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Photocatalytic degradation of acetaminophen in aqueous solution by $Zn_{0.2}Cd_{0.8}S$ catalyst and visible radiation

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ABSTRACT

Photocatalytic degradation of acetaminophen in aqueous solution by $Zn_{0.2}Cd_{0.8}S$ catalyst and visible light radiation was carried out under optimized conditions. The degradation was monitored spectrophotometrically. The degraded products were analyzed by gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry (LC–MS) and their structures were proposed using tandem mass spectrometry data. Various mechanistic pathways were observed involving $^{\bullet}OH$ radicals. The parent compound was converted to lower molecular weight unsaturated carboxylic acids in addition to pyridine derivatives. Based on LC–MS and tandem mass spectrometry MS/MS results, a photocatalytic oxidative mechanism was suggested.

Keywords: Acetaminophen; Photocatalyst; Degradation; LC–MS/MS; $Zn_{0.2}Cd_{0.8}S$; Visible radiation

1. Introduction

Several methods have been suggested for the removal of organic pollutants from wastewaters. These include biodegradation, coagulation, adsorption, advanced oxidation process (AOP) and the membrane process [1–4]. Among these techniques, the AOPs appear to show promising results and have been reported to be effective for the near-complete degradation of soluble organic contaminants from water and soils [5]. Heterogeneous photocatalytic degradation is one such AOP technique, which has taken the lead in this emerging technology for degrading organic compounds [6–8]. The method is more effective as compared with other AOPs because semiconductors are inexpensive and can easily mineralize various organic compounds [9].

The effectiveness of environmentally friendly photochemical methods for wastewater treatment is due to the in situ generation of the strongly oxidizing hydroxyl radicals ($^{\bullet}OH$), which oxidize a broad range of organic pollutants that could be present in water and wastewaters [10,11]. Among the various organic pollutants that are considered to cause environmental hazard, pharmaceutical compounds occupy a prominent position. The presence of trace amounts of these compounds and other synthetic organic molecules in drinking groundwater is of public concern, because little is known about the potential chronic health effects associated with the long-term ingestion of these compounds through wastewater [12]. Acetaminophen also known as 4-hydroxyacetanilide, 4-acetamidephenol or acetaminophen is the most commonly used analgesic and antipyretic drug worldwide and is widely available over-the-counter in many countries [13]. Acetaminophen has been found with a concentration of up to 6 μg/L in European

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sewage treatment plant effluents and up to 10 μg/L in natural waters in USA [14]. To avoid the potential health risk associated with this drug, several methods have been developed for its complete removal from wastewaters. The oxidation of the acetaminophen has been tested by using TiO_2/Fe_2O_3 nanoparticles [15], ozone [16], lanthanum-doped ZnO nanoparticles [17], solar irradiation using TiO_2–ZnO/clay nanoarchitectures [18], electrocatalysis using glassy carbon electrode [19] and sonolysis [20].

The synthesis of CdS quantum dot (QD)-decorated $Cd_xZn_{1-x}S$ cluster by co-precipitation followed with hydrothermal method has been reported in the literature [21]. Photogenerated electrons from CdS QDs have been used to degrade rhodamine B in an aqueous suspension in the presence of visible light. Quantum-sized CdS and $Cd_xZn_{1-x}S$ clusters alter the energy levels of the conduction and valence band edges in the coupled systems, which favor the interparticle electron transfer. Additionally, $Cd_xZn_{1-x}S$ is believed to act in a cooperative manner by increasing the degree of charge-carrier separation, thus improving the incident photon-to-electron conversion efficiency as well as the photocatalytic activity [21].

In this study, we identified the degradation products of acetaminophen in aqueous solution using $Zn_{0.2}Cd_{0.8}S$ and visible irradiation and postulated a plausible mechanistic degradation pathway. The efficiency of photocatalytic oxidation using different proportions of Cd and Zn metal ions with sulfide was also examined. The photocatalytic degradation of acetaminophen was carried out under optimized experimental parameters, such as pH, concentration of drug and time.

2. Experimental procedure

2.1. Photocatalytic degradation of acetaminophen

Acetaminophen drug stock solution of 1×10^{-3} M was prepared in 100 mL of deionized water. Necessary dilutions of this stock were done with deionized water. A given amount of the catalyst ($Zn_{0.2}Cd_{0.8}S$ = 0.05 g) was added to 100 mL of this diluted solution ([acetaminophen] = 1×10^{-5} M). The mixture was allowed to equilibrate for a given time (usually 15–30 min) in dark. The solution was then exposed to visible light source using photoreactor (Luzchem, Canada) which contained 12 lamps of UVA, UVB, UVC, and cool white light, LZC-420 (white phosphore) three lamps for each type). During irradiation, the contents of the solution were agitated continuously to maintain a homogeneous environment. After a certain time interval, the quartz beaker was drawn away from the light source and 10 mL aliquot was withdrawn and centrifuged, and the absorbance of the supernatant solution was monitored immediately on a Specord 210 plus UV/Vis spectrophotometer (AnalyticJena, Germany), using a 1 cm quartz cell. The absorbance value obtained in each case was plotted against time to obtain the rate constant of degradation. All absorbance measurements were recorded in the range of 190–800 nm. The maximum absorption wavelength, experimentally determined to be 257 nm for the acetaminophen drug, was used for the calibration curves and further measurements. The power/intensity of visible light was measured to be 11,930 Lux (or 45 mW/cm^2).

2.2. Catalyst preparation and characterization

The catalyst namely $Zn_{0.2}Cd_{0.8}S$ was prepared according to the previously reported methods from $Cd(NO_3)_2{\cdot}4H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and thioacetamide [21–23]. The characterization was carried out using XRD, SEM and TEM techniques, details of which can be found in the study by Rengaraj et al. [23].

2.3. Product analysis and identification using LC–UV/Vis–MS studies

The chromatographic experiments with high-performance liquid chromatography with ultraviolet/visible light absorption detection (HPLC–UV/vis) system were carried out on a Shimadzu Nexera-i series LC-2040 liquid chromatograph (Shimadzu, Japan) with a quaternary solvent gradient pump, a photodiode array detector and an automatic injector. The degradation products were separated using an Agilent Zorbax® SB-C18 column 150 mm × 4.6 mm packed with 5 μm particle size. The detection system was a diode array detector with detection range between 200–800 nm. The signal acquired from the detector was recorded by Labsolution® software. The mobile phase consisted solutions A and B. Solution A was made from 0.1 M ammonium acetate and acetic acid (pH 5.3), whereas Solution B was acetonitrile. The gradient elution was from 5% to 95% in 25 min. The flow rate was 0.8 mL/min and the injection volume was 50 μL.

The gradient HPLC separation was coupled with a triple quadrupole mass spectrometer LC–MS 8040 (Shimadzu, Japan). The mass spectrometer was equipped with an electrospray ionization (ESI) source and operated in positive polarity. The ESI conditions were as follows: interface bias voltage was +4.5 kV, interface bias current was fixed at 0.73 μA V; the nebulizer gas flow was 1.5 L/min; drying gas flow was 15 L/min and drying temperature was 400°C. The mass range was from m/z 50 to 500.

2.4. Product analysis and identification using gas chromatography–mass spectrometry (GC–MS) studies

10 mL aqueous solution of irradiated acetaminophen was collected at different time intervals and concentrated by vacuum freeze-drying method. Then the samples were derivatized with 200 μL of N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMS) (Supleco, PA, USA) at 70°C for 1 h to convert all free –OH and –COOH groups into their volatile TMS-ether(–$OSiMe_3$) and TMS-ester (–CO_2SiMe_3) derivatives, respectively. 1 μL of the sample was analyzed by GC–MS instrument.

GC–MS analysis was performed on Agilent 7890A GC equipped with a 7693B Autosampler and 7000 Series Triple quadrupole (QQQ) mass spectrometer detector system (Agilent, USA). An Agilent Ultra Inert GC column (Agilent J&W HP-5MS UI 60 m × 0.25 mm × 0.25 μm) was used to provide a highly inert flow path into the detector. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The injector temperature was 200°C and the injection volume was 1 μL. The column temperature was fixed at 80°C for 1 min, and then programmed from 80°C to 150°C at 7°C/min and held for 5 min, then from 150°C to 200°C with the same rate

the final temperature maintained for 5 min. The mass spectrometer conditions were as follows: the transfer line temperature was 280°C, the source temperature was set at 300°C, the MS detector was operated in the electron ionization (EI) mode (70 eV), the quadrupole temperatures for Q1 and Q2 were 180°C and the detector gain was 10. The Agilent Mass Hunter Workstation software B.07.00SP2 was used for data analysis. Product identification was performed using NIST-14 library available through the GC software.

3. Results and discussion

In this work, degradation of acetaminophen was investigated in the presence of a cadmium-based catalyst and visible radiation. Five different catalysts, namely CdS, $Cd_{0.2}Zn_{0.8}S$, $Cd_{0.5}Zn_{0.5}S$, $Cd_{0.8}Zn_{0.2}S$ and ZnS, were prepared and tested for the degradation of acetaminophen under the conditions stated in the experimental section. Table S1 shows the rate constant values for the degradation of the drug when different molar ratios of Cd and Zn were used. The best results were achieved when $Cd_{0.2}Zn_{0.8}S$ was used, thus further investigations were carried out using this catalyst.

The structure of the drug is given in Fig. 1. The drug shows a λ_{max} at 257 nm, which was chosen for monitoring the degradation reaction. Initially, experiments were carried out in the absence and presence of visible radiation or the catalyst alone. The result showed that visible radiation or the catalyst alone was not sufficient for the degradation of this compound. (Fig. S1).

3.1. Degradation of acetaminophen solution

Aqueous drug solution of known concentration was prepared and subjected to visible radiation in the presence of $Zn_{0.2}Cd_{0.8}S$ (0.05 g/100 mL). The change in the absorption spectra of the drug solution was monitored at regular time intervals. The absorption value of drug decreased with irradiation time, indicating degradation of the drug is degrading. The change in the absorption value of the drug can be related in terms of percentage degradation as follows.

$$\%\ \text{Degradation} = \left(\frac{1 - A_f}{A_i}\right) \times 100 \tag{1}$$

where A_i and A_f are the initial and final absorbance values. The variation of absorption for the degradation of the drug as a function of irradiation time is shown in Fig. 2. The data fitted well to pseudo-first-order kinetics with a rate constant of 1.5×10^{-3} min^{-1} and a R^2 value of 0.9957 as shown in Fig. S2.

3.2. Mechanism of acetaminophen degradation

The photocatalytic degradation of drug is believed to take place according to the following mechanism. Energy from visible radiation is absorbed by the catalyst thus promoting its electrons from the valence band to the conduction band. As a result of this phenomenon, an electron–hole pair is produced [24].

$$\text{Catalyst} + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \tag{2}$$

where e_{cb}^- and h_{vb}^+ are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both of these species ($e_{cb}^- + h_{vb}^+$) are highly reactive species which initiate oxidation and reduction reactions on the surface of a catalyst. The oxidation of organic compound is directly performed by positive holes (h_{vb}^+). In aqueous media, h_{vb}^+ reacts with surface bound water molecules and surface HO^- groups to produce $^\bullet OH$, which are known to be strong oxidizing species whereas, e_{cb}^- can react with O_2 to produce superoxide radical anion.

$$H_2O + h_{vb}^+ \rightarrow {}^\bullet OH + H^+ \tag{3}$$

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet -} \tag{4}$$

$$h_{vb}^+ + HO^- \rightarrow {}^\bullet OH \tag{5}$$

The above reactions prevent the combination of the electron and the hole, which are produced in the first step. The $O_2^{\bullet -}$ produced in the above manner can then react with H^+ to produce H_2O_2 which can further produce $^\bullet OH$, and these can react with the drug and is thus responsible for its degradation [25].

$$2H^+ + 2O_2^{\bullet -} \rightarrow H_2O_2 + O_2 \tag{6}$$

$$H_2O_2 + h\nu \rightarrow 2{}^\bullet OH \tag{7}$$

$$^\bullet OH + \text{drug} \rightarrow \text{intermediates} \rightarrow \text{products} \tag{8}$$

3.3. Influence of operating parameters on the photocatalytic degradation of acetaminophen

Operational experimental parameters such as amount of catalyst, drug concentration and pH have a strong

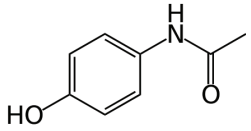

Fig. 1. Structure of acetaminophen.

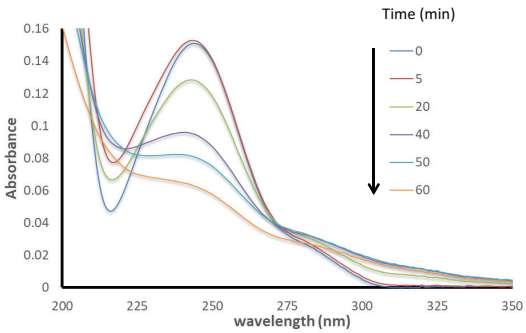

Fig. 2. Absorbance spectra of acetaminophen degradation by $Zn_{0.2}Cd_{0.8}S$ + visible radiation at different time intervals (min). [Acetaminophen] = 1×10^{-5} M, pH = 8, [$Zn_{0.2}Cd_{0.8}S$] = 0.05 g/100 mL solution.

effect on the photocatalytic oxidation rate of a given organic compound. The photocatalytic degradation of acetaminophen (1×10^{-5} M) in aqueous solution with different catalyst concentrations (0.01, 0.025 and 0.05 g/100 mL of solution) was investigated. In the range studied, the effect of catalyst concentration was quite small and within experimental error (<5%). These results are in agreement with other investigations on the optimal operating conditions for acetaminophen photocatalytic oxidation in water [25]. The degradation of acetaminophen (1×10^{-5} M) in aqueous solution was studied under several reaction conditions. In the first experiment, the drug was subjected to visible radiation alone (λ_{max} = 365 nm) for 60 min, and oxygen was bubbled through the reaction. It was observed that no significant degradation of acetaminophen occurred, thus indicating that pure photochemical reactions do not play any role in converting this drug to any other organic compounds. Likewise, no degradation was observed in the presence of the catalyst in dark (Fig. S1). However, when acetaminophen oxidation was performed in the presence of visible radiation and the catalyst with a steady flow of oxygen, the degradation of the drug was observed (Fig. 2).

The adsorption of pollutants on the photocatalyst surface is affected by the pH of the aqueous solution. Therefore, photocatalytic degradation of acetaminophen was observed under different pH conditions (2, 5, 8, 9 and 10) by using HPLC technique. The optimal oxidation was observed at pH = 8 (the natural pH of the aqueous acetaminophen solution). Subsequently, all the degradation

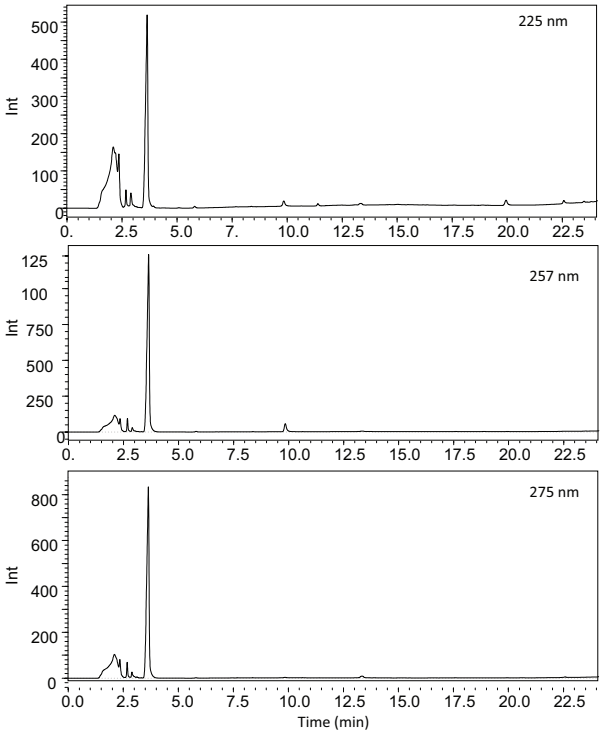

Fig. 3. HPLC–UV/Vis chromatograms of acetaminophen drug after 30 min degradation with $Cd_{0.2}Zn_{0.8}S$ catalyst and visible radiation. Degradation products were monitored at different wavelengths.

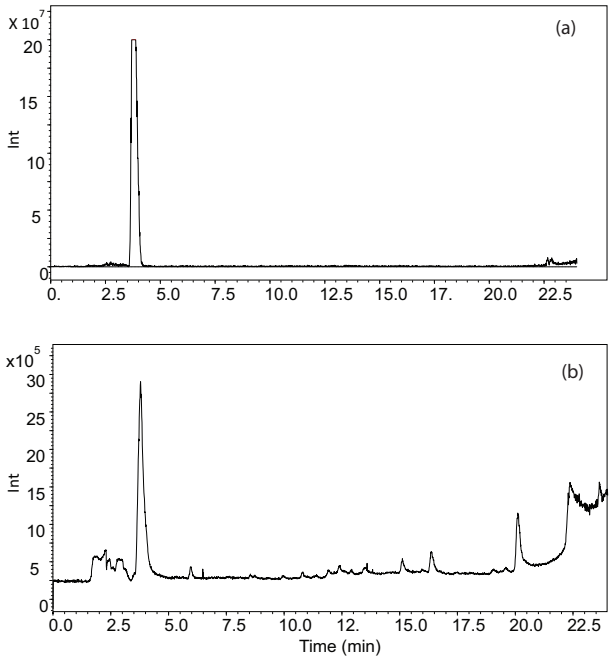

Fig. 4. LC–MS chromatogram of acetaminophen drug (a) before and (b) after photocatalytic degradation for 30 min.

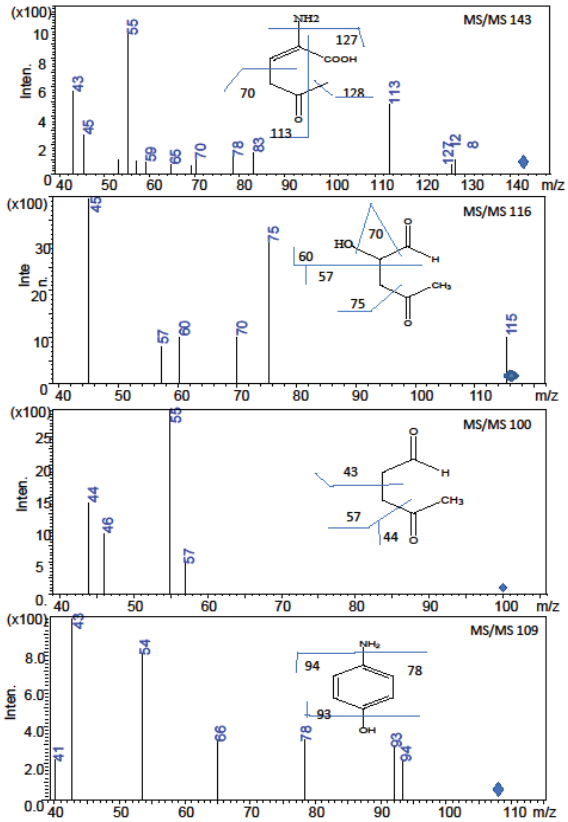

Fig. 5. Tandem mass spectra of degradation products having m/z values 143, 116, 100 and 109, respectively, after photocatalytic degradation.

experiments were performed at this pH value by adding either dilute aqueous HCl or dilute aqueous NaOH solution. The oxidation of acetaminophen is inhibited in strong acidic or basic conditions [14]. In slightly basic pH (8), more hydroxide ions are available on the catalyst surface which are easily oxidized to •OH, which causes the oxidization of acetaminophen molecules [26]. In strongly basic conditions (pH = 10), both the catalyst surface and acetaminophen molecules are negatively charged, thereby increasing electrostatic repulsion between the catalyst surface and the negatively charged (pKa = 9.5) acetaminophen [27].

3.4. LC–UV/VIS–MS studies

The photocatalytic degradation of acetaminophen under optimized conditions was investigated by LC–UV/VIS–MS to determine the intermediate organic compounds formed in the reaction. Fig. 3 shows the LC–UV/VIS chromatograms of the degraded acetaminophen solution as monitored at different wavelengths. Moreover, Fig. 4 shows the LC–MS chromatograms of neat and degraded acetaminophen solution after 30 min of photocatalytic reaction. It was observed that the main peak of acetaminophen which appeared at retention time t_R = 3.9 min, started decreasing gradually and disappeared after 60 min (data not shown). Several other peaks appeared during the degradation experiment as shown in the chromatogram (Fig. 4(b)). These peaks can be ascribed to various intermediates of the acetaminophen degradation. The GC–MS analyses confirmed the presence of some intermediates as shown in Table S2.

3.5. Proposed mechanistic pathways of acetaminophen degradation

It has already been established that the effect of visible radiation on the $Zn_{0.2}Cd_{0.8}S$ leads to the formation of •OH radicals in aqueous medium. Hydroxyl radicals (•OH) have a very short lifetime, so that they can only react where they are formed. The lifetime of •OH radicals is approximately 70 ns in the presence of 1 mM phenol, and its diffusion coefficient is

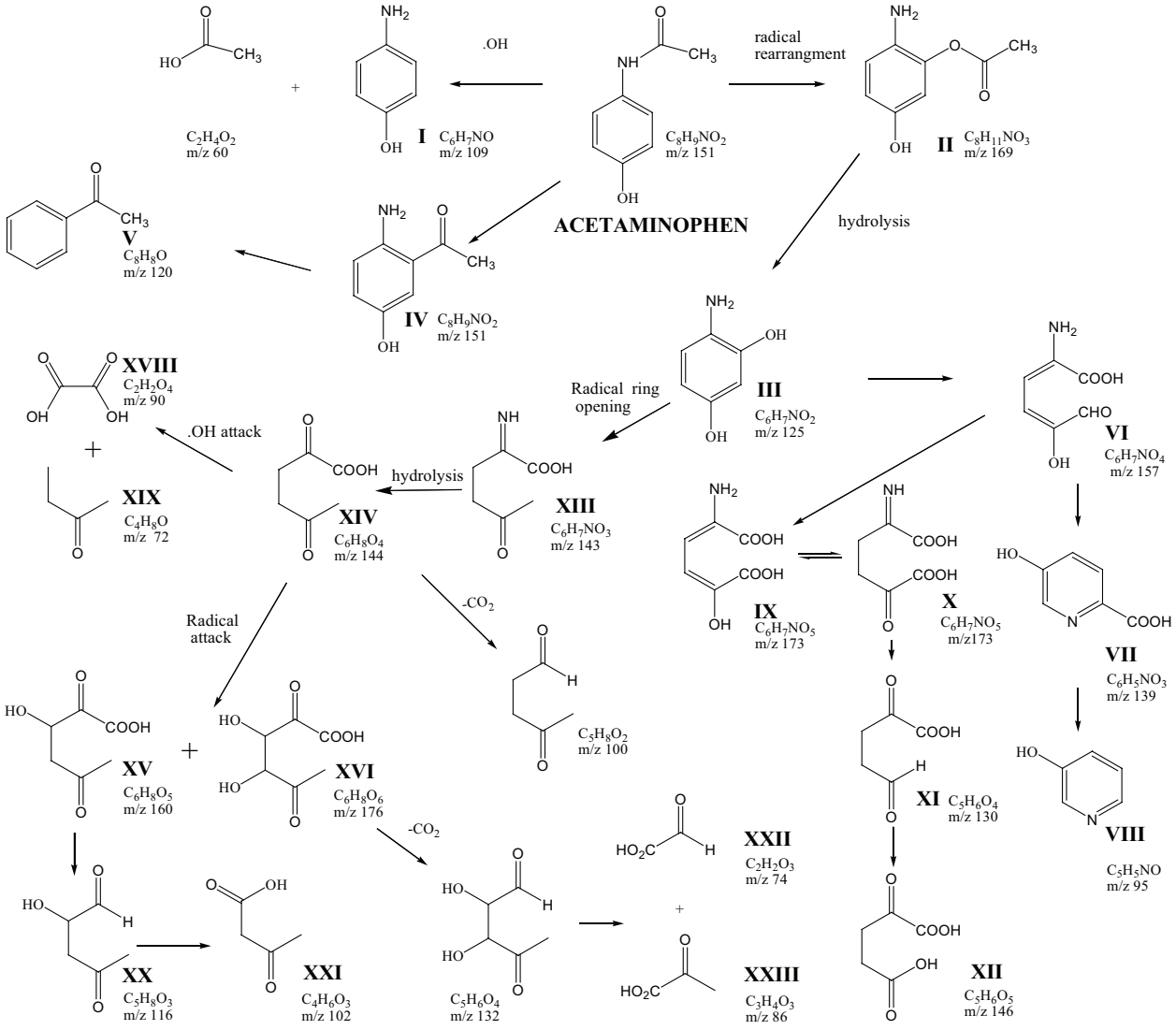

Fig. 6. Proposed radical degradation pathways of acetaminophen.

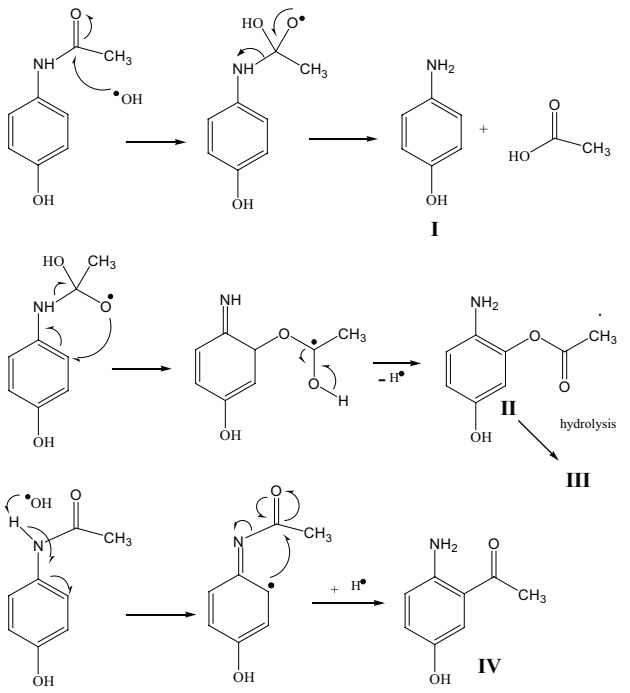

Fig. 7. Mechanism of initial degradation.

estimated to be 2.3×10^{-5} cm^2/s [28]. The •OH radical can diffuse through an average distance of 180 Å, and thus oxidation reactions can be successfully performed in homogeneous media. Because the •OH radicals generated in solution remain in the vicinity of the organic molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the degradation reaction of the organic molecule. The •OH radicals participate in the degradation of acetaminophen either by combining with it to form new hydroxylated compounds or by converting the pollutant into radicals which undergo further reactions. The course of the degradation can be followed by time-lapse analysis of the irradiated acetaminophen samples using LC–MS as shown in Fig. 4. A number of intermediates were observed in LC–MS analysis, and their structures were proposed based on their fragmentation pattern in MS/MS studies (Fig. 5). These intermediates were correlated and are presented in Fig. 6. Several radical-based mechanisms can be inferred and are discussed as follows.

The drug degradation is initiated as a result of ·OH attack on the parent molecule as reported in the literature [29]. The first probable reaction of acetaminophen (m/z 151) is an •OH radical attack on the carbonyl group leading to an oxy radical which then collapses to *p*-aminophenol (I, m/z 109) and an acetate anion (Fig. 7). The oxy radical can also participate in an intramolecular ortho attack on the phenyl ring to produce a phenate ester (II, m/z 169) which is

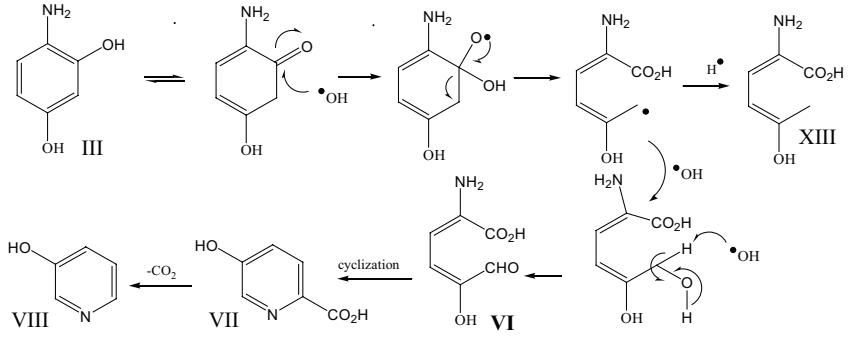

Fig. 8. Degradation of compound III.

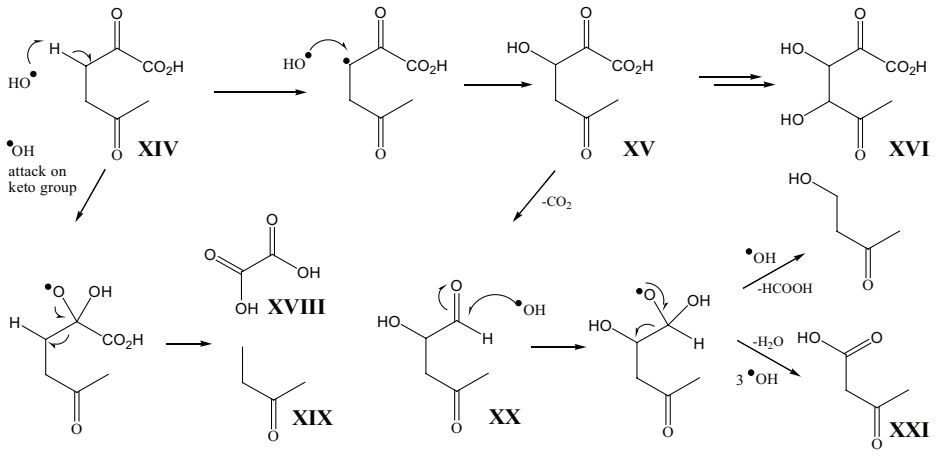

Fig. 9. Degradation of compound XIV.

subsequently hydrolyzed to compound III (m/z 125) (Fig. 7). This compound can be considered as a parent degradation product from which other pathways arise. These are discussed as follows. Another possible radical reaction of acetaminophen is the formation of acetophenone derivative IV (m/z 151), which occurs through the generation of a phenyl radical followed by a 4-exo-trig attack on the amide carbonyl and cleavage of the amide bond. Compound IV is a potential source of acetophenone V (m/z 120).

3.6. Pathways involving parent degradation product III

The degradation compound III can occur through different pathways leading to small molecules such as acetate, oxalate and butanoates. The first notable one is the formation of pyridine derivative VIII (m/z 95). Fig. 8 shows a plausible radical reaction pathway. •OH-mediated cleavage of the phenyl ring produces a carboxylic group and a stable allyl radical, which is then hydroxylated to an allylic alcohol. The latter is oxidized to an aldehyde (VI, m/z 157) and then undergoes a cyclic condensation reaction with the primary amine to produce pyridine derivative VII (m/z 139). Further radical decarboxylation then leads to VIII (m/z 95). The mechanism of the decarboxylation has been reported [30].

The aldehyde VI (Fig. 8) is converted to diacid IX (m/z 173). The latter can be represented in its tautomeric form X. Hydrolysis of imino group and mono-decarboxylation of X produces aldehyde XI (m/z 130), which is then oxidized to XII (m/z 146). The oxidation of the aldehyde to the carboxylic acid is thought to be •OH-radical facilitated as reported in the literature [29].

Another degradation pathway identified in this study also involve compound III. Ring cleavage of III yields compound XIII (m/z 143) from a common radical (Fig. 8). XIII is hydrolyzed to XIV ((m/z 144) which is further degraded to an oxalate (XVIII, m/z 146). and 2-butanone (XIX, m/z 146). The mechanism for this transformation is given in Fig. 9.

Hydroxylation of XIV through •OH leads to alcohol XV (m/z 160) and diol XVI (m/z 176). Decarboxylation of XV offers XX (m/z 116), which is further degraded to butanone derivatives XXI (m/z 102). Likewise, the diol XVI is converted to lower molecular weight compounds XXII (m/z 74) and XXIII (m/z 86).

4. Conclusion

$Zn_{0.2}Cd_{0.8}S$ catalyst was used to degrade acetaminophen under optimized conditions in the presence of visible radiation. More than 60% of the acetaminophen was converted into products in 1 h, and the products were identified by LC–MS–MS and GC–MS. The major products identified were low-molecular weight carboxylic acids in addition to pyridine derivatives. The degradation was initiated by •OH radicals and proceeded through hydroxylation, decarboxylation, isomerization, ring opening and hydrolysis.

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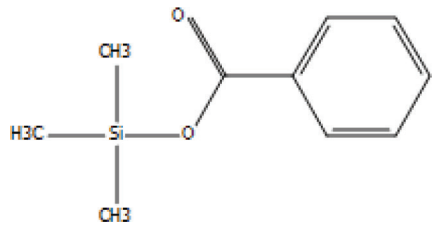
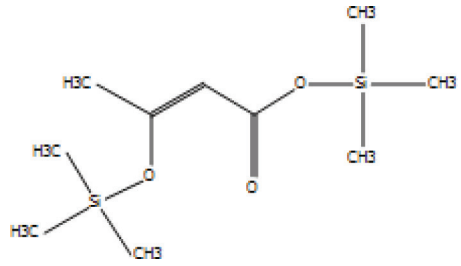
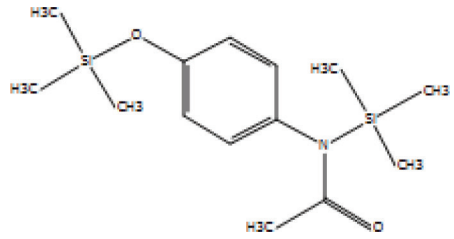
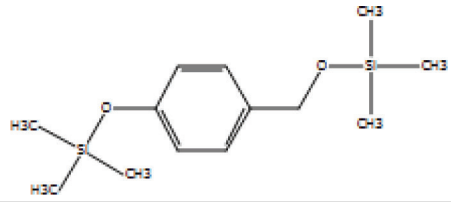
Supplementary materials

Table S1
Rate constant values for the acetaminophen degradation using different molar ratios of Cd and Zn in the catalysts ($Cd_xZn_{1-x}S$)

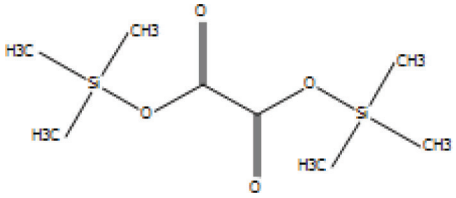
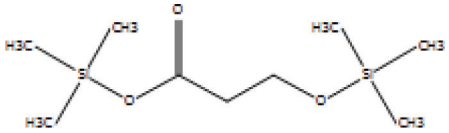
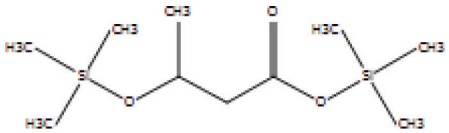
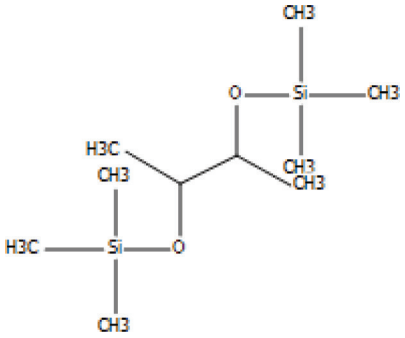
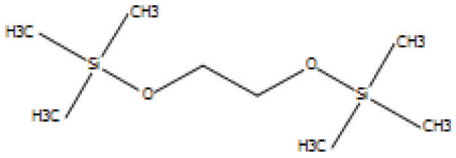
Catalyst	Rate constants (sec^{-1})
CdS	4.00×10^{-4}
$Cd_{0.2}Zn_{0.8}S$	5.00×10^{-4}
$Cd_{0.5}Zn_{0.5}S$	3.00×10^{-4}
$Cd_{0.8}Zn_{0.2}S$	2.00×10^{-4}
ZnS	0.800×10^{-4}

Table S2
List of degradation products of acetaminophen after reaction with $Zn_{0.2}Cd_{0.8}S$ and sunlight radiation

No.	Proposed products	Retention time (min)/ molecular weight	Molecular weight without TMS	Major ion peaks (relative intensity)
1		7.25/194	105	51(10), 77(54), 105(79), 106(7), 135(54), 136(6), 179(100), 180(14), 181(5), 194(7)
2		7.36/234	145	45(20), 67(14), 77(53), 147(100), 148(14), 149(18), 157(22), 231(45), 232(13), 253(13)
3		16.03/223	144	73(100), 74(17), 116(26), 181(26), 182(19), 206(89), 279(56), 280(67), 294(39), 295(39)
4		10.863/268	179	73(100), 91(10), 106(11), 133(14), 163(11), 179(31), 209(14), 253(40), 267(14), 268(30)

(*Continued*)

Table S2 (*Continued*)

No.	Proposed products	Retention time (min)/ molecular weight	Molecular weight without TMS	Major ion peaks (relative intensity)
5		5.27/234	145	43(6), 45(8), 52(9), 66(7), 72(6), 73(100), 74(9), 147(75), 148(10), 149(7)
6		5.466/234	145	56(12), 58(12), 73(73), 101(16), 133(17), 147(100), 148(19), 149(13), 177(17), 219(13)
7		5.756/247	158	45(8), 66(8), 73(67), 75(29), 88(14), 117(45), 147(100), 148(17), 191(23), 233(9)
8		11.321/234	145	44(6), 45(11), 68(6), 73(100), 103(7), 117(95), 118(11), 135(6), 147(26), 218(15)
9		12.687/206	117	73(81), 74(9), 103(15), 147(51), 148(13), 155(11), 191(100), 192(25), 193(15), 244(13)

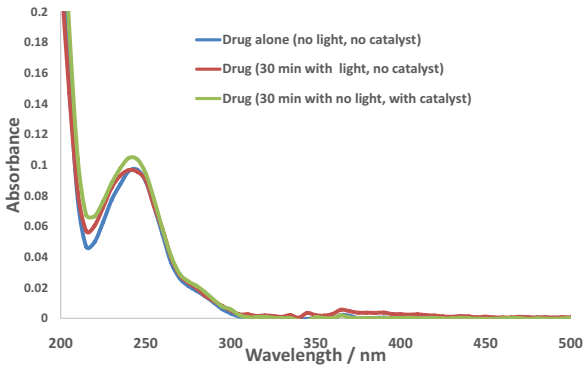


Fig. S1. UV–Vis spectra of acetaminophen with catalyst alone (no light) and acetaminophen with light but without catalyst.

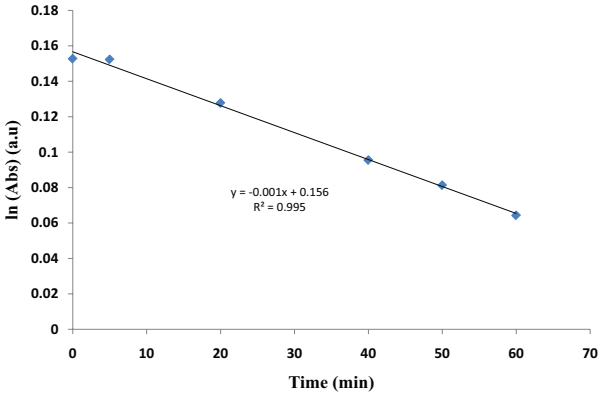


Fig. S2. Change in absorbance value of acetaminophen vs. time.