



Removal of acetaminophen from water by simulated solar light photodegradation with ZnO and TiO₂ nanoparticles: Catalytic efficiency assessment for future prospects



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ABSTRACT

This study aims to comparatively assess TiO₂ and ZnO catalysts in photodegradation of aqueous acetaminophen solution. Commercial TiO₂ (anatase and rutile phases), synthetic TiO₂ (rutile) commercial ZnO (wurtzite), and synthetic ZnO (wurtzite) are all described; the synthetic ZnO and TiO₂ were synthesized by thermal precipitation method. XRD, SEM, UV-vis spectroscopy, and BET/BJH were used for catalysts characterization. The photocatalytic experiments have been carried out using solar simulated radiation (0.0146 W/cm²). A 50 mL solution of an appropriate acetaminophen concentration was studied. The ZnO systems showed higher catalytic efficiency than the TiO₂ counterparts. Among the TiO₂ systems, the commercial anatase showed highest activity, followed by the synthetic system (rutile). Among the ZnO systems, the synthetic catalyst shows higher efficiency than the commercial counterpart. Based on its superior efficiency, the synthetic ZnO has been singled out for further investigation to find optimal working conditions. The pH plays a main role in photodegradation process, the synthetic ZnO photodegraded ~97 % of acetaminophen at pH = 9 in 1 h of irradiation. The acetaminophen photodegradation in basic to neutral condition is better than acidic solutions. The synthetic ZnO particles completely mineralized acetaminophen within 120 min at pH = 7. This is confirmed by electronic absorption spectrophotometry, high-performance liquid chromatography and total organic carbon measurements. The photodegradation rate was increased with increasing the amount of loaded ZnO up to a steady-state limit of 0.1 g. Effects of different reaction parameters, on synthetic ZnO catalyst efficiency in acetaminophen photodegradation, are studied to find out the optimal conditions.

1. Introduction

Pharmaceutical compounds have become serious water contaminants, with some exceeding the threshold limit in drinking water [1,2]. Different water purification methods are widely used including, physical, biological and chemical processes [3–6]. For example, chlorination is effective in water purification but may cause production of more chlorinated hydrocarbons in water [7]. Ozonation and UV radiation are effective but are costly and limited to small scale usage [8]. Advanced oxidation processes (AOPs) can be an alternative. In AOPs,

powerful oxidizing species such as ([·]OH) are produced upon expose of semiconductor particle catalyst to light [5,9–16,18–29]. Chemically stable semiconductors like TiO₂ and ZnO have the ability to produce active species upon irradiation with suitable wavelengths [30,31]. The resulting active species ([·]OH) can completely mineralize water organic contaminants [32]. The suggested schematic mechanism is shown in Scheme 1.

TiO₂ (with its two forms the less stable and more active anatase, and the more stable but less active Rutile), and ZnO can use the UV radiations present in the oncoming solar light. Both natural solar light and

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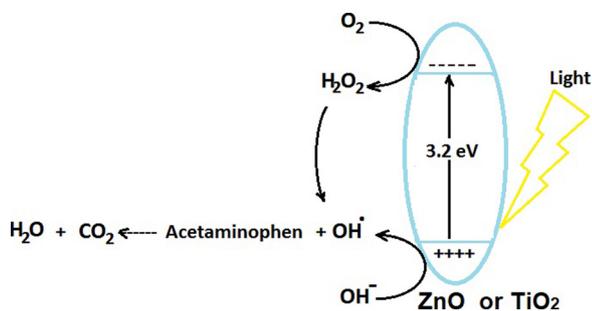
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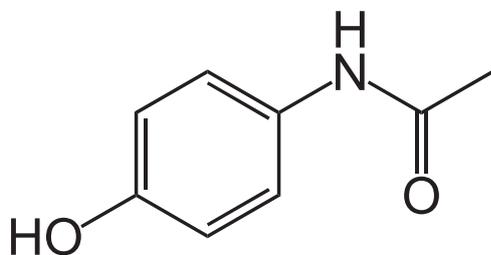
Scheme 1. Schematic of photocatalytic mechanism of TiO₂ or ZnO.

solar simulated light contain a UV tail (~5 %). Both ZnO and TiO₂ systems can be excited by this small UV tail and catalyzed photodegradation water organic contaminants [16,30,33]. The ability of these catalysts to function under direct solar light is due to their sensitivity to the UV tail, not due to the visible light region itself as claimed in different places [34–39]. Therefore, the relative catalytic efficiency is presumably determined by the ability of the solid to absorb in the solar UV tail. Visible region can also be used in cases for doped TiO₂ systems [40–45].

Despite the higher stability of TiO₂ under different conditions [46–48], the ZnO has higher absorptivity for the UV tail present in solar radiation [49]. Therefore, a critical comparative assessment for the two catalytic systems under solar simulated light is useful. This is one major goal of this communication. Different types of ZnO and TiO₂ solids, all in the nano-scale, are involved to find the best photocatalyst conditions, keeping in mind natural conditions where water purification is needed under solar simulated light instead of pure UV irradiation.

Acetaminophen contaminant has not been arbitrarily chosen. Acetaminophen (Paracetamol), with molecular structure shown below (Scheme 2), has been globally used in medication for many years. It is commercially produced in huge amounts [50]. Acetaminophen and structural analogs are ubiquitous in the natural environment and easily accumulate in the aquatic environment, which has been detected in surface waters, wastewater, and drinking in different areas [51,52]. Contamination with this compound is more profound in densely populated urban areas [53]. Aquatic environments and drinking water are being contaminated with acetaminophen [51]. It is among the top three drugs prescribed in England and among the top 200 drugs prescribed in the USA [54,55]. For these reasons, complete removal of acetaminophen contaminant from waters is imperative.

TiO₂ and ZnO were reported in photodegradation of acetaminophen [56,57] under UV radiation [58] but not under direct or simulated solar light to our knowledge. Alternatively, the present study aims at finding an efficient catalyst that functions under direct solar light (or at least solar simulated light) while using conditions that resemble natural conditions, with minimal processing cost. To find out the most efficient catalyst, different solids TiO₂ (commercial anatase, commercial rutile, and lab synthesized rutile) and ZnO (commercial wurtzite and lab synthesized wurtzite) powders were investigated here. All solids have been characterized by X-ray diffraction (XRD), scanning electronic microscopy (SEM) and UV–vis spectroscopy. Photocatalytic study has



Scheme 2. Acetaminophen molecular structure.

then been comparatively performed. As the most effective catalyst system is the synthetic wurtzite ZnO, its optimal working conditions have then been studied. The effects of pH, contaminant concentration and catalyst concentration, on catalytic efficiency in the photodegradation of acetaminophen, have been studied to check the suitability of the process for natural water purification under natural conditions.

As this work shows lab scale study results, they can be scaled up to pilot plant processes for future large scale study. For this purpose, a future vision on how to extend this study to involve continuous flow rate processing is proposed. Multi-use of the semiconductor catalyst under photodegradation processes is also envisioned in this work.

2. Experimental

2.1. Chemicals

Zinc oxide (Product No. 544906, CAS Number 1314-13-2), titanium dioxide Anatase (Product No. 232033, CAS Number 1317-70-0), and Rutile (Product No. 637262, CAS Number 1317-80-2) nanopowders have been purchased from Sigma Aldrich Co. Other chemicals, ZnCl₂, NaOH, HCl, TiCl₃ and others, are have also been purchased from Sigma Aldrich Co. Acetaminophen (a pharmaceutical compound commercially known as Paracetamol) was kindly donated by Pharmicare Co., Ramallah in pure form.

2.2. Equipment

Different characterization measurements were made for ZnO and TiO₂ nanopowder systems. A Shimadzu model TCC-260 spectrophotometer was used for UV–vis electronic absorption spectral measurement in aqueous dispersion form. The dispersions were made by mixing different powders (0.10 g) in 100 mL distilled water. A Philips XRD X'PERT PRO diffractometer, with Cu Kα ($\lambda = 1.5418 \text{ \AA}$) as a source, was used for X-ray diffraction (XRD) measurement. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements were achieved using FE-SEM/EDS Jeol microscope, Model JSM-6700 F. Brunauer-Emmett-Teller (BET) method was employed to assess the specific surface area based on the nitrogen adsorption/desorption isotherms using a traditional lab manually prepared vacuum line system.

A 1525 Binary Waters HPLC with a dual absorbance detector using a Symmetry C18 column and a mobile phase of 1% acetic acid aqueous solution and methanol (40:60) was used for acetaminophen analysis. A SHIMADZU Total Organic Carbon analyzer (TOC-L) was used for total organic carbon analysis.

2.3. Catalyst preparation

2.3.1. ZnO nanopowder preparation

The ZnO nanoparticles have been synthesized by direct and simple thermal precipitation method, that does not need an autoclave step as in the case of utilizing the hydrothermal method. A solution of NaOH (250 mL, 0.9 M) was heated to 55 °C with magnetically stirred, then ZnCl₂ solution (250 mL, 0.45 M) was added dropwise to the stirred NaOH solution in a period of an hour [11]. The produced white precipitate was left to settle, the supernatant was drained out, and the precipitate was rinsed with distilled water many times to ensure removal of all foreign ions. The ZnO precipitate nanopowder was then dried, calcined at 450 °C and left for further characterization and uses.

2.3.2. TiO₂ nanopowder preparation

A precipitation method was followed to prepare TiO₂ nanopowder. A solution of NaOH (200 mL, 0.5 M) was magnetically stirred, then a 50 mL TiCl₃ (12 % in HCl solution) was placed in a burette and dropwise added to the NaOH solution with continuous stirring [13]. The pH of

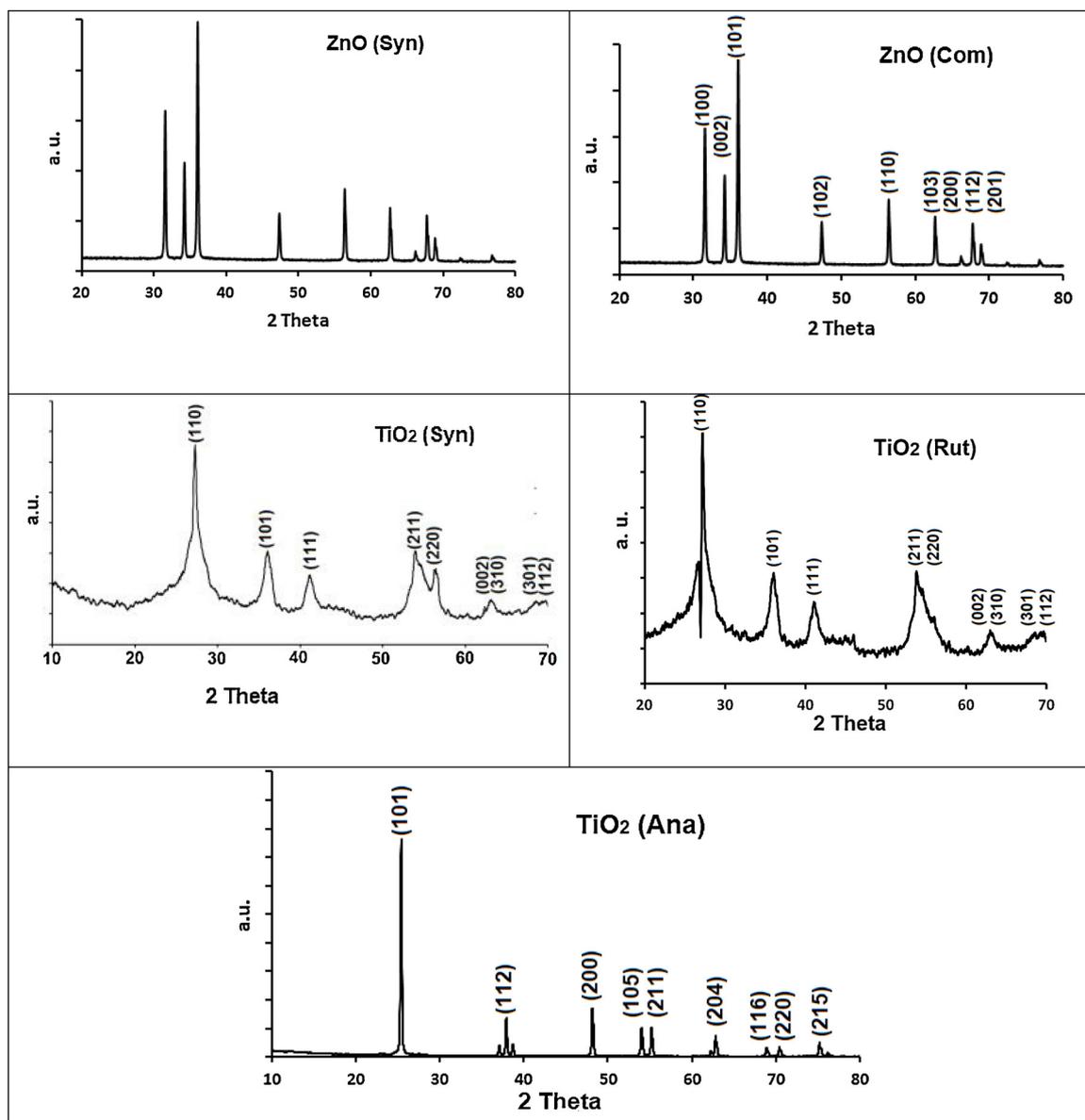


Fig. 1. XRD patterns measured for different solid catalyst systems.

the solution was then adjusted to ~ 3.5 . The resulting white TiO_2 nanopowder was separated and rinsed many times for further purification from foreign ions. The produced TiO_2 powder was dried and calcined at 550°C for an hour and then kept for further characterization and use.

2.4. Photocatalytic experiments

Different photocatalytic experiments have been conducted to reach the best catalyst and optimum conditions for acetaminophen photodegradation. Five types of nano-size catalysts were investigated; commercial anatase TiO_2 , commercial rutile TiO_2 , commercial ZnO, synthesized TiO_2 , and synthesized ZnO were all examined. The photocatalytic experiments were conducted by stirring a specific amount of the catalyst in 50 mL solution of known acetaminophen concentration. The solution pH was adjusted by adding drops of dilute HCl or NaOH solution. The solution was exposed to light with stirring and thermostated at 25°C ($\pm 2^\circ\text{C}$) for an hour. A 400 W Osram Tungsten Halogen lamp was used as a source of solar simulated light. The lamp spectrum is a bell curve with little ($\sim 5\%$) in the UV region, just like the natural sun radiations that reach earth. The incident

radiation intensity at the reaction mixture surface was 0.0146 W/cm^2 . Small aliquots of solution were syringed out from reaction vessel at different reaction times then centrifuged at 5000 r/m for 5 min. The supernatant was then transferred to a quartz cell and spectrophotometrically analyzed at 243 nm, as described in literature [59].

Complete mineralization of acetaminophen under photodegradation experiments was confirmed by different analysis techniques. A beaker containing (100 mL, 40 ppm) acetaminophen with 0.2 g synthetic ZnO (the superior catalyst) was thermostated at 25°C ($\pm 2^\circ\text{C}$). The mixture was stirred under solar simulated light. Aliquots of solution were syringed out from reactor with time periods (0, 30, 60, 90, and 120 min) during the photodegradation experiments and centrifuged. As per Quality Assurance, the Quality Control Manual by National Water Quality Laboratory [60] was followed during sample collection, storage and analysis. After centrifugation, the liquid phase samples were kept refrigerated in the dark inside polyethylene tubes for analysis.

The supernatants were analyzed by UV-vis spectrophotometry, HPLC and TOC. HPLC analysis was performed using a C18 column and isocratic elution with a flow rate of 1.0 ml/min, as described in Section 2.2 above. All solvents were filtered through a $0.45\ \mu\text{m}$ Millipore filter

before use and degassed in an ultrasonic bath. Volumes of 10 μl samples were injected into the column, and quantification was performed by measuring at 254 nm. The total organic carbon TOC analysis was calculated as a difference between total carbon (TC) and total inorganic carbon (TIC) for the same sample.

Each analysis method was validated and controlled by standard materials analysis based on known procedures for lab analysis [61]. In electronic absorption analysis of remaining acetaminophen, a calibration curve was constructed using known concentrations with triplicate measurement for each concentration. The resulting calibration curve (with $R^2 = 0.995$) was used for acetaminophen analysis in samples taken as described above with time. To further check measurement reliability and validity, a sample with known concentration of acetaminophen was routinely used during the analysis.

To check the reliability of the TOC analysis, a sample of known acetaminophen concentration (known carbon content) was analyzed for TOC. The TOC analysis was measured three times for each sample, and the mean and standard deviation values were calculated and tabulated in the Results Section.

To validate BET specific surface area (SSA) measurements, a dried TiO_2 standard powder sample of known SSA of $50 \text{ m}^2/\text{g}$ was purchased from Sigma-Aldrich. The dried standard sample was used to check the validity of BET SSA results for other solid materials.

A standard crystalline silicon sample was used to calibrate the XRD analysis equipment. The pH meter was calibrated before each set of measurements. The light intensity was measured and adjusted at the beginning, middle and end of each experiment using a Lux-meter.

3. Results and discussions

3.1. Catalyst characterizations

3.1.1. X-Ray diffraction analysis

XRD patterns for all used catalyst systems are shown in Fig. 1. The XRD patterns confirm the wurtzite type for both commercial ZnO and synthesized ZnO. The particle sizes for all solids were estimated based on the Scherrer equation for specific XRD pattern reflections. The average particle sizes were $\sim 43 \text{ nm}$ for commercial ZnO and $\sim 38 \text{ nm}$ for synthesized ZnO. The synthesized TiO_2 was in the stable rutile type based on XRD pattern, with average particle size $\sim 33 \text{ nm}$ based on the Scherrer equation. The average particle size is $\sim 35 \text{ nm}$ for commercial rutile TiO_2 and $\sim 30 \text{ nm}$ for commercial anatase TiO_2 , Table 1. There is no significant changes in particles size of the synthesized ZnO and TiO_2 comparing to commercialized ZnO and TiO_2 .

3.1.2. Scanning electron microscopy (SEM)

The SEM images measured for all solids are shown in Fig. 2. The SEM images show nanorods with $\sim 20 \text{ nm}$ in width and $\sim 70 \text{ nm}$ in length for both commercial ZnO and synthesized ZnO. The ZnO nanoparticles are agglomerated into larger aggregates ($\sim 150 \text{ nm}$). The SEM images confirm the presence of agglomeration ($\sim 200 \text{ nm}$) of smaller nano-scale particles confirmed by XRD ($\sim 33 \text{ nm}$) for the synthesized TiO_2 . The micrographs also show that the commercial rutile TiO_2 has large agglomerates ($\sim 230 \text{ nm}$), involving nanoparticles (average $\sim 35 \text{ nm}$) as confirmed by XRD. Based on SEM, the anatase TiO_2 has agglomerates ($\sim 250 \text{ nm}$), with average nanoparticles in the range $30 - 35$

Table 1

The XRD results of different catalyst systems showing the JCPDS card No., Reflection peaks used in Scherrer calculations, and the crystalline particle sizes.

Catalyst system	JCPDS card no.	Reflection peaks used in Scherrer calculation	Average crystalline size based on Scherrer (nm)
ZnO (Com)	JCPDS card no. 79- 2205	100, 002, 101	43
ZnO (Syn)	JCPDS card no. 79- 2205	100, 002, 101	38
TiO_2 (Syn)	JCPDS card no. 21-1276	110, 101, 111	33
TiO_2 (Rut)	JCPDS card no. 21-1276	110, 101, 111	35
TiO_2 (Ana)	JCPDS card no. 21-1272	101, 112, 200	30

nm as confirmed by XRD.

The specific surface area values, the average pore volume, and the average pore size were calculated based on Nitrogen adsorption/desorption isotherms. The calculations followed the BET/BJH method [62]. All measurements were carried out by using a traditional lab manually prepared vacuum line system. The results for all solid catalysts are presented in Table 2. The specific surface area of the five catalyst systems was relatively low. This reduction in the BET surface area is attributed to the lack of porosity. This is confirmed by the small values of the calculated pore volumes, Table 2.

3.1.3. Electronic absorption spectra

UV-vis absorption spectra (200–800 nm range) have been measured for ZnO and TiO_2 nanopowders suspended in water, Fig. 3. The synthesized ZnO shows an intense absorption maximum at $\sim 380 \text{ nm}$, while commercial ZnO shows lower intensity band at the same wavelength. Anatase TiO_2 shows absorption edge at $\sim 380 \text{ nm}$ with significant intensity compared with other TiO_2 absorptions. The rutile TiO_2 shows less intense absorption with a maximum at $\sim 380 \text{ nm}$, while the synthesized TiO_2 shows a less intense broad absorption at $\sim 380 \text{ nm}$.

3.2. Photocatalytic experiments

3.2.1. Effect of catalyst type

The photodegradation of acetaminophen (50 mL, 20 ppm) catalyzed by different catalyst systems (0.1 g) using solar simulated light for 1 h was examined, Fig. 4. The comparative efficiency results, expressed in terms of turnover frequency (TF, number of reacted contaminant molecules per catalyst formula unit per an hour) and quantum yield (QY, number of reacted contaminant molecules per incident photon) for different catalysts are summarized in Table 3.

The commercial anatase TiO_2 exhibits higher efficiency than commercial rutile TiO_2 . The superiority of anatase TiO_2 is due to its ability to have longer electron/hole lifetime than the rutile, as described earlier [63,64]. This behavior explains the ability of anatase type to degrade more acetaminophen ($\sim 50 \%$) compared to rutile type (17 %). The synthetic rutile TiO_2 shows higher acetaminophen photodegradation ($\sim 20 \%$) compared to commercial rutile TiO_2 .

ZnO system shows higher photocatalytic efficiency than the TiO_2 system. That's attributed to the higher sensitivity and absorptivity of ZnO in the UV tail present in solar and solar simulated light, as reported earlier [65].

The synthetic ZnO system degrades about 83 Percentage of acetaminophen in 1 h irradiation, while the commercial ZnO degrades only about 60 % of the contaminant in the same time. The superiority of synthetic ZnO particles compared to commercial particles is due to its smaller size. This increases the catalyst specific surface area, and consequently increases the amount of produced active species during irradiation.

3.2.2. Effect of pH on catalyst photodegradation efficiency

The effect of pH on the photocatalytic efficiency of different catalyst systems (0.1 g) on acetaminophen (50 mL, 20 ppm) has been investigated. The pH value can influence the solid catalyst surface charge and can affect the equilibrium structure state of the contaminating

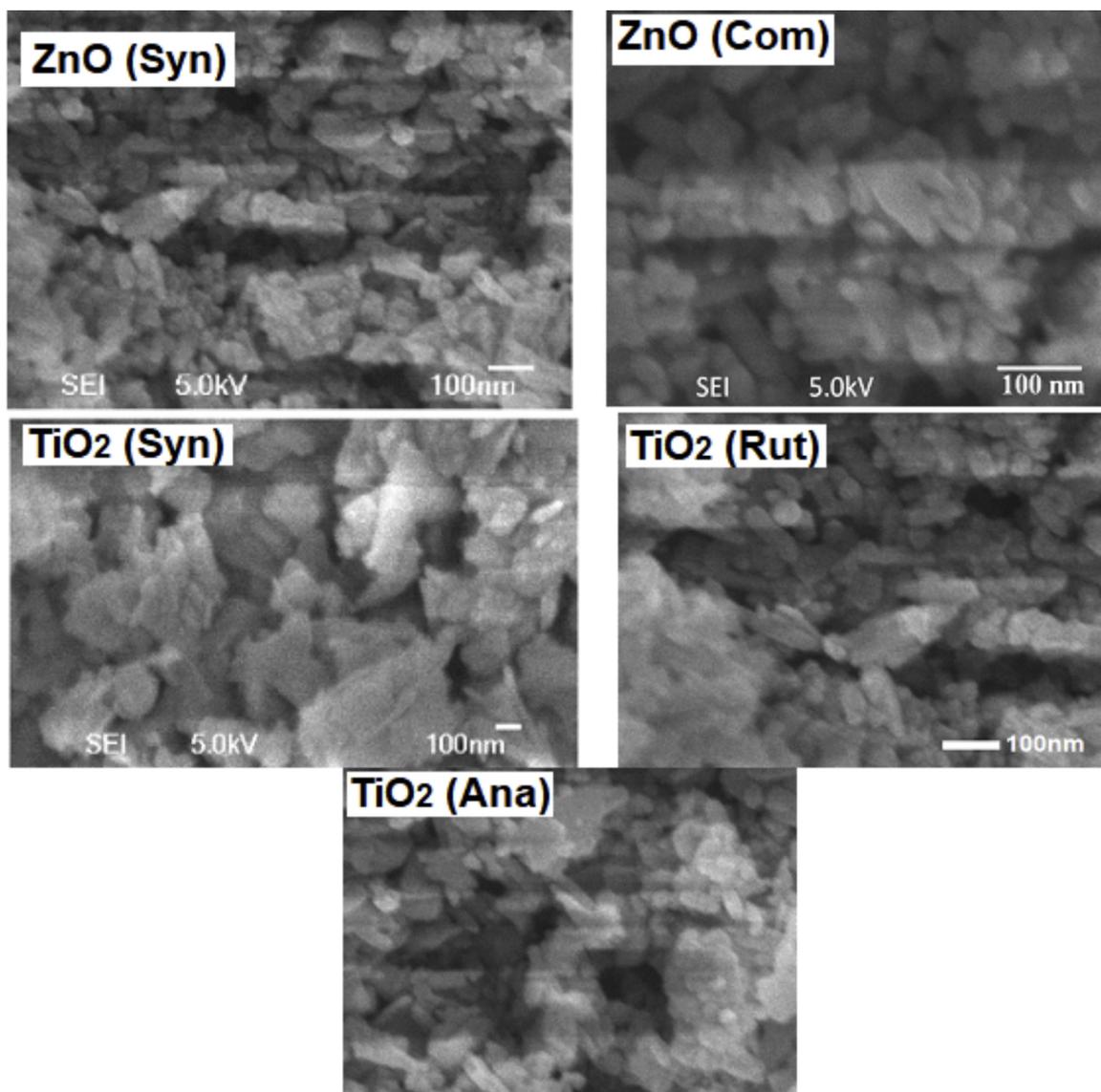


Fig. 2. SEM images for measured for different solid catalysts.

Table 2

Different catalyst system surface area, average pore volume, and average pore size. Calculations are based on BET/BJH nitrogen adsorption isotherms.

Catalyst system	BET specific surface area, (m ² /g)	Average pore volume, (cm ³ /g)	Average pore size, (nm)
ZnO (Com)	18	0.038	2.1
ZnO (Syn)	27	0.043	2.3
TiO ₂ (Syn)	20	0.032	2.5
TiO ₂ (Rut)	14	0.028	2.0
TiO ₂ (Ana)	18	0.023	2.2

molecules. The zero point of charge (pH_{zpc}) of the solid plays a main role in the adsorption and desorption between the contaminant molecules and the catalyst solid surface. This makes the studying of photodegradation at a wide pH range is necessary. Different pH values (3, 5, 7, 9 and 11) were used, keeping in mind that natural waters have pH values in the range 5–9 [66]. Fig. 5 summarizes the effect of pH on different catalyst systems exposed to solar simulated light for 1 h. Quantitative efficiency comparative results are summarized in Table 4. The ZnO systems show higher photocatalytic efficiencies at all pH values than TiO₂ systems.

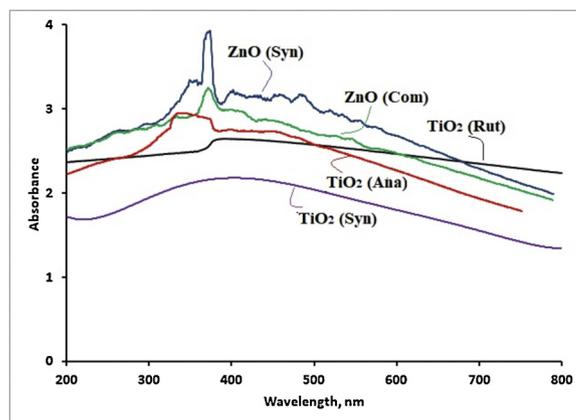


Fig. 3. Solid electronic absorption spectra measured for different solid catalyst systems suspended in water. Water is used as baseline.

For ZnO systems, photodegradation of acetaminophen was superior at $\text{pH} = 9$, followed by a neutral medium. Similar behavior also occurred for TiO₂ systems. The pH value affects the surface charges of solid ZnO and TiO₂. Acetaminophen structure is also affected by pH

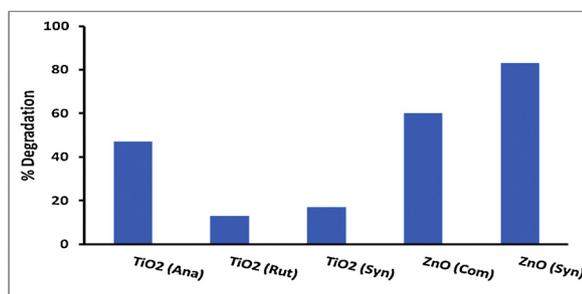


Fig. 4. Comparison between efficiencies for different catalysts in acetaminophen degradation. Experiments conducted using acetaminophen (50 mL, 20 ppm) mixed with 0.1 g catalyst at pH = 7. Exposure time 60 min. Ana is anatase, Rut is rutile, Syn is synthetic, Com is commercial.

value [67].

In ZnO systems, the photodegradation of acetaminophen occurs more readily at pH 9 than at pH 11. This is because acetaminophen (with $pK_a \approx 9.3$) occurs as charged anions at pH higher than pK_a [68]. As the ZnO catalyst surface is also negatively charged at pH > pH_{pzc} (~9.2) [67], the acetaminophen molecules are retarded away from the catalyst surface and away from the nearby $\cdot OH$ radicals [69]. The lowering in photodegradation activity of ZnO in neutral and acidic solutions is attributed to the positively charged ZnO surface at pH < 9 (pH_{pzc}) [70]. Acetaminophen is neutral with different resonance structures at pH < pK_a (9.3) [71]. At pH < 9.3 the acetaminophen acts as Lewis base, towards positive ZnO surface, by the lone pairs present on nitrogen and oxygen atoms. The photodegradation activity increase with pH, up to pH = 9, is due to an increase in the concentration of OH^- which is the main source for $\cdot OH$ (main active species in the photodegradation mechanism) [67,72].

The TiO₂ system, with surface zero point charge $pH_{pzc} \sim 6.2$, has a negatively charged surface at pH > 6.2 and a positively charged at pH < 6.2. The photodegradation rate of acetaminophen increase with higher pH, up to pH = 9, is understandable. Acetaminophen assumes neutral charge up to pH < pK_a (9.4), as discussed above. Therefore, repulsion and retardation are not the main factors. Photodegradation rate increase with pH in this range is thus due to increasing concentration of OH^- that is a source of hydroxyl radical ($\cdot OH$). At pH 11, which is higher than pH_{pzc} of TiO₂ and higher than acetaminophen pK_a , the TiO₂ is negatively charged and acetaminophen exists in its anionic form. Acetaminophen is thus retarded away from TiO₂ surface, leading to some inhibition in the photodegradation process [67].

Among different catalyst systems, the synthesized ZnO shows superiority in photodegradation of acetaminophen at different pH values. Therefore, all photocatalytic studies described below are performed using synthesized ZnO nanopowder, unless otherwise stated. Effects of different factors described below show the optimal working conditions for the synthesized ZnO photocatalyst.

3.2.3. Effect of acetaminophen concentration on photodegradation with synthesized ZnO

Different acetaminophen concentrations (10, 20, 30, and 40 ppm, in 50 mL solution) were studied using synthetic ZnO (0.1 g) under solar

Table 3

Comparison between efficiencies of different catalyst systems. Experiments conducted using acetaminophen (50 mL, 20 ppm) mixed with 0.1 g catalyst at pH = 7. Exposure time 60 min.

Catalyst	%Degradation	Degraded molecules ($\times 10^{18}$) per an hour	TOF ($\times 10^{-3}$) (molecules/formula unit. h)	QY ($\times 10^{-4}$) (molecule/photon)
TiO ₂ (Ana)	47 %	1.88	2.50	6.48
TiO ₂ (Rut)	13 %	0.52	0.69	1.79
TiO ₂ (Syn)	17 %	0.68	0.91	2.34
ZnO (Com)	60 %	2.40	3.24	8.28
ZnO (Syn)	83 %	3.32	4.06	11.45

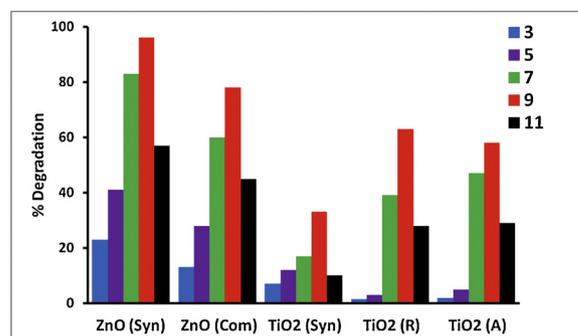


Fig. 5. Effect of pH on acetaminophen percentage degradation on different catalyst efficiencies. Experiments conducted on acetaminophen (50 mL, 20 ppm) mixed with different catalysts (0.1 g) using different pH values. Exposure time 60 min.

Table 4

Comparative efficiency values for different catalyst systems under different pH values in acetaminophen degradation. Experiments conducted on acetaminophen (50 mL, 20 ppm) mixed with different catalysts (0.1 g) using different pH values. Exposure time 60 min.

Catalyst	pH	% Degradation	Degraded molecules ($\times 10^{18}$)	TOF (molecules/formula unit. h) ($\times 10^{-3}$)	Q.Y (molecule /photon) ($\times 10^{-4}$)
TiO ₂ (Ana)	3	2	0.08	0.11	0.28
	5	5	0.2	0.27	0.69
	7	47	1.88	2.51	6.48
	9	58	2.32	3.09	8.00
	11	29	1.16	1.55	4.00
TiO ₂ (Rut)	3	1.5	0.06	0.08	0.21
	5	3	0.12	0.16	0.41
	7	39	1.56	2.08	5.38
	9	63	2.52	3.36	8.69
	11	28	1.12	1.49	3.86
TiO ₂ (Syn)	3	7	0.28	0.37	0.97
	5	12	0.48	0.64	1.66
	7	17	0.68	0.91	2.34
	9	33	1.32	1.76	4.55
	11	10	0.4	0.53	1.38
ZnO (Com)	3	13	0.52	0.70	1.79
	5	28	1.12	1.51	3.86
	7	60	2.4	3.24	8.28
	9	78	3.12	4.22	10.76
	11	45	1.8	2.43	6.21
ZnO (Syn)	3	23	0.92	1.24	3.17
	5	41	1.64	2.22	5.66
	7	83	3.32	4.49	11.45
	9	96	3.84	5.18	13.24
	11	57	2.28	3.08	7.86

simulated light for 60 min, Fig. 6. The range of acetaminophen concentrations was chosen here based on applicable range that used in literature [55,73,74]. Fig. 6a shows that the photodegradation initial rate increases with higher acetaminophen concentration. Fig. 6b shows that the values of acetaminophen percentage photodegradation decrease with increased concentration. Despite the lowering in percentage

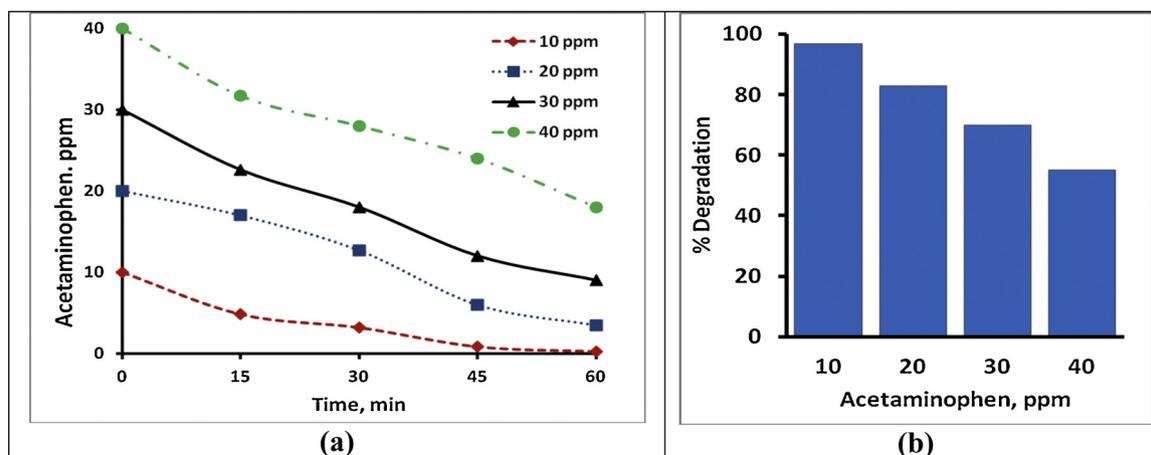


Fig. 6. Effect of acetaminophen concentration of photodegradation process. a) Reaction profiles with time, and b) Values of acetaminophen percentage photo-degradation. Experiments were conducted using acetaminophen (50 mL) mixed with synthesized ZnO (0.1 g) at pH = 7.

Table 5

Effect of acetaminophen concentration of ZnO photocatalytic efficiency in photodegradation. Experiments were conducted using acetaminophen (50 mL) mixed with synthesized ZnO (0.1 g) at pH = 7.

Acetaminophen concentration (ppm)	%Degradation	Number of degraded molecules ($\times 10^{18}$)	TOF (molecules/formula unit.h) ($\times 10^{-3}$)	QY (molecule/ photon) ($\times 10^{-4}$)
10	97	1.94	2.62	6.69
20	83	3.32	4.49	11.45
30	70	4.20	5.68	14.48
40	55	4.40	5.95	15.17

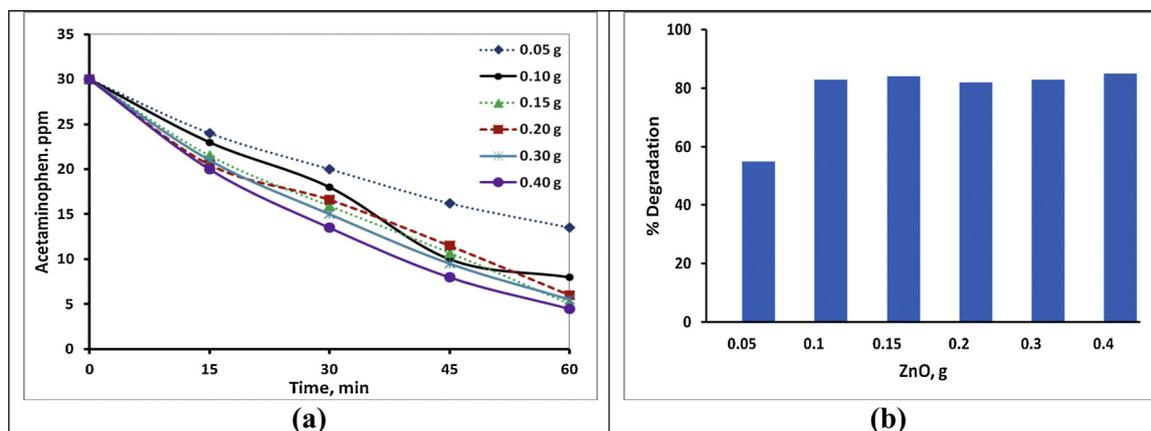


Fig. 7. Effect of ZnO catalyst loading on acetaminophen photodegradation. a) Reaction profiles with time, and b) Value of percentage photodegradation with time. Experiments were conducted under solar simulated light using acetaminophen (50 mL, 30 ppm) mixed with a specific amount of synthesized ZnO at pH = 7.

Table 6

Effect of ZnO catalyst loading on its catalytic efficiency in acetaminophen photodegradation. Experiments were conducted under solar simulated light using acetaminophen (50 mL, 20 ppm) stirred with different loadings of ZnO at pH = 7.

Catalyst amount (g)	%Degradation	Number of degraded molecules ($\times 10^{18}$)	TOF (molecules/formula unit.h) ($\times 10^{-3}$)	QY (molecule /photon) ($\times 10^{-4}$)
0.05	55	2.20	5.95	7.58
0.10	83	3.32	4.49	11.45
0.15	83	3.32	3.00	11.45
0.20	80	3.20	2.16	11.03
0.30	83	3.32	1.50	11.45
0.40	85	3.40	1.15	11.73

photodegradation, the absolute amount of degraded acetaminophen is higher in cases of higher acetaminophen concentration. Table 5 confirms this logic, as catalytic efficiency (TOF and QY) of ZnO increases with increased contaminant concentration. The results show the feasibility of using the photocatalytic process in a range of contaminant concentrations.

3.2.4. Effect of synthesized ZnO loading on photodegradation of acetaminophen

The effect of catalyst amount on photodegradation of acetaminophen has been studied. Different amounts of synthetic ZnO (0.05, 0.10, 0.15, 0.20, 0.30 and 0.40 g) were stirred with acetaminophen solutions (50 mL, 30 ppm) under solar simulated light for 60. The results are shown in Fig. 7. Fig. 7a shows that the photodegradation initial rate increases with increasing the catalyst loading up to a steady-state limit (0.10 g). At higher loading, there is no increase in the photodegradation rate. This can be explained as increasing catalyst amount

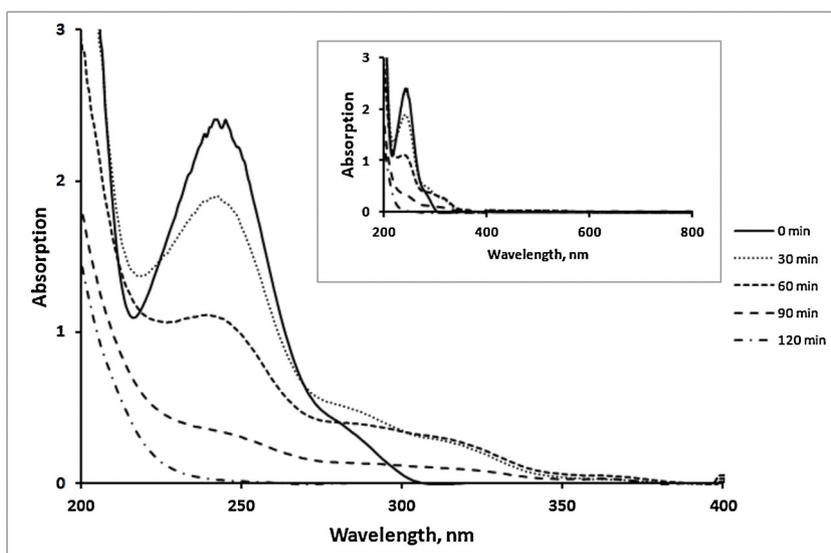


Fig. 8. UV-vis spectra for acetaminophen solution measured after different times (0, 30, 60, 90, and 120 min). Experiments are performed using acetaminophen (100 mL, 40 ppm) mixed with synthesized ZnO (0.2 g) at pH = 7 under solar simulated light.

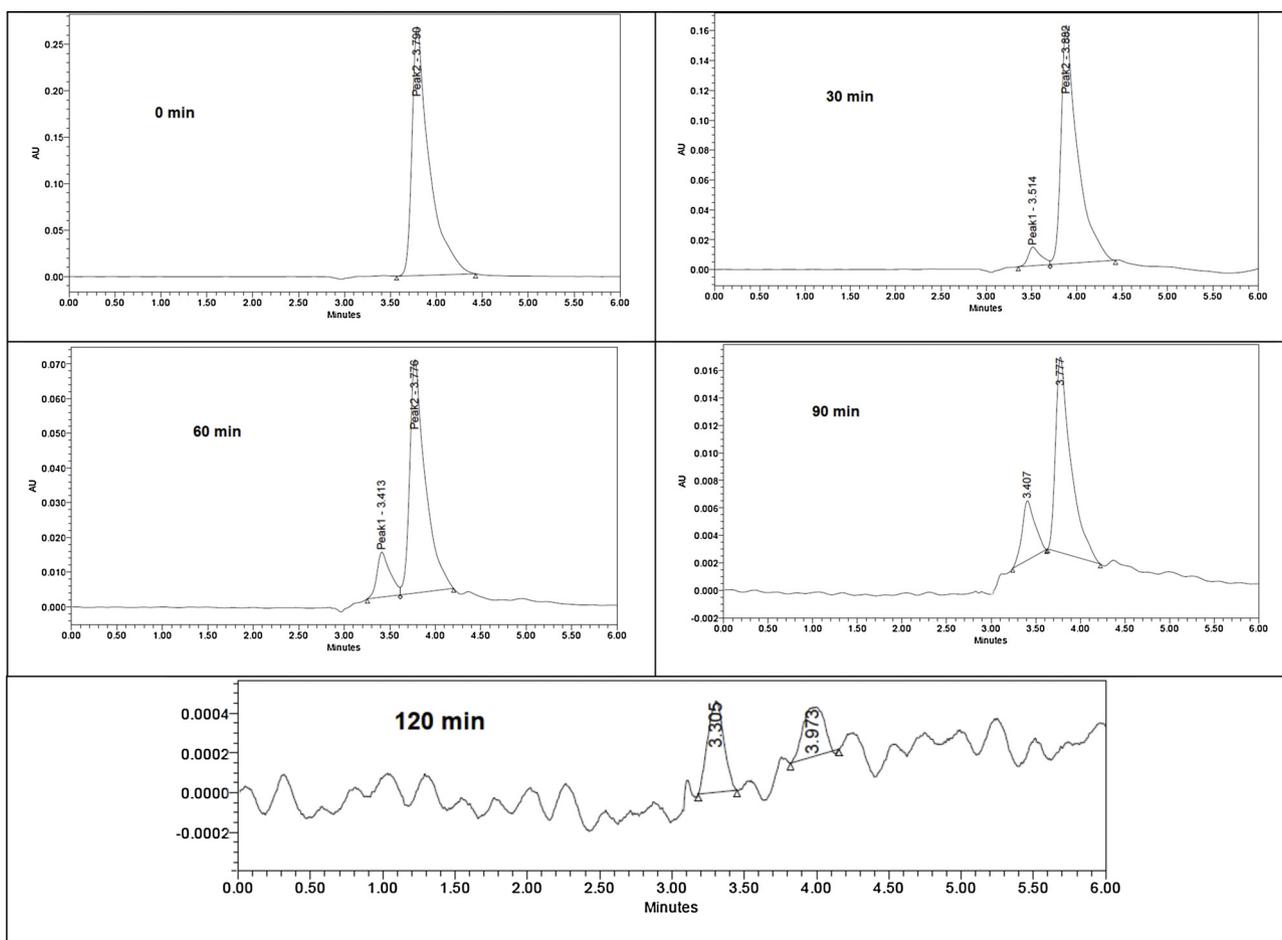


Fig. 9. HPLC chromatograms measured for acetaminophen solution (100 mL, 40 ppm) for different times. Experiments conducted using synthesized ZnO (0.2 g) at pH = 7 for 120 min.

causes screening the light from reaching internal catalyst particles that dispersed in the container bulk. In conclusion, the active catalysts are those presented on the container surface and directly exposed to light radiation. This result is consistent with earlier reports [11,19,20]. The acetaminophen percentage photodegradation value increases with the

catalyst loading as shown in Fig. 7b, but this does not mean increased catalytic efficiency. Table 6 shows how catalytic efficiency values for ZnO decreases with higher catalyst loading. The results suggest that for lower catalyst loading is recommended for future large scale application of water purifications.

Table 7

Value of HPLC peak area and TOC measured for acetaminophen solution irradiated with solar simulated light using ZnO catalyst.

Time (min)	HPLC chromatograph areas		Total organic carbon mg/L (ppm)
	$t_R = 3.5 \text{ min } \mu\text{V} \cdot \text{S} \times 10^3$	$t_R = 3.8 \text{ min } \mu\text{V} \cdot \text{S} \times 10^3$	
0	0	3514.9	26.00
30	121.2	2026.3	18.00
90	130.1	802.0	10.20
150	43.2	170.0	2.32
210	3.5	2.6	0.02

* t_R is retention time.

3.3. Complete mineralization confirmation

Complete mineralization of reacted acetaminophen molecules under photodegradation conditions was confirmed by different methods. Special experiments were made for this purpose, Acetaminophen (100 mL, 40 ppm) was stirred with synthetic ZnO (0.2 g) under solar simulated light for enough time (120 min). Aliquots were taken at a different time (0, 30, 60, 90, and 120 min) during the experiment. The aliquots were centrifuged at 5000 rpm for 3 min and the supernatant was analyzed by UV-vis spectrophotometry, HPLC and TOC.

The UV-vis spectrophotometric analysis results of the solutions with photodegradation time are shown in Fig. 8. The acetaminophen decaying spectra (at ~243 nm) show how its concentration decreases with photodegradation time, reaching about zero after 120 min of irradiation. In parallel to the 224 nm peak lowering, a new absorption peak (300–350 nm) appears during the early times of photodegradation experiment. The new peak itself then starts to decay to zero at the end of photodegradation course. This absorption is attributed to organic transient products formed during the photodegradation of acetaminophen. After enough time, the absorption declines indicating complete mineralization of acetaminophen and any other produced organic intermediates.

The HPLC analysis results of acetaminophen are shown in Fig. 9. The acetaminophen chromatographic retention time was ~3.8 min, as shown in Fig. 9a. During the reaction progress, a peak at retention time ~3.5 min appears indicating the production of a new species as described above, as shown in Fig. 9b and c. After longer irradiation time, both peaks ($t_R = 3.8 \text{ min}$ and $t_R = 3.5 \text{ min}$) fade away. The results of Fig. 9 are summarized in Table 7.

TOC values were measured to determine the amount of organic contents in the solution during the photodegradation process. The TOC results show a continuous decrease in the organic content with photodegradation time, reaching nearly complete disappearance after 250 min. Table 6. This value is lower than the maximum TOC values allowed in drinking water (2–4 mg/L) [75].

Collectively, the UV-vis spectra, HPLC and TOC results confirm complete removal of acetaminophen from water by solar simulated light when synthetic ZnO powder is used as a catalyst. All methods

Table 8

The efficiency of ZnO and TiO₂ (This work) in photodegradation of acetaminophen comparing with other previous studies.

Contaminant (concentration)	Catalyst (amount)	Nature of irradiation (time)	degradation% (pH)	Ref.
Acetaminophen (20 ppm, 132 μM)	ZnO (0.1 g /50 mL)	Solar simulated light (60 min)	100 % (9)	This work
Acetaminophen (20 ppm, 132 μM)	TiO ₂ (Rutile) (0.1 g /50 mL)	Solar simulated light (60 min)	68 % (9)	This work
Acetaminophen (20 ppm, 132 μM)	TiO ₂ (Antase) (0.1 g /50 mL)	Solar simulated light (60 min)	60 % (9)	This work
Acetaminophen (27 μM)	TiO ₂ /Cellulose (0.4 g/L)	Low-pressure mercury lamp (200–280 nm UV) (150 min)	82 % (9)	[67]
Acetaminophen (66 μM)	(3% WO ₃)/TiO ₂ /SiO ₂ (1.0 g/L)	500W UV-vis xenon lamp (240 min)	79 % (9)	[76]
Acetaminophen (66 μM)	TiO ₂ (1.0 g/L)	500 W UV-vis xenon lamp (240 min)	35 % (9)	[76]
Acetaminophen (165 μM)	TiO ₂ (6 g/L)	125 W UV mercury lamp (240 min)	80 % (9)	[77]
Acetaminophen (660 μM)	ZnO (0.1 g/100 mL)	60 W fluorescent lamp (180 min)	80 % (7)	[78]
Acetaminophen (50 μM)	ZnO (0.1 g/100 mL)	UV lamp (180 min)	90 % (9)	[79]

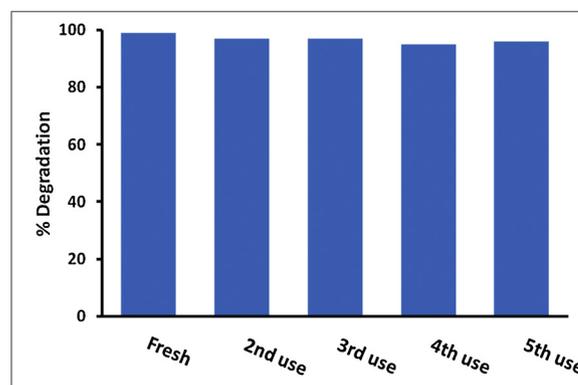


Fig. 10. Stability of the synthesized ZnO catalyst on recovery and reuse. Values of acetaminophen percentage degradation percent measured for the catalyst after multiple reuses.

indicate the appearance of new organic materials, during acetaminophen degradation, but disappear after 120 min of irradiation. The results highlight the potential of using synthetic ZnO catalyst for complete removal of acetaminophen from with solar simulated light. A comparison between ZnO and TiO₂ (This work) efficiency in photodegradation of acetaminophen with literature results is represented in Table 8.

3.4. Catalyst recovery and reuse

The synthesized nano-size catalyst can be recovered and reused many times. Separate experiments have been performed for this purpose. The fresh acetaminophen (100 mL, 40 ppm) and synthesized ZnO (0.2 g) reaction mixture has been irradiated with solar simulated light for 120 min, the mixture was left to completely settle in dark. A sample of the supernatant was syringed out and analyzed for the un-degraded acetaminophen, and then the mixture is carefully decanted for catalyst recovery. Fresh acetaminophen (100 mL, 40 ppm) has been added to the recovered catalyst, and the suspension was exposed to solar simulated light for another 120 min. The procedure has been repeated four times. Fig. 10 shows percentage of photodegradation values for different reused catalyst systems. No significant loss in the catalyst efficiency occurs after the 5th use. Any loss in percentage photodegradation value is due to loss of catalyst during decantation and recovery.

In experiments performed at lower pH values, trace concentrations (< 5 ppm) of Zn²⁺ ions have been detected using atomic absorption spectra (AAS) in the catalytic reaction mixture. The ions result from dissolution of the ZnO catalyst. In TiO₂ experiments no Ti⁴⁺ ions were detected. While these results indicate that the TiO₂ is preferable over ZnO, this should not be taken as disadvantage for the latter. The Zn²⁺ ion concentrations are far less than the daily requirement for adult humans (15–22 mg/day) [80]. Moreover, zinc ions are recommended as supplementations for humans and agriculture [9,81]. The resulting Zn²⁺ ion concentrations here are lower than being health hazardous

[82].

The present results are based on lab scale study. For future larger scale applications, methods to recover the catalyst are being investigated in these laboratories. Supporting the ZnO nanoparticles onto insoluble supports, such as low graphite or clay, and recovering them by simple filtration, are underway. Attaching the ZnO particles to the surface of the glass reactor is another strategy with promising results. In this method the contaminated water solution is allowed to flow over glass-supported ZnO catalyst where it is exposed to solar light in a continuous flow mode. Glass sheet supported plates can be produced commercially and furnished to society at relatively low cost as both glass and ZnO catalyst are non-costly. Therefore, the results will have impact for different societies, in both industrialized and low-income countries. Optimizing the continuous flow method is an important part so as to come out with a practical method for contaminated natural waters. The catalyst is expected to effectively function not only for acetaminophen degradation but to any other organic contaminant as well.

As per cost analysis, the process is promising even at the lab scale stage. ZnO (and TiO₂) are commercially available at low cost. Solar radiation is abundant in many places worldwide. Moreover, the process is environmentally friendly as it yields water with no organic remains in solution. Once tested at continuous-flow pilot-plant scale, the results potentially have commercial value.

4. Conclusion

Acetaminophen, a widespread water contaminant can be effectively mineralized leaving no organic contaminants by simple photodegradation with solar simulated radiation on ZnO or TiO₂ nanopowder catalysts. ZnO shows higher efficiency in photodegradation of acetaminophen comparing with TiO₂. ZnO effectively functions at different pH values, for different contaminant concentrations (10–50 ppm), the steady-state efficiency of the loaded catalyst was reached at 0.10 g, and the efficiency of photodegradation was higher in neutral to basic solutions, mainly at pH = 9. The p*H*_{pzc} plays the main role in the photodegradation efficiency. ZnO shows an acceptable efficiency in natural pH (pH = 7). The UV–vis spectroscopy, HPLC, and TOC analysis confirmed the complete mineralization of acetaminophen (100 ml, 40 ppm) in 120 min of irradiation. The ZnO shows the ability to be recovered and reused without significantly losing its efficiency. The lab-scale results lay down foundations for more future continuous flow rate study at the pilot plant scale.

Authors contributions

The results shown here are partly based on Sh. H. thesis [83] (supervised by H. S. H. and A. H. Z.). A. H. A. and A. Z. performed extra needed experiments. S. Z., N. Q. and A. H. performed SEM and additional XRD measurements in the laboratories of UAE Alain University, UAE. Sh. Z. helped in TOC analysis. M. H. helped with the literature review, pharmaceutical concepts and formulating the study. A. H. Z. and H. S. H. wrote up the manuscript. All Authors read and approved the manuscript

Credit author statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication before its appearance in the Journal of Environmental Chemical Engineering.

Declaration of Competing Interest

The authors declare that they have no competing interests

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