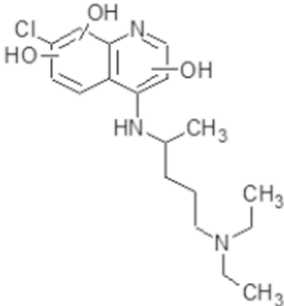
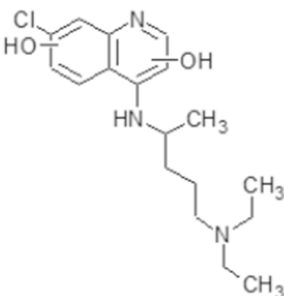
Sl. No.	Chemical Formula	m/z value	Structure
1	$C_{18}H_{32}ClN_3O_8P_2$	515	 <p style="text-align: center;">Chloroquine (Parent compound)</p>
2	$C_{18}H_{28}N_3O_4Cl$	386	
3	$C_{18}H_{28}N_3O_3Cl$	368	
4	$C_{18}H_{28}N_3O_2Cl$	354	

Table 1 (continued)

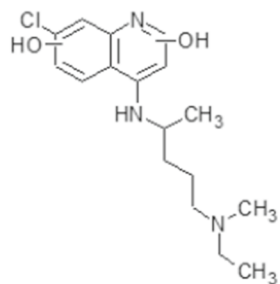
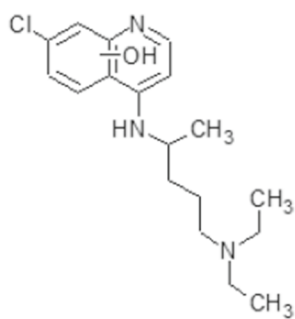
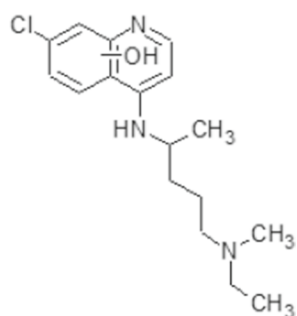
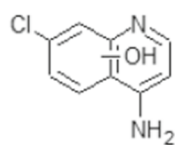
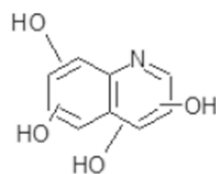
5 $C_{17}H_{26}N_3O_2Cl$ 3406 $C_{18}H_{26}N_3OCl$ 3367 $C_{17}H_{24}N_3OCl$ 3228 $C_9H_7N_2OCl$ 1959 $C_9H_5NO_4$ 192

Table 2 The comparison of the current chosen method with other established methods

Sl. no.	Chosen method in the present study	Other methods
1	The source of energy chosen here is sunlight which is inexpensive and renewable. The method can remove even the last traces of contaminant from water. The method is simple, easy to operate environment-friendly, and flexible in application. The catalyst can be recycled multiple times after simple physical treatment.	Conventional water treatment methods such as flocculation, sedimentation, filtration, chemical treatment, and thermal treatment do not entirely remove toxic pollutants from water. Further, such methods are energy-intensive, expensive, and less environment-friendly.
2	The photocatalyst used here is simple widely available ZnO, with effective solar activity. This makes the process applicable even in less affluent societies.	Other photocatalytic treatment methods are expensive as they use expensive doped/supported/immobilized catalysts.

form hydroxyl radicals. Thus, alkaline pH results in more $\bullet\text{OH}$ radical formation and better adsorption of CLQ on the surface of ZnO, leading to better degradation (Wu et al., 2010; Kadhim et al., 2020).

The effect of pH on the heterogeneous photocatalytic degradation of organics is very complex and depends on the characteristics of the pollutant and the catalyst and the multitude of interactions between various reactive species including those formed in situ. In such systems, the pH effect is often explained based on the ZPC of the catalyst.

3.2.6 Recycling of Used Catalyst

From the environmental and economic angles, the potential for the reuse of the catalyst is very important. To verify the reusability of ZnO, the used catalyst was separated by filtration, washed with deionized water, and dried at 200°C for 2 h. The recycling experiment was done under conditions optimized for fresh catalysts. Under SL (Fig. 13), CLQ showed 98% decomposition in the 1st run, 98% in the 2nd run, 96% in the 3rd run, 94% in the 4th run, and 93% in the 5th run, respectively after 240 min of irradiation time. The decrease in degradation is only marginal thereby confirming the reusability of the catalyst for many runs.

3.2.7 The Effect of Anions

Various anions are present in real water. The effect of the presence of anions such as Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , NO_3^- , F^- , Br^- , and I^- individually and as a mixed solution on the performance of ZnO/SL/CLQ system was

investigated. The effect of anions on the CLQ degradation is presented in Fig. 14, which indicates that the presence of anions in water can either increase or decrease the degradation efficiency. The inhibition was observed in the presence of carbonate, bicarbonate, and iodide. It may be because they scavenge $\bullet\text{OH}$ radicals resulting in the formation of the radical anion and subsequently decreasing the availability of oxidizing agent (ROS) for CLQ degradation. Enhancement of the degradation of CLQ by chloride, fluoride, and nitrate can be partially explained based on the hypothesis that the radicals $\text{Cl}_2^{\bullet-}$, $\text{F}^{\bullet-}$, $\text{NO}_3^{\bullet-}$ etc. undergo slower radical-radical recombination or deactivation compared to $\bullet\text{OH}$. Hence, these radical anions are more readily available for a longer time than $\bullet\text{OH}$ to react with substrate and effect degradation. Thus, the relatively lower reactivity (of the radical anion) is compensated by the better availability for reaction with the substrate (Gayathri et al., 2019). The anion Sulphate and the mixed ions showed almost no effect on the degradation of CLQ. The effect of anions in AOPs can be very complex and inconsistent. The reaction conditions, the activation source, the characteristics of the reaction system, the relative concentration of various components, etc. can influence the anion effect on inhibition or enhancement (Jyothi et al., 2018). Hence, the effect of every anion has to be individually evaluated in every system and general conclusions may not be applicable in many cases.

3.2.8 The Effect on the COD

The real measure of the efficiency of removing a pollutant from water is its total mineralization

into harmless end products such as CO_2 , H_2O , and salts, resulting in the complete elimination of chemical oxygen demand (COD). In this context, the COD of the system after different times of solar irradiation is measured and the results are shown in Fig. 15. Complete removal of the original COD was achieved in 480 min of irradiation under SL.

3.2.9 Photodegradation Mechanism and Intermediates

The mechanism of semiconductor-mediated photocatalytic degradation of pollutants in water is well established (Gayathri et al., 2019) and may be briefly presented as in Reactions (8)–(15).



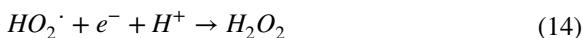
(Recombination of electron-hole pairs)

Formation of primary radicals by valence band holes: (10) and (11)

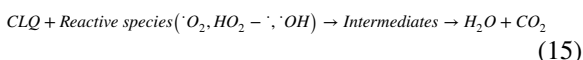


(Scavenging of conduction band electrons (Eq. 12))

Formation of multiple peroxide species shown in Eqs. (13) and (14):



CLQ reacts with ROS to give intermediate products and further gives CO_2 and H_2O (Eq. 15).



The mineralization/degradation, proceeds through a number of intermediates, as is verified by LC-MS analysis of the reaction solution at approximately 50% degradation of CLQ. Eight transformation products were identified depending on their mass-to-charge (m/z) ratio. The structure

of some of these intermediates are as follows (Table 1):

The comparison of the current method with other established methods is briefly given in the Table 2.

4 Summary and Conclusions

In summary, ZnO-mediated solar photocatalysis is demonstrated to be an efficient method for the removal of CLQ pollutants from water. The relevant reaction parameters such as catalyst dosage, CLQ concentration, pH, presence of oxidants such as H_2O_2 and persulfate are optimized experimentally. When the concentrations of CLQ and ZnO nanoparticles were 20 mg/L and 0.1 g/L, respectively, with natural pH of 7–7.2, CLQ removal reached 100% under solar irradiation. The kinetics of CLQ depletion follows pseudo-first-order. The pollutant is completely mineralized into harmless products such as CO_2 and water as is seen by the complete elimination of COD. LC-MS analysis identified some of the CLQ degradation intermediates. The influence of salts present in water on the degradation of CLQ is moderate and varies from enhancement to ‘no effect’ or inhibition. The photocatalytic process primarily involves the formation of $\cdot\text{OH}$ radicals which interact with the pollutant on the surface of the catalyst as well as in the bulk. The application of solar energy, which is renewable and available in plenty, as the source of activation makes the process especially relevant for the inexpensive and environment-friendly removal of toxic pollutants such as CLQ from water.

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Author Contribution PVG conceived the idea, conducted the research work, and wrote the manuscript. SJ did overall supervision, and gave suggestions for improving the manuscript. All authors read, edited, and approved the final manuscript.

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Data Availability The datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical Approval All ethics were followed during the preparation of the manuscript.

Competing Interests The authors declare no competing interests.

References

- Anju, S. G., Yesodharan, S., & Yesodharan, E. P. (2012). Zinc oxide mediated sonophotocatalytic degradation of phenol in water. *Chemical Engineering Journal*, 189, 84–93. <https://doi.org/10.1016/j.cej.2012.02.032>
- Balakrishna, K., Rath, A., Praveenkumarreddy, Y., Guruge, K. S., & Subedi, B. (2017). A review of the occurrence of pharmaceuticals and personal care products in Indian water bodies. *Ecotoxicology and environmental safety*, 137, 113–120. <https://doi.org/10.1016/j.ecoenv.2016.11.014>
- Bottoni, P., Caroli, S., & Caracciolo, A. B. (2010). Pharmaceuticals as priority water contaminants. *Toxicological & Environmental Chemistry*, 92(3), 549–565. <https://doi.org/10.1080/02772241003614320>
- Chander, V., Sharma, B., Negi, V., Aswal, R. S., Singh, P., Singh, R., & Dobhal, R. (2016). Pharmaceutical compounds in drinking water. *Journal of xenobiotics*, 6(1), 5774. <https://doi.org/10.4081/xeno.2016.5774>
- Chen, Y., Yang, J., Zeng, L., & Zhu, M. (2022). Recent progress on the removal of antibiotic pollutants using the photocatalytic oxidation process. *Critical Reviews in Environmental Science and Technology*, 52(8), 1401–1448. <https://doi.org/10.1080/10643389.2020.1859289>
- Cheng, H., Song, D., Liu, H., & Qu, J. (2015). Permanganate oxidation of diclofenac: The pH-dependent reaction kinetics and a ring-opening mechanism. *Chemosphere*, 136, 297–304. <https://doi.org/10.1016/j.chemosphere.2014.11.062>
- Clesceri, L. S., Greenberg, A. E., & Eaton, A. E. (1998). *APHA AWWA, W.P.C.F. Standard methods for the examination of water and wastewater* (20th ed.). American Public Health Association.
- Cruz, D. M., Mostafavi, E., Vernet-Crua, A., Barabadi, H., Shah, V., Cholula-Díaz, J. L., Guisbiers, G., & Webster, T. J. (2020). Green nanotechnology-based zinc oxide (ZnO) nanomaterials for biomedical applications: A review. *Journal of Physics: Materials*, 3(3), 034005. <https://doi.org/10.1088/2515-7639/ab8186>
- da Silva-Rackov, C. K., Lawal, W. A., Nfodzo, P. A., Vianna, M. M., & do Nascimento, C.A. and Choi, H. (2016). Degradation of PFOA by hydrogen peroxide and persulfate activated by iron-modified diatomite. *Applied Catalysis B: Environmental*, 192, 253–259. <https://doi.org/10.1016/j.apcatb.2016.03.067>
- Dhanalakshmi, R., Priya, P., & Sivamurugan, V. (2022). Pharmaceutical pollutants in water: Origin, toxicity hazards, and treatment. In *Organic Pollutants* (pp. 293–320). Springer. https://doi.org/10.1007/978-3-030-72441-2_12
- Feliciano, A. R. S., Andrade de Lucena, A. L., da Rocha Santana, R. M., Zaidan, L. E. M. C., Michelle da Silva, P., Napoleão, T. H., Duarte, M. M. M. B., & Napoleão, D. C. (2020). Advanced oxidation processes employment for the degradation of lamivudine: Kinetic assessment, toxicity study and mathematical modeling. *Water Quality Research Journal*, 55(3), 249–260. <https://doi.org/10.2166/wqrj.2020.010>
- Gasmi, A., Peana, M., Noor, S., Lysiuk, R., Menzel, A., Gasmi Benahmed, A., & Bjørklund, G. (2021). Chloroquine and hydroxychloroquine in the treatment of COVID-19: The never-ending story. *Applied microbiology and biotechnology*, 105(4), 1333–1343. <https://doi.org/10.1007/s00253-021-11094-4>
- Gayathri, P. V., Suguna, Y., & Yesodharan, E. P. (2017). Purification of water contaminated with traces of rhodamine B dye by microwave-assisted, oxidant-induced and zinc oxide catalyzed advanced oxidation process. *Desalination and Water Treatment*, 85, 161–174. <https://doi.org/10.5004/dwt.2017.21286>
- Gayathri, P. V., Yesodharan, S., & Yesodharan, E. P. (2019). Microwave/Persulphate assisted ZnO mediated photocatalysis (MW/PS/UV/ZnO) as an efficient advanced oxidation process for the removal of RhB dye pollutant from water. *Journal of Environmental Chemical Engineering*, 7(4), 103122. <https://doi.org/10.1016/j.jece.2019.103122>
- Glaze, W. H. (1987a). Drinking-water treatment with ozone. *Environmental science & technology*, 21(3), 224–230. <https://doi.org/10.1021/es00157a001>
- Glaze, W. H., Kang, J. W., & Chapin, D. H. (1987b). The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone: Science & Engineering*, 9(4), 335–352. <https://doi.org/10.1080/01919518708552148>
- Hamza, A., Fatuase, J. T., Waziri, S. M., & Ajayi, O. A. (2013). Solar photocatalytic degradation of phenol using nano-sized ZnO and $\text{I}^{\pm}\text{-Fe}_2\text{O}_3$. *Journal of Chemical Engineering and Materials Science*, 4(7), 87–92. <https://doi.org/10.5897/JCEMS2013.0162>
- Hariharan, C. (2006). Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles: Revisited. *Applied Catalysis A: General*, 304, 55–61. <https://doi.org/10.1016/j.apcata.2006.02.020>
- Hosny, M., Fawzy, M., & Eltaweil, A. S. (2022). Green synthesis of bimetallic Ag/ZnO@ Bioharnanocomposite for photocatalytic degradation of tetracycline, antibacterial and antioxidant activities. *Scientific Reports*, 12(1), 1–17. <https://doi.org/10.1038/s41598-022-11014-0>
- Jyothi, K. P., Yesodharan, S., & Yesodharan, E. P. (2018). Contaminant salts as enhancers of sonocatalytic degradation of organic water pollutants: Effect of concentration, reaction time and adsorption on the efficiency of enhancement and the fate of concurrently formed H₂O₂. *Journal of environmental chemical engineering*, 6(3), 3574–3589. <https://doi.org/10.1016/j.jece.2016.12.053>

- Kadhim, M. J., Mahdi, M. A., & Hassan, J. J. (2020). Influence of pH on the photocatalytic activity of ZnO nanorods. *Materials International*, 2, 0064–0072. <https://doi.org/10.33263/Materials21.064072>
- Karungamye, P. N. (2020). Methods used for removal of pharmaceuticals from wastewater: A review. *Applied Journal of Environmental Engineering Science*, 6(4), 6–4. <https://doi.org/10.48422/IMIST.PRSM/ajeess-v6i4.23828>
- Khezrianjoo, S., & Revanasiddappa, H. D. (2012). Langmuir-Hinshelwood kinetic expression for the photocatalytic degradation of metal yellow aqueous solutions by ZnO catalyst. *Chemical Sciences Journal*, 45, 1–7. <https://doi.org/10.4172/2150-3494.1000058>
- Khuroo, M. S. (2020). Chloroquine and hydroxychloroquine in coronavirus disease 2019 (COVID-19). Facts, fiction and the hype: A critical appraisal. *International journal of antimicrobial agents*, 56(3), 106101. <https://doi.org/10.1016/j.ijantimicag.2020.106101>
- Kiejza, D., Kotowska, U., Polińska, W., & Karpińska, J. (2021). Peracids-New oxidants in advanced oxidation processes: The use of peracetic acid, peroxymonosulfate, and persulfate salts in the removal of organic micropollutants of emerging concern— A review. *Science of The Total Environment*, 790, 148195. <https://doi.org/10.1016/j.scitotenv.2021.148195>
- Lee, J., Von Gunten, U., & Kim, J. H. (2020). Persulfate-based advanced oxidation: critical assessment of opportunities and roadblocks. *Environmental science & technology*, 54(6), 3064–3081. <https://doi.org/10.1021/acs.est.9b07082>
- Lozano, I., Pérez-Guzmán, C. J., Mora, A., Mahlkecht, J., Aguilar, C. L., & Cervantes-Avilés, P. (2022). Pharmaceuticals and personal care products in water streams: Occurrence, detection, and removal by electrochemical advanced oxidation processes. *Science of The Total Environment*, 827, 154348. <https://doi.org/10.1016/j.scitotenv.2022.154348>
- Mahdizadeh, H., Nasiri, A., Gharaghani, M. A., & Yazdapanah, G. (2020). Hybrid UV/COP advanced oxidation process using ZnO as a catalyst immobilized on a stone surface for degradation of acid red 18 dye. *Methods X*, 7, 101118. <https://doi.org/10.1016/j.mex.2020.101118>
- Miettinen, M., & Khan, S. A. (2022). Pharmaceutical pollution: A weakly regulated global environmental risk. *Review of European, Comparative & International Environmental Law*, 31(1), 75–88. <https://doi.org/10.1111/reel.12422>
- Mirzaeifard, Z., Shariatinia, Z., Jourshabani, M., & Rezaei Darvishi, S. M. (2020). ZnO photocatalyst revisited: effective photocatalytic degradation of emerging contaminants using S-doped ZnO nanoparticles under visible light radiation. *Industrial & Engineering Chemistry Research*, 59(36), 15894–15911. <https://doi.org/10.1021/acs.iecr.0c03192>
- Mohan, S., & Sruthy, S. (2022). Human health risk assessment due to solvent exposure from pharmaceutical industrial effluent: Deterministic and probabilistic approaches. *Environmental Processes*, 9(1), 1–21. <https://doi.org/10.1007/s40710-022-00571-1>
- Ortuzar, M., Esterhuizen, M., Olicón-Hernández, D. R., González-López, J., & Aranda, E. (2022). Pharmaceutical pollution in aquatic environments: A concise review of environmental impacts and bioremediation systems. *Frontiers in microbiology*, 13, 869332. <https://doi.org/10.3389/fmicb.2022.869332>
- Pandis, P. K., Kalogirou, C., Kanellou, E., Vaitis, C., Savvidou, M. G., Sourkouni, G., Zorpas, A. A., & Argiris, C. (2022). Key points of advanced oxidation processes (AOPs) for wastewater, organic pollutants and pharmaceutical waste treatment: A mini review. *Chem Engineering*, 6(1), 8. <https://doi.org/10.3390/chemengineering6010008>
- Pham, T. A. T., Tran, V. A., Le, V. D., Nguyen, M. V., Truong, D. D., Do, X. T., & Vu, A. T. (2020). Facile preparation of ZnO nanoparticles and Ag/ZnO nanocomposite and their photocatalytic activities under visible light. *International Journal of Photoenergy*, 2020, 1–14. <https://doi.org/10.1155/2020/8897667>
- Raizada, P., Sudhaik, A., & Singh, P. (2019). Photocatalytic water decontamination using graphene and ZnO coupled photocatalysts: a review. *Materials Science for Energy Technologies*, 2(3), 509–525. <https://doi.org/10.1016/j.mset.2019.04.007>
- Rebeaud, M. E., & Zores, F. (2020). SARS-CoV-2 and the use of chloroquine as an antiviral treatment. *Frontiers in medicine*, 7, 184. <https://doi.org/10.3389/fmed.2020.00184>
- Reza, K. M., Kurny, A. S. W., & Gulshan, F. (2017). Parameters affecting the photocatalytic degradation of dyes using TiO₂: a review. *Applied Water Science*, 7(4), 1569–1578. <https://doi.org/10.1007/s13201-015-0367>
- Rzymiski, P., Drewek, A., & Klimaszuk, P. (2017). Pharmaceutical pollution of aquatic environment: an emerging and enormous challenge. *Limnological Review*, 17(2), 97. <https://doi.org/10.1515/limre-2017-0010>
- Sanna, V., Pala, N., Alzari, V., Nuvoli, D., & Carcelli, M. (2016). ZnO nanoparticles with high degradation efficiency of organic dyes under sunlight irradiation. *Materials Letters*, 162, 257–260. <https://doi.org/10.1016/j.matlet.2015.10.031>
- Saravanan, A., Kumar, P. S., Jeevanantham, S., Anubha, M., & Jayashree, S. (2022). Degradation of toxic agrochemicals and pharmaceutical pollutants: Effective and alternative approaches toward photocatalysis. *Environmental Pollution*, 298, 18844. <https://doi.org/10.1016/j.envpol.2022.118844>
- Sayadi, A. R., Asadpour, M., Shabani, Z., & Sayadi, M. H. (2012). Pharmaceutical pollution of the ecosystem and its detrimental effects on public health. *Journal of Rafsanjan University of Medical Sciences*, 11(3), 269–284. <http://journal.rums.ac.ir/article-1-1435-en.html>
- Shibin, O. M., Yesodharan, S., & Yesodharan, E. P. (2015). Sunlight induced photocatalytic degradation of herbicide diquat in water in presence of ZnO. *Journal of Environmental Chemical Engineering*, 3(2), 1107–1116. <https://doi.org/10.1016/j.jece.2015.04.026>
- Vaudin, P., Augé, C., Just, N., Mhaouty-Kodja, S., Mortaud, S., & Pillon, D. (2022). When pharmaceutical drugs become environmental pollutants: Potential neural effects and underlying mechanisms. *Environmental Research*, 205, 112495. <https://doi.org/10.1016/j.envres.2021.112495>
- Wu, J., Jiang, Y., Zha, L., Ye, Z., Zhou, Z., Ye, J., & Zhou, H. (2010). Tetracycline degradation by ozonation, and evaluation of biodegradability and toxicity of ozonation byproducts. *Canadian Journal of Civil Engineering*, 37(11), 1485–1491. <https://doi.org/10.1139/L10-100>

Zawadzki, P., & Deska, M. (2021). Degradation efficiency and kinetics analysis of an advanced oxidation process utilizing ozone, hydrogen peroxide and persulfate to degrade the dye rhodamine B. *Catalysts*, *11*(8), 974. <https://doi.org/10.3390/catal11080974>

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