CHEMICAL ENGINEERING TRANSACTIONS
VOL. 56, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim
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ISBN978-88-95608-47-1; **ISSN** 2283-9216
DOI: 10.3303/CET1756276

Study on ZnO Catalytic Activity in Salycilic Acid Degradation by Sonophotocatalysis

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The preparation of ZnO via sol-gel preparation and the study on sonophotocatalytic activity are reported. ZnO was prepared by zinc acetate precursor and the characterisation of the material was conducted by XRD, gas sorption analyser, SEM-EDX and Diffuse Reflectance UV-Visible spectrophotometry. Catalytic activity of the semiconductor material was investigated using varying methods of salicylic acid destruction - photocatalytic, sonocatalytic and sonophotocatalytic. The results indicated that prepared ZnO has photocatalytic activity with the band gap energy value of 3.22 eV. From the tested catalytic system, sonophotocatalytic gives the best rate of salycilic acid destruction. The kinetic rate of each treatment gives the information that there is a synergistic index between photocatalysis and sonocatalysis.

1. Introduction

Treatment of organic compounds in contaminated wastewater including pharmaceutical industries is a concern for environmental protection. There are so many techniques for water remediation that have been developed and one of them is advance oxidation process. Several works have adopted photocatalysis in the presence of nanoparticle, one of the main categories of advanced oxidation process (AOP), to eliminate detrimental effects of pharmaceutical compounds. With this scheme, titanium dioxide (TiO_2) has been gaining attention for the application since it is known as cheap, non-toxic and have wide band gap energy for the effective photocatalytic mechanism (Lekshmi et al., 2014). The use of ZnO instead of TiO_2 as a photocatalyst material for the application has also been investigated (Cho et al., 2012). With similar band gap energy values as TiO_2, the synthesis of ZnO with tailored physicochemical properties has been attempted by various methods and innovations such as the use of plant extract as templating agent in nanoparticle synthesis as well as other routes for the specific form of the nanoparticles (Lazar et al., 2012). Another mechanism that can be adopted from the utilisation of metal oxide semiconductor is sonocatalysis which has been developed intensively since 1990 (Anju et al., 2012).
The difference between both methods is that photocatalysis occurs based on the photonic activation of the catalyst by light irradiation while sonocatalysis is the ultrasonically induced acoustic cavitation. Both processes predominantly involve the formation of free radicals and other reactive moieties which consequently react with and destroy the pollutant species (Lazar et al., 2012). The advantages of sonocatalytic mechanism are that it is safe and clean, has high penetrability in water medium and degradation efficiency, and optimum energy conservation without any generation of secondary pollutants. Some researchers reported that ultrasonic irradiation process is capable of degrading various organic compounds such as dyes, phenol compounds, chloro-aromatic compounds, aqueous carbon tetrachloride, pesticides, and aromatic/polycyclic aromatic hydrocarbons. To improve the treatment effectivity, a combined method of photocatalytic and sonocatalytic for organic compounds degradation called sonophotocatalytic had been developed (Ahmedchekkat et al., 2011). This research aims to evaluate sonophotocatalytic using ZnO as catalyst for efficient pharmaceutical wastewater treatment (Kavitha et al., 2011). The production of salicylic acid in the pharmaceutical industry leads to wastewater discharge and needs to be removed effectively and choosing salicylic acid as the model is reasonable for this study. Research aims to synthesise ZnO using sol-gel mechanism and evaluate the physicochemical characteristic and catalytic activity of the material. Physicochemical characterisation was

Please cite this article as: Fatimah I., Pradita R.Y., Nurfalinda A., 2017, Study on zno catalytic activity in salycilic acid degradation by sonophotocatalysis, Chemical Engineering Transactions, 56, 1651-1656 DOI:10.3303/CET1756276

performed by some evaluation methods: x-ray diffraction (XRD), gas sorption analysis for determination of specific surface area, pore volume and pore distribution, scanning electron microscope-energy dispersive x-ray (SEM-EDX) and diffuse-reflectance UV-Vis (DRUV-Vis). The kinetics of sonocatalytic, photocatalytic and sonophotocatalytic treatments of salicylic acid was studied to evaluate the effectiveness of combined method.

2. Materials and Methods

2.1 Materials

Chemicals consist of zinc acetate dehydrate, isopropanol, acetic acid, copper sulphate pentahydrate, and salicylic acid were acquired from Merck (Germany) and cetyl trimethyl ammonium bromide (CTMA-Br) was purchased from Aldrich (Germany).

2.2 Methods

Zinc acetate solution was prepared by diluting zinc acetate salt in water solvent followed by stirring. A solution of CTMA in isopropanol : water (1 : 1) was dispersed slowly into the zinc acetate solution and the final mixture was continuously stirred for 4 h. The solvent was evaporated before drying and calcination at 500 °C for 5 h.
For characterisation, XRD Shimadzu X-6000 with monochromatic radiation source of Cu Kα at 40 kV and filament current of 30 mA was used. Measurements were made with a diffraction angle 2θ from 5° to 70° with step of 0.02° at a speed of 1.2° min^{-1}. The specific surface area, pore volume and pore radius determination were performed using a NOVA 1200e gas sorption analyser. The sample (about 100 - 200 mg) was degassed at 90 °C for 2 h before purging with N_2 at 77 K. The specific surface area parameter was calculated based on Brunair-Emmet-Teller (BET) equation. Surface morphology of the material was obtained by using SEM JEOL.
For catalytic activity testing, UV Lamp of Philips 40 W and ultrasonic (US) batch reactor were used. Catalytic activity of ZnO was tested in various process listed in Table 1.

Table 1: Detail condition of various treatments

Process	Condition
Photolysis	Salicylic acid solution + UV
Photocatalytic	Salicylic acid solution + ZnO + UV
Photooxidation	Salicylic acid solution + ZnO + H_2O_2 + UV
Sonocatalysis	Salicylic acid solution + US
Sonooxidation	Salicylic acid solution + H_2O_2 + US
Sonophotocatalysis	Salicylic acid solution + ZnO + US
Sonophotooxidation	Salicylic acid solution + ZnO + H_2O_2 + US

H_2O_2 was added as oxidant for oxidation mechanism and for each catalytic treatment, ZnO powder was added at a dosage of 0.2 g / 500 mL. UVB Lamp Philips with the power of 20 W was used in an immersed condition as described in Figure 1. Ultrasound compartment for sonocatalysis, sonophotocatalysis and sonophotooxidatin was assembled by using Neytech sonicator operated at a frequency of 35 kHz and output power of 300 W. Catalytic activity was evaluated based on spectrophotometric analysis of treated solution at varied time of sampling. A HITACHI U-2010 spectrophotometer was utilised.

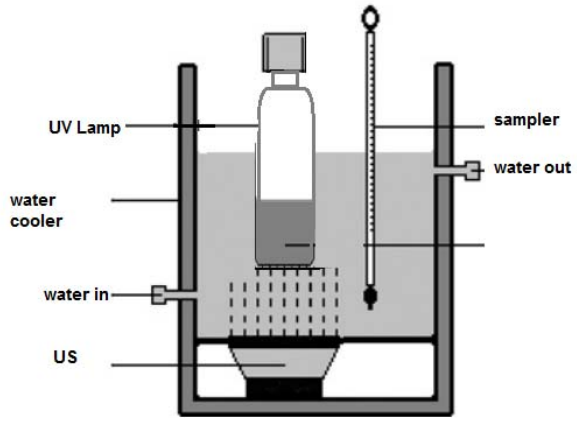

Figure 1: Reactor set-up

3. Results and Discussion

Figure 2 represents the XRD pattern of the prepared ZnO powder. Some characteristic peaks located at 31.84°, 34.52°, 36.33°, 47.63° and 56.71° are associated with the presence of hexagonal wurtzite phase of ZnO according to JPCDS card number: 36-1451. It is also confirmed that the synthesised ZnO was free of impurities as there is no other peaks except ZnO. The average particle size of ZnO sample is 15.6 nm calculated by using Debye-Scherrer formula:

$$d = 0.89\ \lambda\ \beta \cos\theta \quad (1)$$

where 0.89 is the Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane ⟨101⟩.

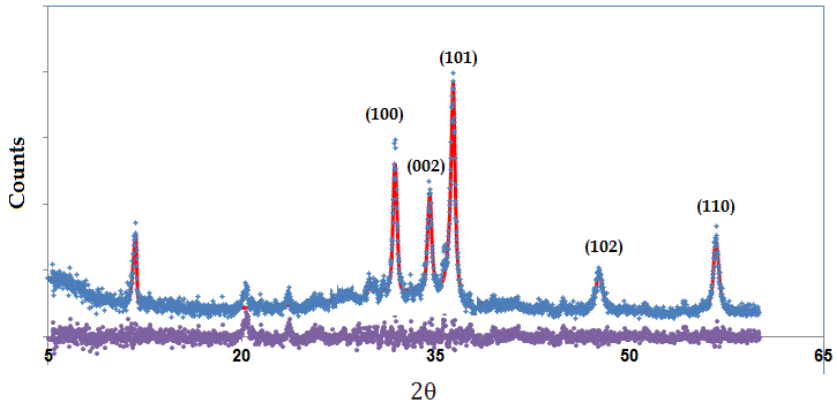

Figure 2: XRD pattern of prepared ZnO

The specific surface area, pore volume and pore radius of the prepared ZnO is presented in Table 2 based on the adsorption-desorption data in Figure 3. The patterns expressed the combination of mesoporous and microporous pattern of material structure and is supported by the pore distribution curve, which demonstrated the modal pores around the region at lower than 20 Å, 20 Å and 50 Å regions. The morphology of the material reflected flower-like structure as described in Figure 4. From the DRUV-Vis analysis data, the calculated band gap energy is 3.08 eV. The value is sufficient for photocatalysis fitted with UV light energy (Figure 5).

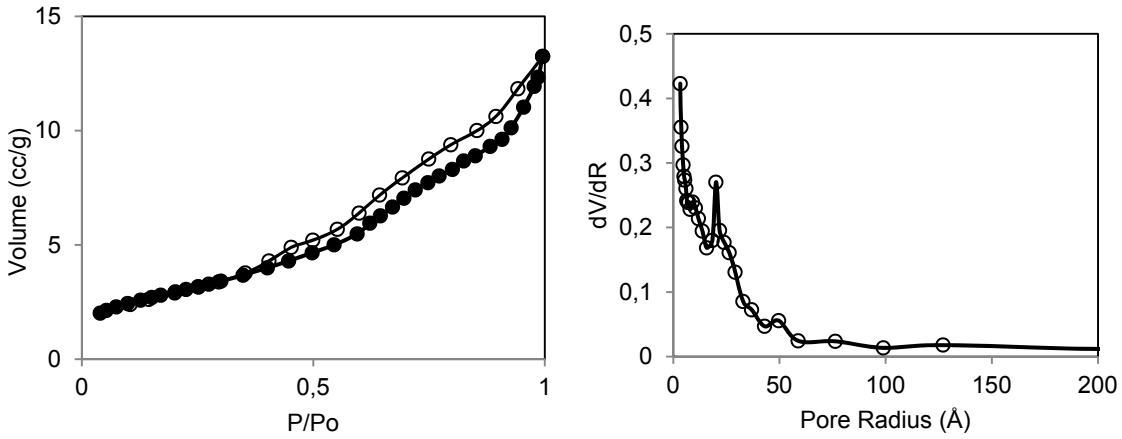

Figure 3: Adsorption-desorption pattern of prepared ZnO

The photoactivity and sonoactivity of ZnO is shown by the kinetics of salicylic acid degradation over varied treatments in Figure 6. From the kinetics curves, it is found that the combined method gives the higher salicylic acid reduction as represented by the lower concentration of rest molecule in treated solution for the same time of sampling.

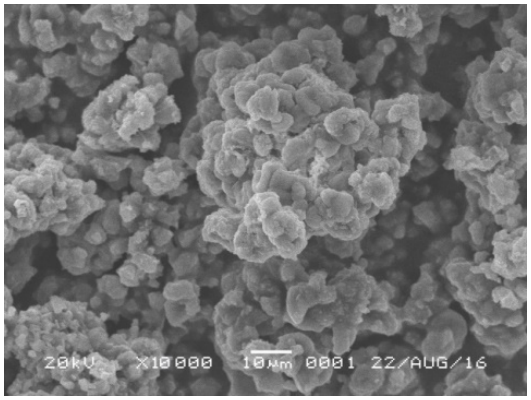

Figure 4: SEM profile of ZnO

In both mechanisms, the US treatment produced lower rate of the degradation compared to the UV treatment. From the evaluation on the catalysis (without H_2O_2) and catalytic oxidation (with H_2O_2) mechanisms, it is concluded that the presence of H_2O_2 accelerated the degradation reaction. The possible mechanism from the presence of components in the treatments are presented in Figure 5.

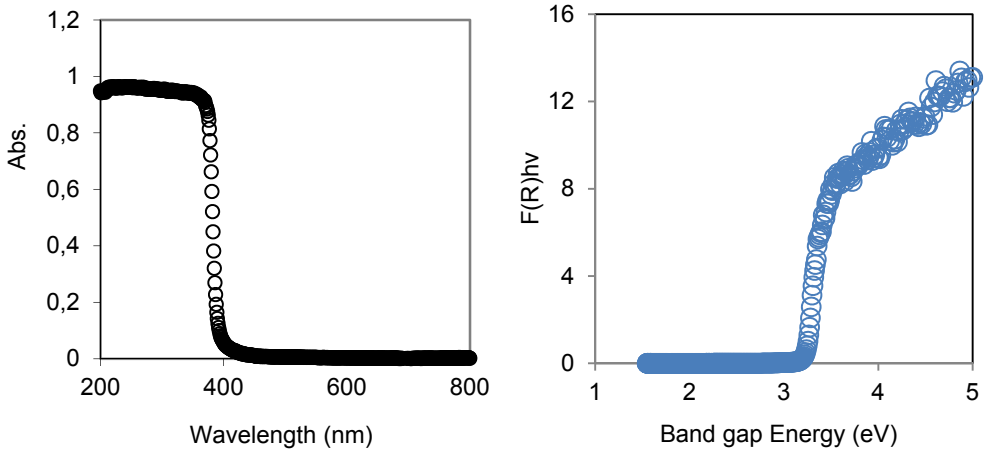

Figure 5: DRUV-Vis of ZnO

Table 2: Surface profile of ZnO

Specific surface area (m^2/g)	Pore Volume (cm^3/g)	Pore radius (Å)
17.46	0.034	19.80

Catalytic activity of ZnO in varied treatments is demonstrated by the change of spectra of treated solution from various process, where one of these is the spectral change from ZnO + UV treatment represented in Figure 6. Figure 6(a) exhibits the trend of salicylic acid degradation over various treatments and it shows that UV treatment gave the lowest degradation rate. From the pattern, it is concluded that the absorbance of the solution reduced as time of treatment increased. The kinetics of salicylic acid degradation from the examined process is depicted in Figure 7. It means that the presence of UV only was not enough to produce radicals from the water molecules cleavage. The use of US also gave significant change of the degradation indicating that the energy consumption from US can potentially destroy the molecule from its interaction with the solvent. ZnO complemented the photocatalytic and sonocatalytic activities as indicated by the increasing degradation rate by the combination of either ZnO and US or ZnO and UV compared to the treatment using US and UV individually. The additional treatment contributed to the increase in salicylic acid destruction and the highest rate was achieved by the combination of ZnO, US, UV and H_2O_2 addition. The trend on synergistic index along time variation is exhibited in Figure 8.

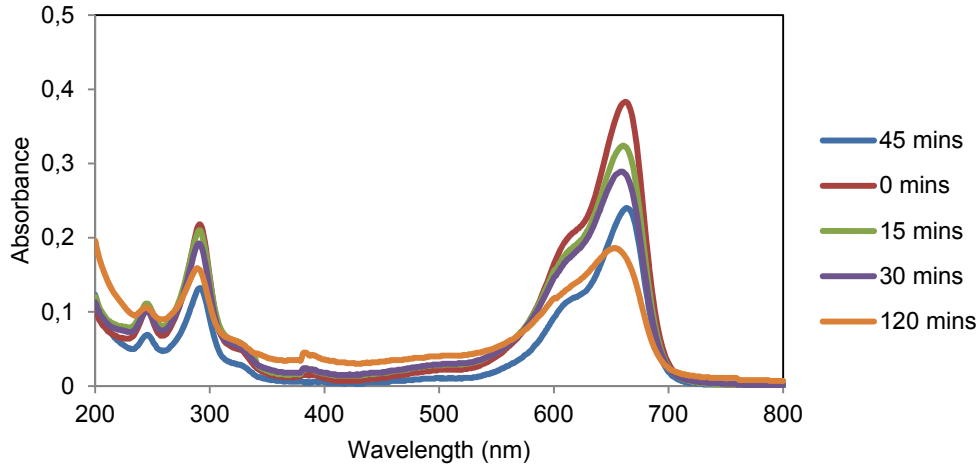

Figure 6: Spectra of treated salicylic acid solution at varied time under ZnO+UV treatment

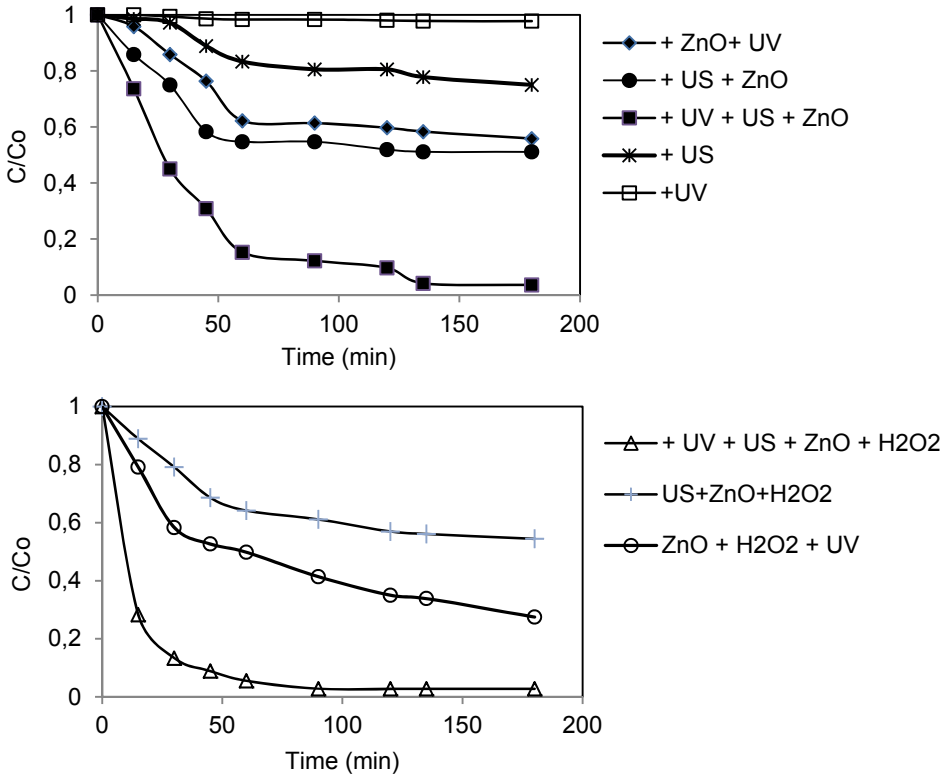

Figure 7: Kinetics of salicylic acid degradation over varied treatments (a) without H_2O_2 (b) with H_2O_2

The synergistic index of the proses using catalytic degradation and also catalytic oxidation degradation was calculated using Eq(2) and Eq(3).

$$\text{Synergistic index} = \frac{(\%\ \text{Reduction})_{\text{Sonophotocatalysis}}}{(\%\ \text{Reduction})_{\text{sonocatalysis}} + (\%\ \text{Reduction})_{\text{photocatalysis}}} \quad (2)$$

Where

$$\%\ \text{Reduction} = \left(1 - \frac{C}{C_o}\right) \text{x } 100\ \% \quad (3)$$

From the values, it is concluded that the combined methods gave synergistic effect as indicated by the values that are more than 1 for sonocatalysis. However, the values reduced the treatment time for more than 90 mins for sonophotooxidation process. This phenomenon is caused by the formation of radicals at initial time followed by propagation reaction such that the effect of synergism between two mechanisms is not significant (Eqs(4) – (7)).

$$H_2O_2 + US \rightarrow 2\ \bullet OH \quad (4)$$

$$ZnO + US \rightarrow ZnO\ (h^+) + (e^-) \quad (5)$$

$$e– + O_2 \rightarrow \bullet O_2^- \quad (6)$$

$$h^+ + H_2O \rightarrow \bullet OH \quad (7)$$

The presence of H_2O_2 accelerated the formation of radicals faster at the early stage of the treatment.

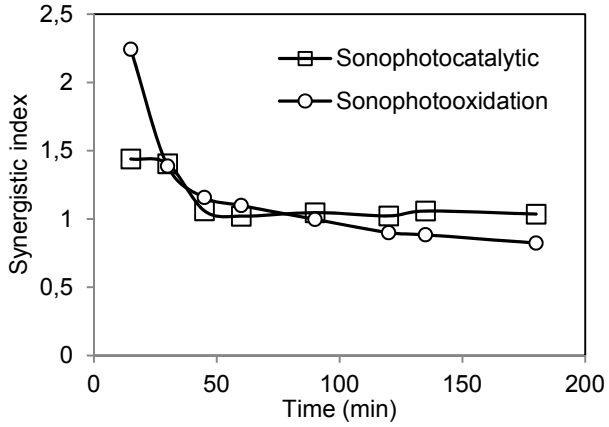

Figure 8: The trend on synergistic index of sonocatalytic and sonophotocatalytic along time variation

4. Conclusion

ZnO was successfully prepared and gave activities in sonocatalysis, photocatalysis and sonophotocatalysis. The physio-chemical characterisation of the material revealed that ZnO was formed in wurtzite phase with the band gap energy of 3.08 eV. The kinetic study on salicylic acid degradation showed the synergistic effect of the sonocatalytic and photocatalytic mechanisms.

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