

RESEARCH PAPER

An efficient method for the synthesis of photo catalytically active ZnO nanoparticles by a gel-combustion method for the photo-degradation of Caffeine

Rajesh B. Jagannatha, Shwetha Rani Ramu, Mahesh Padaki* and R. Geetha Balakrishna*

Centre for Nano and Material Sciences, Jain University, India

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ABSTRACT

In this study, Zinc oxide nanoparticles were synthesized by gel-combustion method using a novel bio-fuel tapioca starch pearls, derived from the tubers of *Mannihot esculenta*, to investigate the photocatalytic degradation of caffeine. The ZnO photocatalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-visible spectroscopy. X-ray diffractometry result for the ZnO nanoparticles exhibit normal crystalline phase features. All observed peaks can be indexed to the pure hexagonal wurtzite crystal structures. There are no other impurities in the diffraction peak. In addition, SEM measurement shows that most of the nanoparticles are spongy and spherical in shape and fairly mono dispersed. A significant degradation of the Caffeine was observed when the catalyst was added into the solution even without the UV light exposure. In addition, the photo degradation increased with the photocatalyst loading. Besides the photocatalyst loading, the effect of some parameters on the photo degradation efficiency such as initial concentration and pH were also studied.

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INTRODUCTION

There are a great variety of pharmaceuticals and personal care products for human and veterinary health in the medical field. The wide occurrence of pharmaceutical and personal care products (PPCPs) in natural aquatic environment received extensive scientific interest as well as public awareness recently due to their potential hazardous effect on human beings and ecological system. The environmental fate of these PPCPs, including transportation and transformation, is still largely unknown. The continuous appearance of new chemicals in water sources reflecting habits from modern standards of living establishes new priorities in current investigations on wastewater

treatment. The widespread occurrence of pharmaceuticals in surface waters attests their lack of efficient removal during wastewater treatment and/or their relative persistence in receiving waters. Reclaimed wastewater has a variety of possible uses, such as the irrigation of agricultural and urban areas, cooling water for industrial plants and recharging groundwater bodies. Caffeine or 1, 3, 7-Trimethylxanthine is a plant product and it is ranked as the number one drug worldwide, with a massive production of hundreds of tons [1]. Usually employed as a stimulant, caffeine is commonly found in coffee, tea, chocolate, cocoa, and soft drinks [2]. Buerge et al. reported that an estimated global average consumption is 70 mg Caffeine/person/day. In the United States alone,

* Corresponding Author Email: br.geetha@jainuniversity.ac.in
sp.mahesh@jainuniversity.ac.in

the daily average consumption per-person rate is 210 mg [2]. Caffeine is widely metabolized by humans, the disposal of the unconsumed coffee and caffeinated soft drinks being the predominant source of caffeine, introduced into the wastewater treatment system and makes its way through wastewater-treatment plants globally [3] and some amount of Caffeine will inevitably be deposited into aquatic receiving systems. Long term intake of Caffeine is known to affect memory and performance of human brain, especially in due course of withdrawal which then leads to decreased attentiveness, increased cloudiness of the brain, physical and mental dependence. Caffeine persists in water. It is detected at the concentrations of 1.5 to 300 ppm in influent and effluent of sewage treatment plants, while around 0.3 to 106 ppm was found in drinking water and raw water, respectively. Also adverse effects of Caffeine include increased frequencies of headaches and fatigue during Caffeine withdrawal. The present need for additional information on Caffeine toxicity has accompanied increasing concerns about its prevalence and mixture with other wastewater components. Bantle et al. [4] found that caffeine concentrations in water were high enough to affect *Xenopus laevis* egg development when exposed for 96 hours (LC50 = 0.22 to 0.37 mg/mL). Sub lethal end points were more sensitive for *P. promelas*. Mean 5-day EC50 and LOEC values for *P. promelas* were 70 and 20 mg/L. The International Uniform Chemical Information Database (2004) reported 120-hour, *X. laevis* LC50 values between 0.13 and 0.19 mg/mL. Further research is needed to ensure that Caffeine levels present in contaminated streams do not present a risk to freshwater species. Reported caffeine concentrations from New York STP effluents ranged from 0.19 to 9.9mg/L [2, 5]. Reported Caffeine concentrations in Swiss lakes and rivers are ranging from 6-250 ng/L. Whereas, Swiss STP effluents ranged from 0.03 to 9.5mg/L. Any chemical introduced by sewage to aquatic realm can lead to continual multigenerational exposure for aquatic organisms [6]. If Caffeine is profusely discharged from anthropogenic sources into an environment, it could constantly replenish levels regardless of the amount of caffeine degraded, creating a dynamic equilibrium. Due to the last advances in light related technologies, heterogeneous photocatalysis is becoming more relevant amongst the existing advanced oxidation technologies (AOTs). One of the main reasons is

the ability of the process to achieve the degradation and mineralization of many organic pollutants at normal conditions of temperature and pressure, with a fairly clean technology [7-9]. Semiconductor photocatalysis is a highly competitive Advance Oxidation Process for water remediation in spite of a limited industrial implementation.

Metal oxide nanoparticles, by virtue of their dimensions find application in different fields ranging from catalysis to drug delivery to cosmetics. Of all the metal oxides, ZnO and TiO₂ nanoparticles have a special place in photocatalysis [10-13], antimicrobial agent in medicine [14-15] optoelectronics and sensors. ZnO (3.37 eV, band gap) is a superior semiconductor compared to TiO₂ (3.0 eV, band gap). This makes it a good photocatalyst in the degradation of organic and toxic chemicals in the visible as well as in the UV region of the spectrum. The use of ZnO photocatalyst for environmental clean-up has been of great interest due to its non-toxic nature, photochemical stability and low cost when sunlight is used as the source of irradiation. When ZnO is exposed to the light of energy equal to or greater than the band gap energy (3.37 eV), an electron is excited from the ZnO valance band into the ZnO surface where they initiate the redox reactions with organic species adsorbed on the surface. Many organic contaminants can be oxidized into CO₂ and H₂O.

EXPERIMENT

Zinc nitrate hexahydrate (Zn (NO₃)₂ · 6H₂O), 2-Hydroxy 4 Methoxy- Benzophenone, Ammonium persulphate were purchased from Merck, Arva synthesis and Fischer synthesis respectively. Methanol and Caffeine used in the experiments were of HPLC and analytical grade purchased from Merck and Fisher Scientific India Pvt. Ltd., (Mumbai, India) and used without further purification. Tapioca pearls were purchased from the local market in Bangalore. The pH of the solution was adjusted with 0.01 M sodium hydroxide solution and 0.01M Formic acid. Double distilled water was used throughout the experiments.

Preparation of Tapioca starch

The processed form of tapioca was prepared as follows, initially tapioca pearls involved hand-picking, then washing with tap water and rinsing with water to remove suspended impurities. To 500g tapioca pearls in a beaker, a known volume of water was added, heated on a hot plate at 150 °C for

an hour. When the pearls became transparent and viscous, the contents were transferred to a clean plastic sheet. The sheet was covered with a thin cloth to prevent dust contamination and dried by exposing to the sunlight for a week.

Synthesis of ZnO nanoparticles using Tapioca starch

Preparation and characterization of ZnO nanoparticles are conducted as per our earlier reported article [16]. 2:1 ratio of zinc nitrate hexahydrate (oxidizer, 10g) and tapioca starch (fuels, 5g) were mixed well with 40 mL water in a beaker and heated on a hot plate at 200 °C till it formed a gel. The gel was introduced to a pre-heated muffle furnace maintained at ± 475 °C. Sputtering and smoldering type of the reaction was observed. The reaction was completed in 5 min and voluminous flaky white product of ZnO nanoparticles was obtained. The product was calcined at 500 °C for 5 h to remove the impurities.

Characterization

X-ray diffraction (XRD) patterns were obtained on a Philips X'pert PRO XRD system. Surface morphology (SEM) was studied using scanning electron microscope (Carl Zeiss 55). HPLC system, Waters' make HPLC, was connected to photodiode array detector. Water Empower software chemstation was used for HPLC instrument. The absorption spectrum of the sample was measured using Shimadzu UV 1800 PC UV-Vis spectrometer consisting of software UV probe.

Photocatalytic Experiment

Photocatalytic activity of ZnO nanoparticles were evaluated on the degradation of caffeine in a solar light (700 W/m², average value) illumination. The solar light illumination experiments were carried out between 10 am – 4 pm. Known weight of the catalyst was dispersed in a known volume of the caffeine along with an electron scavenger ammonium persulphate and the resultant mixture was stirred throughout the experiment for uniform exposure of the catalyst to light. 10 mL aliquots were withdrawn every 20 minutes, filtered through Millipore syringe filter (0.45 μ m pore size) to remove the catalyst during the course of the reaction. The degradation of the Caffeine was monitored after removal of photocatalyst by centrifugation at 4000 rpm and measured the decrease in the absorption maxima at 272 nm. The extent of degradation of the pollutant was also studied by using the same

solution by HPLC at a desired time interval during irradiation. The residual concentration of Caffeine was estimated by HPLC method from the calibration curve of absorbance versus concentration of the Caffeine at a steady value of $\lambda_{max} = 272$ nm. Waters' HPLC equipped with a Empower series, quaternary pump, auto sampler and connected with photodiode array detector was used to study the degradation of Caffeine quantitatively. Chromatographic separation was achieved on an RP-HPLC column (Lichrocart * 250-4, RP-18e (C18) 5 μ m, Merck make) through isocratic delivery of a mobile phase methanol: water [60%:40% v/v] at a flow rate of 1 mL/min. UV absorbance was recorded at 272 nm at room temperature. Retention time of Caffeine was 3.0 ± 0.5 min. Linearity check/calibration curve of the method was performed by the use of standard Caffeine solutions of known concentration {0.1-10 ppm, ($R^2 = 0.999$)}.

Photodegradation

The % degradation was calculated from the following equation

$$\% \text{ Degradation} = \frac{1 - A_t}{A_0} \times 100 \quad (1)$$

where A_t = absorbance at time t , and A_0 = absorbance at zero time (t_0).

The photocatalytic degradation was studied by varying the experimental parameters like concentration of caffeine, catalytic load, pH, stirring time and recycling.

RESULTS AND DISCUSSION

Fig. 1 shows XRD spectrum of ZnO nanoparticles prepared by Combustion method. The diffraction peaks in (Fig. 1) can be perfectly indexed to the hexagonal structures of ZnO (JCPDS Card No. 36-1451) No characteristic peaks of impurities are detected in the XRD pattern, implying the formation of single phase crystals. The strong and narrow diffraction peaks indicates that the product has good crystallinity. Furthermore, the observed diffraction peaks are broad and less sharp, indicating that as prepared ZnO particles with small dimension. The average crystallite size (D_p in nm) of ZnO particles can be estimated according to the diffraction reflection by using Debye-Scherrer equation:

$$D_P = \left(\frac{K\lambda}{\beta_{1/2} \cos \theta} \right) \quad (2)$$

where K is a constant equal to 0.89, λ is the X-ray wave length equal to 1.54 \AA , $\beta_{1/2}$ is the full width at half maximum and θ is the half diffraction angle. Particle size of ZnO is found to be 55 nm.

Fig. 2a shows the typical FESEM micrographs of ZnO under different magnifications. It is clear from the SEM that, single-phase spherical shaped organized particles with good surface area were observed. The particles are united together to form

sponge- like structure with more pores. The FTIR spectrum as depicted in Fig. 1 b results shows that the peaks around 900- 1200 cm^{-1} and 780- 980 cm^{-1} are due to formation of Zn-O- O-Zn bonds and peaks at 394 and 508 cm^{-1} are due to stretching vibrations of Zn-O bond [17]. The chemical composition of ZnO was investigated by EDS analysis. Fig. 2c depicts the typical EDS spectrum taken from ZnO. The chemical analysis

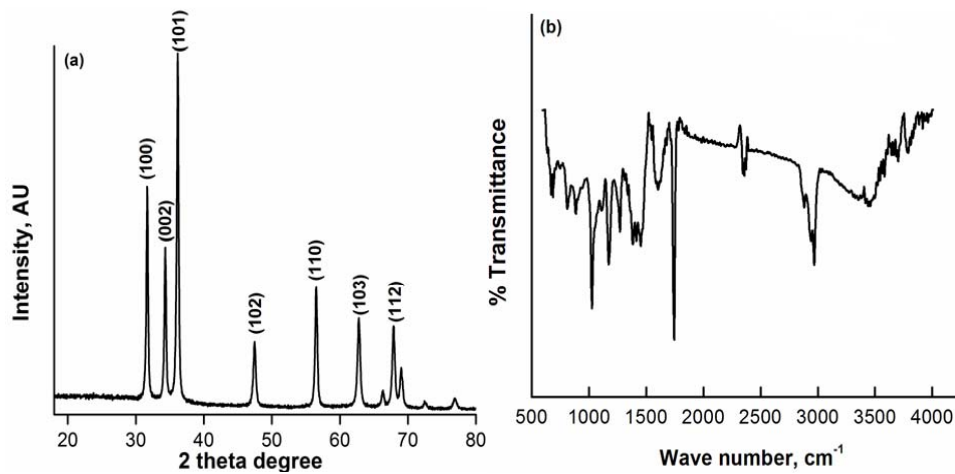


Fig. 1. (a) X- ray diffraction pattern, (b) FTIR spectrum of the synthesized ZnO nanoparticles

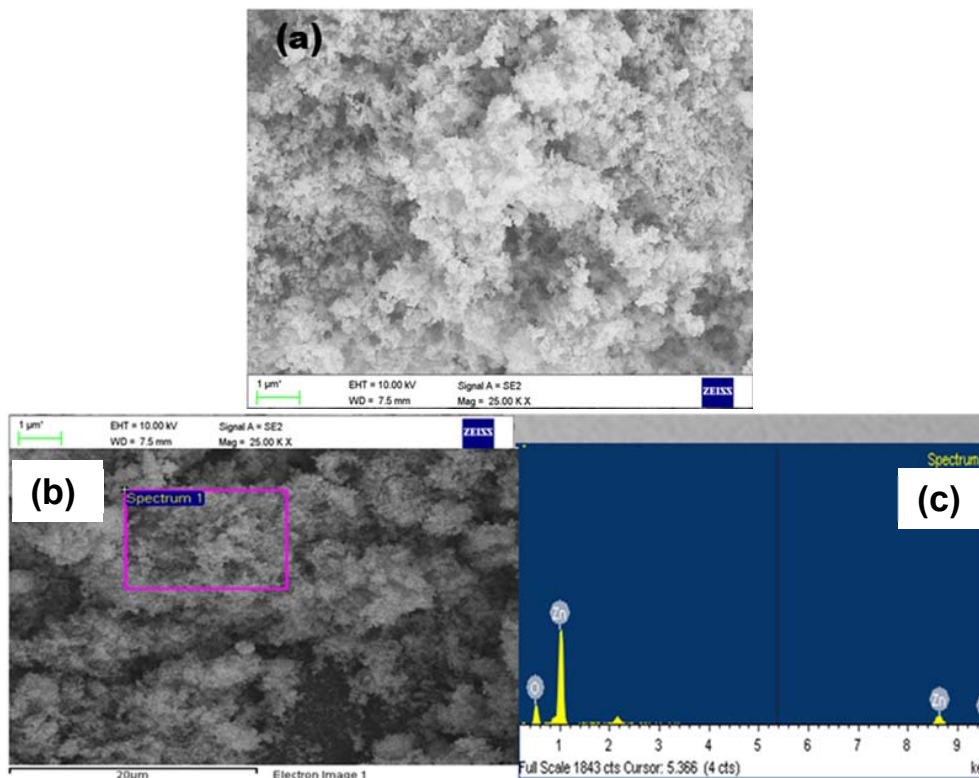


Fig. 2. (a) FESEM image, (b) SEM image and (c) EDS spectrum of ZnO nanoparticles

Fig. 1. (a) X- ray diffraction pattern, (b) FTIR spectrum of the synthesized ZnO nanoparticles

Name of the element	Theoretical % composition	Obtained % composition
Zinc	80.3	83.7
Oxygen	19.7	16.3

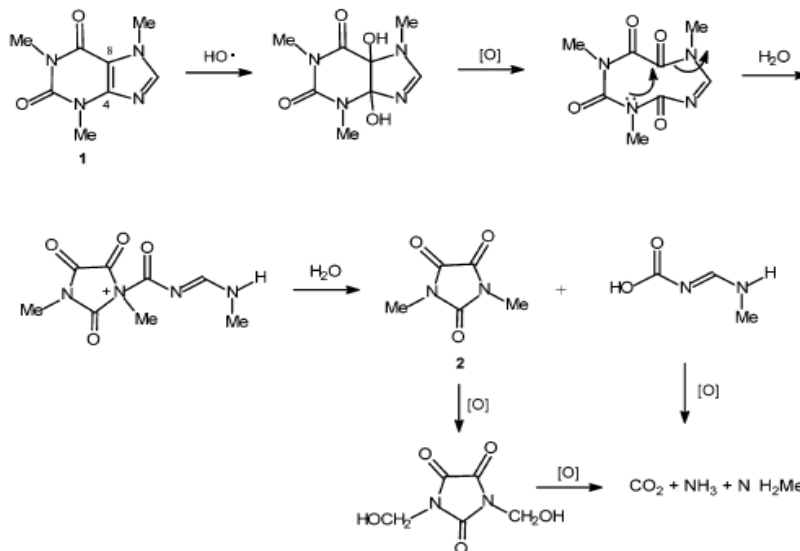
of the prepared nanoparticles measured by EDS analysis shows that only Zn and O signals have been detected. The elemental composition of the samples obtained by EDS is shown in Table 1.

No signal of secondary phase or impurity was detected except for carbon, indicating the high purity of ZnO nanoparticles [18].

The UV-Vis spectra of Caffeine

Fig. 3 displays the UV spectra of Caffeine taken before any irradiation. Caffeine has an

absorption profile spanning from 200 to 300 nm, with absorption peaks at 206 and 270 nm. The concentration of Caffeine becomes diminution for nano- ZnO photodecomposition. It was found that when Caffeine is irradiated in sun light with the photo catalyst ZnO and an oxidizing agent APS, first, the intensity of peak at 270 nm decreases steeply after 60 min of irradiation, second is that the 206 nm absorption peak gradual red- shift reaches to 6-7 nm , third is that the absorption spectral intensity of Caffeine increases significantly at 206 nm. All the peaks disappear after 120 min of sun light irradiation and this has been confirmed by HPLC, as shown in (Fig. 5). The retention time of Caffeine was 3.0 ± 0.5 min. The initial peak area of 1 ppm and 6 ppm Caffeine solution at before sunlight irradiation was 99554 AU and 387555 AU, respectively, and the same reduces to 1208 AU



Scheme 1: Mechanism of Caffeine degradation by reactive oxygen species

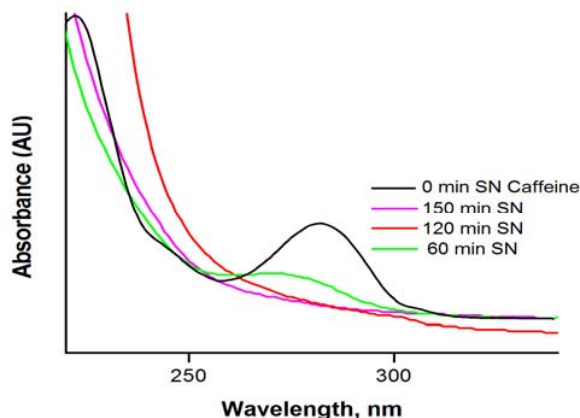


Fig.3 UV- Vis absorption spectra of Caffeine degradation

and 1055 AU after 120 min of sunlight irradiation, as depicted in (Fig. 5). When the APS is added to the solution, it bores abundantly hydroxyl radical (OH•) to impact the structure of Caffeine leading to the absorption peak variation. The degradation of organic compounds in situ occurs by the formation of hydroxyl radicals as proposed by [19]. Caffeine degradation occurs by the attack of hydroxyl radicals to the C4= C8 double bond of caffeine to form Dimethyl parabenic acid. Successive hydroxylation, oxidation and mineralization of

reaction intermediates, forms slowly CO₂, NH₃ and NH₂. Thus, based on this assumption, it can be proposed that caffeine is initially oxidized by free hydroxyl radicals to yield Dimethyl parabenic acid and also other intermediates and finally to form CO₂ NH₃ [20].

Photolysis and photocatalysis degradation of Caffeine

ZnO nanomaterials are efficiently tested as photocatalyst for degradation of Caffeine under solar light. The effect of different parameters such

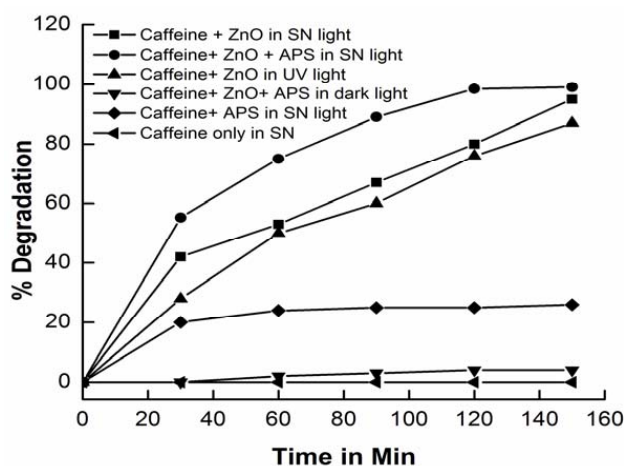


Fig. 4. Effect of sunlight, and dark light on the degradation of Caffeine

HPLC chromatograms of 1 and 6 ppm Caffeine degradation studies

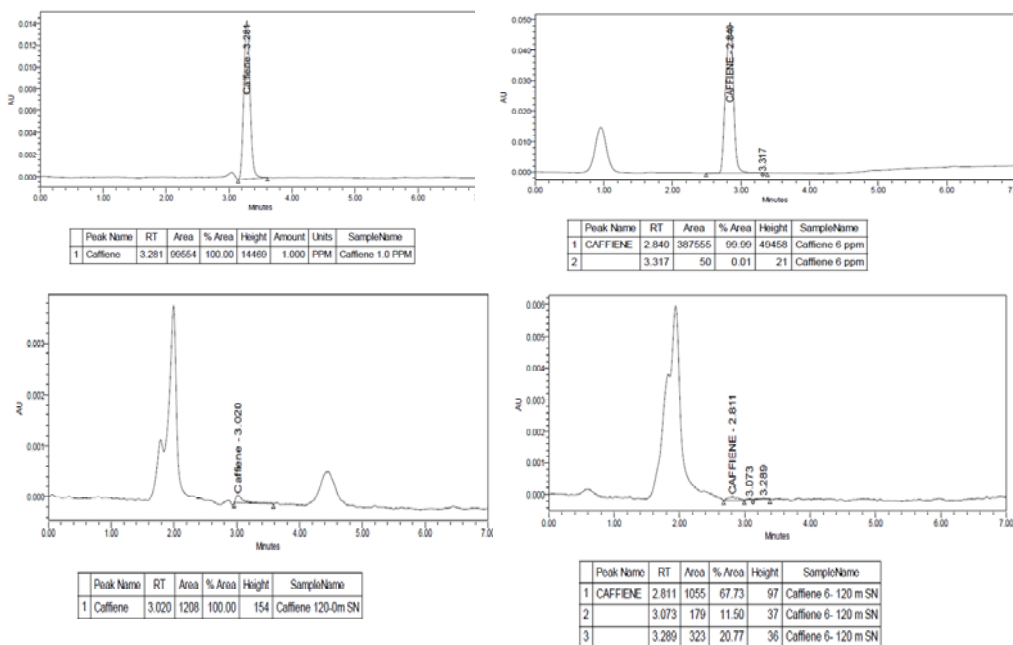


Fig. 5. HPLC Chromatograms of Caffeine standard solution and reaction mixture

as catalyst loading, concentration, solution pH on photodegradation was evaluated using ZnO nanoparticles under solar light. Photocatalytic activity was also studied using the different concentrations of ammonium per sulphate. In darkness, 3% degradation was observed whereas on illumination (sunlight) 95% degradation occurred. There are some pollutants that degrade on exposure to light (photolysis). Though the electron scavenger is attributed to the whopping 25% degradation, a nearly complete degradation (99%) was possible only when both the photocatalyst and electron scavenger were present together.

Photocatalytic degradation of Caffeine and Control experiments were conducted in dark with ZnO and without (ZnO-free), sunlight and UV light irradiation conditions. The results in (Fig. 4) show minimal Caffeine adsorption to ZnO surfaces and no susceptibility to surface-catalyzed dark reactions. Furthermore, no Caffeine degradation advances in dark light with ZnO and APS, in UV light irradiation, Caffeine degradation was found to be 85% , and in sunlight it was 98.6% of 1 ppm caffeine solution, with a light irradiation period of 120- 140 min. Direct photo catalysis of caffeine in UV light is less than that in the sunlight. These results suggest that photocatalytic degradation is primarily responsible for removing Caffeine. Synthesized ZnO is very sensitive/ reactive in sunlight. The use of sunlight being an abundant natural energy source can significantly reduce the costs of the Photo degradation process [21-23].

Effect of initial concentration of Caffeine

The effect of initial concentration of Caffeine in the range of 1 to 6 mg/L on its photocatalytic

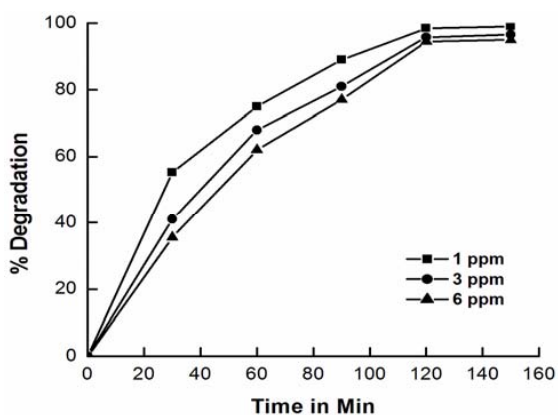


Fig. 6. Caffeine photocatalytic degradation with the variation in the feed concentration

degradation was examined with constant catalyst load of 0.70 g/L, and 2 mL of 0.015 M APS was also studied. Increase the concentration of the pollutant from 1 ppm to 6 ppm decreases the extent of degradation from 99% to 95.5 % as depicted in Fig. 6. Caffeine has conjugated carbon-carbon double bonds in its structure. The degradation might be due to cleavage of these conjugated carbon-carbon double bonds. [24] The increase in the concentration of Caffeine caused the suppression of the photodegradation rate. For the initial Caffeine concentration of 1 mg/L, the almost complete degradation was achieved after 120- 140 min. As the initial Caffeine concentration increased, photo degradation percentages were also decreased due to more concentrated solutions prevented the penetration of light to the surface of the catalyst. Hence, the amount of oxidizing species generated on the catalyst surface decreased.

Effect of Catalyst Loading

Fig. 7 shows the dependency of the photo degradation efficiency of Caffeine on the catalyst loading. The results showed that photodegradation efficiency is increased with an increase in catalyst loading to an optimum loading, and after which it is decreased. The set of experiments were conducted by changing the catalytic load from 0.35 to 1 g /L of Caffeine by maintaining the constant concentration of pollutant constant (1 ppm). There was an increase in the degradation when the catalytic load was increased from 0.35 to 0.7g (72% to 99% degradation) due to the increase of active sites on ZnO surface. Maximum degradation of Caffeine was found to be at 0.70 g/L and beyond this catalyst load, the photocatalytic activity

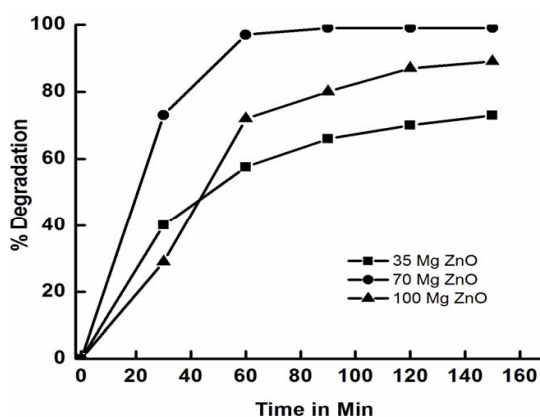


Fig. 7. Caffeine photocatalytic degradation with the variation of catalyst load

decreases due to the formation of turbidity which reduces the light penetration into the solution, and enhances the light scattering [25]. This observation can be explained in terms of the availability of active sites on the surface of the catalyst and the penetration of solar radiation into the suspension. An increase in catalyst dosage results in an increase in total active surface area of catalyst which in turn results in an increase in the photodegradation efficiency [26]. However, this effect is counteracted at high catalyst dosages due to increased turbidity of the suspension. This is also due to aggregation of catalyst particles, which reduces the interfacial area between the reaction solution and the photo catalyst [25]. The increased turbidity reduces penetration of the solar radiation much needed due to scattering, hence a decrease in photodegradation efficiency at high catalyst dosage. On this respect, it was concluded that 0.7g/L ZnO catalyst can be used as an optimum amount for further reactions. The photocatalytic efficiency of the recycled ZnO was tested. The used catalyst was recovered by centrifugation followed by repeated washing with distilled water and dichloromethane (AR grade) several times and finally it was dried in a hot air oven at 100 °C for 3 h for further process. Photocatalytic degradation efficiency of the recycled catalyst was tested for reusability and the results are as depicted in Fig. 1 of SI.

Effect of APS concentration

The photo degradation efficiencies increased significantly when ammonium persulfate was used in the presence of UV and sunlight radiation, as shown in (Fig. 5). Ammonium persulfate is a strong oxidizing agent, its oxidation potential is 2.1 V and that of sulfate radical is 2.6 V. The

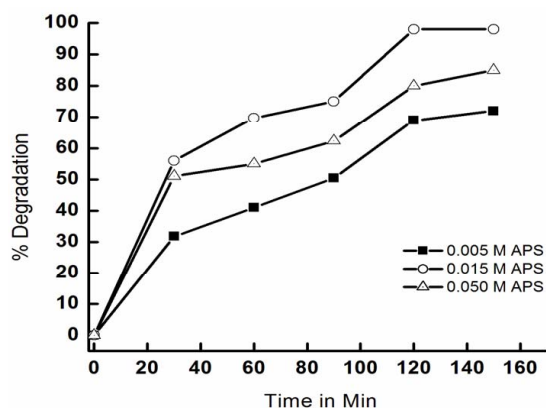
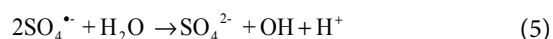
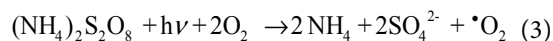


Fig. 8. Caffeine photocatalytic degradation with the variation in the APS concentration

effect of this electron scavenger on the photo catalytic degradation was investigated by varying its concentration from 0.005 M to 0.05 M. The efficiency was found to be maximum for 0.015 M (99% degradation) as depicted in (Fig. 8), and beyond which it was decreases. Moreover, high concentration of ammonium persulfate acts as scavenger itself, thereby decreasing the concentration of hydroxyl radicals and reducing compound elimination efficiency [27]. Therefore, ammonium persulfate should be added at an optimum concentration to achieve the best degradation. The hydroxyl radicals generated attack the Caffeine framework at different sites like unsaturation points etc. In several such attacks the Caffeine gets converted into CO₂ and hetero-atoms which are further mineralized. The probable role of ammonium persulfate in the degradation process is as follows:



Effect of pH on ZnO

Effect of pH on the photo degradation of Caffeine is an important parameter which should be studied as industrial effluents containing organic compounds that may not be neutral. Experiments were carried out in acidic, basic and neutral media with the optimized parameters under sunlight irradiation. Describing the effect of pH on photocatalytic degradation is an important task because of its multiple roles, namely, hydroxyl radical attack, direct oxidation by the positive holes and direct reduction by the electron in the conduction band. The importance of each one depends on the nature of the substrate and pH. In the current study, it is presumed that the reaction is due to hydroxyl radical attack, favored by high concentration of hydroxyl radical at basic pH. The rate of reaction taking place on the surface of ZnO, an amphoteric oxide, is governed by pH of the dispersion which influences the surface charge properties of the photo catalyst [28, 29]. The acid base property of ZnO surface can be explained on the basis of zero point charge (zpc). The zpc for ZnO is 9.0 ± 0.3 .

Fig. 9 illustrates the degradation of Caffeine in ZnO /sunlight system under various pH values. The degradation rate of caffeine is the highest as 11 of pH. The pH of the aqueous solution influences

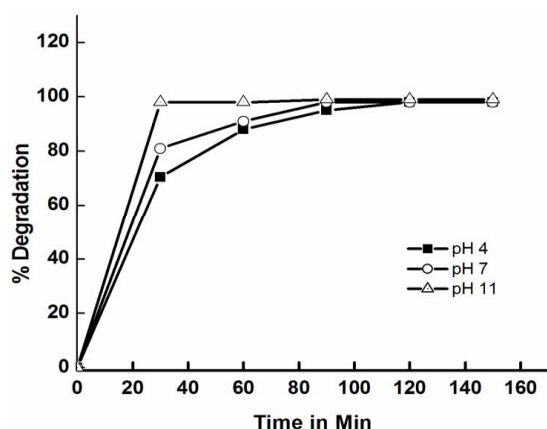


Fig. 9. Caffeine photocatalytic degradation at different pHs

the physicochemical properties of ZnO, including the charge on the particle, the aggregation number of particles, and the position of the conduction and valence band [30]. The isoelectric point of ZnO (pzc is 9.0 ± 0.3). At low pH (acidic) ZnO carries a net positive charge, Caffeine and reaction intermediates formed are primarily negatively and neutrally charged. Therefore at acidic pH ZnO facilitates the adsorption of the organic molecule and enhances photocatalytic degradation. However the degradation rate of Caffeine is decreased when the pH is so low that the electron-hole pairs recombine easily. Nevertheless, better removal efficiency of Caffeine in ZnO/UV/sunlight system under alkali conditions is found in our experiments. One possible explanation is that the photocatalytic transformation of Caffeine does not involve hydroxyl radical ($OH\bullet$) exclusively. Direct electron transfer and surface sorption reactions also contribute significantly to the disappearance of Caffeine in ZnO suspensions. Although there is no semiconductor excited in the solution of direct photolysis system, hydroxyl radical ($OH\bullet$) and hydrated electrons can be formed when water is irradiated with high energy UV / Sunlight. Therefore, higher pH value can provide higher concentration of hydroxyl ions to react with holes to form hydroxyl radicals, subsequently enhancing the photodecomposition rate of Caffeine [31], while the degradation ratio of Caffeine is inhibited when the pH value is so high that hydroxyl ions compete with caffeine ions on the surface absorption of ZnO.

CONCLUSIONS

ZnO nanoparticles were synthesized by gel-combustion method using a novel and effective fuel, tapioca pearls starch and characterized by XRD, FTIR SEM and EDS. On the basis of the

results presented the synthesized ZnO is a very good sunlight active photocatalyst and Caffeine degradation has only taken place in the presence of the photocatalyst, which without catalyst, photodegradation might take a very long time. Experimental results showed that in the presence of ZnO nanoparticles, the photodegradation of Caffeine is significantly enhanced which implies the great potential of this material in the waste water treatment system. The degradation has been studied with changes in parameters like catalytic load, pH and ammonium persulfate and for different initial concentrations of Caffeine. The study attains significance in synthesizing sunlight activated ZnO catalyst that can ideally degrade the hazardous EDC pollutants in waste water.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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