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Characteristics of ZnO Synthesized by Combined Sol-Gel and Hydrothermal Methods for the Removal of Nitrobenzene

M. G. Liman[1*], A. H. Abdullah[2], M. Z. Hussein[3] and Z. Zainal[2]

1. Department of Pure and Applied Chemistry, Faculty of Science, Usmanu Danfodiyo University,
Sokoto. **NIGERIA**
2. Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Selangor D. E.,**MALAYSIA**
3. Institute of Advanced Technology, Universiti Putra Malaysia, Selangor D. E., **MALAYSIA**
Email: gidado.liman@udusok.edu.ng

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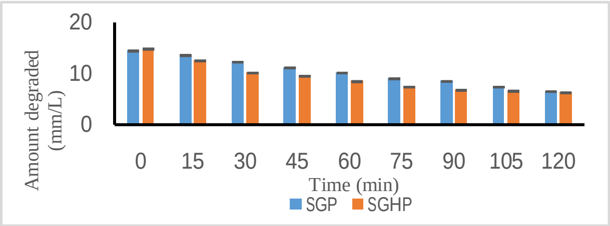
ABSTRACT

Ever-increasing world population and rapid industrial development across the globe is not without problem, especially in terms of availability of potable drinking water. The photocatalytic oxidation of zinc oxide, ZnO, under UV irradiation on organic pollutants in water is well established and nitrobenzene, NB, has been classified under persistent organic pollutants and reported as being carcinogenic.In this study, ZnO catalyst was synthesized via sol-gel method, SGP and for the first time via combination of sol-gel and hydrothermal method, in the presence of polyethylene glycol surfactant, SGHP. The resulting powder was calcined at 500^0*C for a 2 hcalcination period. The prepared samples were characterized using X-ray Diffraction (XRD, Transmission Electron Microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), Surface Area Measurement (BET method) and Diffuse Reflectance Spectroscopy (DRS). All the ZnO samples were spherical with hexagonal structure and particle size ranges from 16 to 96 nm. The photocatalytic activity of the prepared ZnO was evaluated by degradation of NB and 2h of UV light irradiation. ZnO prepared by a combined sol-gel and hydrothermal method, SGHP exhibits the highest photocatalytic activity (75% of NB removal) than SGP. This is attributed to high surface area and small particle size. The degradation of NB follows first-order reaction with a rate constant* k_1 *equals to* 2.16×10^{-2} mgL^{-1} min^{-1} *and a half-life period of 32 min.*

Graphical Abstract



Degradation trend of NB by the ZnO samples synthesized using two different methods (Solgel and Solgel-Hydrothermal) for 2 h duration.

Keywords: Hydrothermal, Nitrobenzene, PEG, Photocatalyst, Nanoparticle, Sol-gel, Zno

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INTRODUCTION

There is no disputing the fact that, rapid globalization and industrialization brought about by advancement in science and technology has been a source of blessing to this world. However, the development has not being without many challenges. The major of these challenges is inadequacy of clean and sanitized drinking water. It was estimated that around 4 billion people worldwide are suffering from clean and sanitized water supply and millions people died due to severe water borne diseases annually [1].Richardson [2] and Wintgens [3] reported that, the discharge of wastewater and chemical spillage from industries into water channels has exacerbated the water quality crisis. For instance, Yang and Cheng [4] and Lu et al. [5] have reported that, by-products of disinfection process generated from chlorination are carcinogenic to human health, thus leading the world researches to develop more efficient water treatment technologies to remove the persistent organic contaminants from wastewater. Many efforts have been devoted to develop technologies that are capable to eradicate the hazardous materials from wastewater [6, 7]. Among many options, the development of processes to transform the toxic and hazardous pollutants into harmless compounds is one of the most effective solutions. However, initially, traditional methods were employed in the purification of water which later turns out to be nondestructive [8], because of their inability to degrade the organic pollutants. Allegre et al. [9], Padmanabhan et al. [10] and Gaya and Abdullah [11] indicated that further treatment is required to destroy the pollutants into final harmless products such as CO_2 and H_2O, which indirectly increases operational cost [11]. Other researchers worked on Advanced Oxidation Processes [12 – 17]. The advanced - oxidation processes -are designed based on the generation of highly reactive species such as $H_2O_2, {}^{\bullet}OH, {}^{\bullet}O_2^-$ and O_3 for the complete destruction of refractory organic compounds (Konstantinou and Albanis, 2004 and Pera-Titus et al., 2004). The commonly used semiconductorsemployed in the photocatalytic processes include, $\mathrm{TiO_2, ZnO, CuO, Nb_2O_5}$ and ZnS. The photocatalytic process is normally undertaken under ambient condition and atmospheric oxygen [18]. Daneshvar, Salari, & Khataee [19] and Akyol et al. [20] both viewed ZnO as a suitable alternative to TiO_2 because of the former's having nearly the same band gap as the latter, follows the same mechanism of photodegradation and sometimes rated high in photocatalytic performance. Gaya and Abdullah have extensively reviewed the papers related to the use of TiO_2 in heterogeneous photocatalytic degradation of organic contaminants. In their review, they have identified important achievements and problems recorded in recent work done until 2007 [11].Nitroaromatic compounds such as nitrobenzene and nitrophenols are largely synthesized and particularly often occur in water bodies as toxic pollutants. The degradation of these compounds in the environment via direct photolysis and by biological treatment is difficult and usually slow. Experimental results suggested the UV:H_2O_2 process as an effective and efficient technology for complete mineralization of nitrobenzene and nitrophenols. Comprehensive reaction mechanism for nitrobenzene photolysis was proposed with detailed discussions [21]. The degradation mechanism of p-nitrophenol (p-NP) exposed to 254 nm UV light was studied in the presence and absence of oxygen respectively via both steady-state photolysis and time-resolved laser flash photolysis (LFP) experiments [22]. Liman et al.reported an enhanced photoactivity of ZnO modified with cobalt against nitrobenzene [23].Many efforts have been devoted to develop technologies that are capable to eradicate the hazardous materials from wastewater. In recent times, photocatalysis has been found to be a very reliable approach towards addressing water pollution problems, even though it is not without its own lapses too.Nitroaromatic compounds such as nitrobenzene and nitrophenols are largely synthesized and particularly often occur in water bodies as toxic pollutants. The degradation of these compounds in the environment via direct photolysis and by biological treatment is difficult and usually slow. Experimental results suggested the UV:H_2O_2 process as an effective and efficient technology for complete mineralization of nitrobenzene and nitrophenols. Comprehensive reaction mechanism for nitrobenzene photolysis was proposed with detailed discussions. The degradation mechanism of p-nitrophenol (p-NP) exposed to 254 nm UV light was studied in the presence and absence of oxygen respectively via both steady-state photolysis and time-resolved laser flash photolysis (LFP) experiments. Nitrobenzene is a nitro aromatic hydrocarbon used to produced aniline and it was nominated by the National Institute of Environmental Health Sciences for listing in the Report on carcinogens based on the conclusions of an International Agency for Research on Cancer (IARC) working group that there is sufficient evidence of its carcinogenicity in experimental animals and that it is possibly carcinogenic to humans [24]. Minero *et al.*,[25] reported that degradation of nitrophenols is slightly faster than that of nitrobenzene. They also reported that TiO_2 showed better efficiency on the degradation of nitrobenzene than ZnO. Nitrobenzene is considered to be highly toxic aromatic compound which is widely used in explosives, pesticides, prepharmo, dye production and so on[12] yet very little work were conducted on its removal. Qiang-Rong*et al.*,[26] reported the use of excimer UV lamp (λ = 172 nm) in degrading nitrobenzene and confirmed that, the degradation is more efficient with UV/H_2O_2 combination than using UV alone. Particularly titania, TiO_2 and zinc oxide, ZnO have been extensively studied and were found to be very good semiconductors involved in wastewater treatment operation in the presence of light. Initially the attention was more on the Titania but with several advantages of Zinc oxide over Titania, the attention is now being focused on Zinc oxide [27]. The work by Qamar and Muneer found that TiO_2 samples and ZnO can efficiently catalyze the photomineralization of vanillin in the presence of light and oxygen [28]. Some misconceptions in the photocatalytic studies mainly originating from scientists without proper understanding of heterogeneous catalysis has been reported [29]. Zhang and co-workers have succeeded in preparing ZnO nanoparticles by a surfactant-assisted complex sol-gel method using zinc nitrate [30]. In the same manner, a lot of researches were conducted in which semiconductor photocatalysts were used for the photodegradation of some pollutants [31-35]. A. M. Turkey studied the catalytic oxidation of CO over pure and doped over Cu-Ni-O system [36].

MATERIALS AND METHODS

ZnO was synthesized via sol-gel method by dissolving a known amount of $Zn(NO_3)_2.6H_2O$ and a known amount of $C_6H_8O_7.H_2O$ (1:1) in a mixture of $100cm^3$ of deionized water and $10cm^3$ of 1 % $C_2H_6O_2$.The solution was magnetically stirred for few minutes to allow for complete dissolution. The pH of the solution was adjusted to pH 7 using conc. NH_4OH. The solution is then warmed in a steam bath at 80^oC for 4 hours after which it is aged at room temperature for another 4 hours and then magnetically stirred at 85^oC for 15 hours. The resulted gel is dried in an oven at 100^oC for 12 h. The dried sample is grinded and calcined at 500^oC for 2 h in a Carbolite furnace with a heating rate of 10^oC min^{-1}. However, to investigate the changes in physical and catalytic properties, Ethylene glycol was interchanged with Polyethylene glycol surfactant and calcination time was changed to 4 and 6 h. Temperature could likely be one of the factors that can affect the structure or crystallinity of the catalyst and hence affects its photoactivity. For this reason, the effect of calcination temperature was studied for the catalyst prepared through sol-gel method and without modification. In doing this, same preparation procedure was adopted with only variation at the calcination stage. At the calcination stage, three samples prepared in the same manner were calcined at 400, 500 and 600^oC. The effect is studied using the characterization and photodegradation results. ZnO was synthesized via the combination of sol-gel and hydrothermal methods using the same amount of the reagents. However, after obtaining the gel solution, it is placed Teflon-line stainless steel vessel and placed inside hydrothermal oven at 80^oC for 18 h. The precipitate formed is filtered, washed using deionized water and finally dried in the oven at 100^oC for 12 h. The sample was then calcined as the above calcination procedure.

RESULTS AND DISCUSSION

Characterization: The two different samples (SGP and SGHP) synthesized via a sol-gel method and a combined sol-gel and hydrothermal methods were characterized by XRD technique and the result presented in figure 1. From the figure it could be seen that five peaks are found within (2Θ = 20 – 60) and almost all the peaks are sharp but with slight variation in intensity. The XRD analysis conducted on the SGP and SGHP samples have shown that the samples depict a typical hexagonal wurtzite crystal structure of ZnO, matching the hexagonal structure of ZnO (JCPDS No: 98-000-2485). A significant difference in terms of peak position and peak intensity between SGHP and SGP is obvious as illustrated in figure 1 could point to why SGHP has a better photoactivity than SGP. The crystallite size of SGHP calculated using Scherer's formula (Table 1), is slightly smaller than that of SGP, though the difference is insignificant. Table 1 shows the comparison of the crystallite size with the particle size measured from TEM for the two samples.

Table1. Comparison of crystallite size of SGP with SGHP calculated using Scherer's formula with particles size measured using TEM

Sample	XRD (nm)	Particle Size from TEM (nm)
SGP	34.75	34 – 75
SGHP	32.38	28 – 48

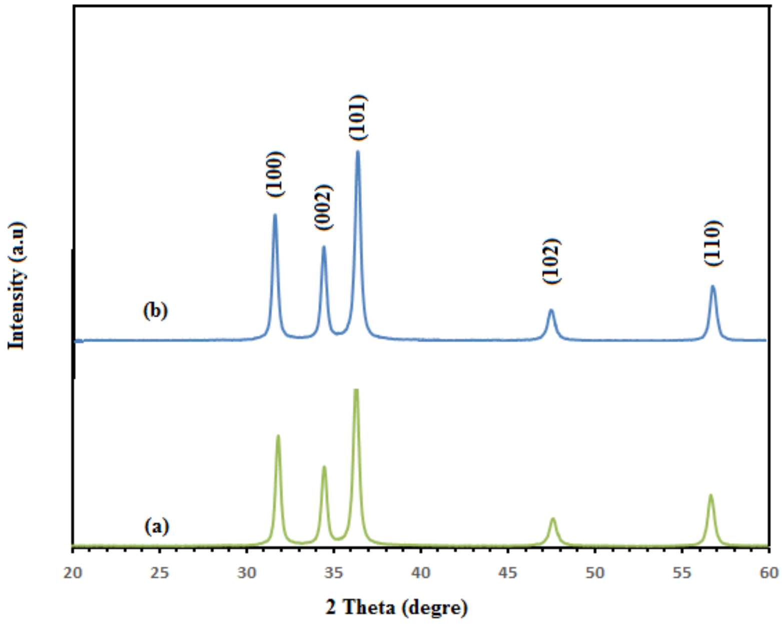

Figure 1. XRD patterns for ZnO synthesized using different method (a) SGP and (b) SGHP

Figures 2 and 3 represent the TEM and FESEM images of SGP and SGHP. From the figures, it could be seen that the shapesare spherical in nature and with small particle sizes. There is no much difference when compared with those of SGP. A closer examination of the TEM images reveals that the particle size of SGHP is smaller than that of SGP1 (Table 4) with less agglomeration.

Surface area is one of the important characteristics of semiconductor catalyst that speaks about its photoactivity. The surface area of the samples (SGP and SGHP) synthesized via two different methods are shown in table 2. Barrett-Joyner-Hollander (BJH) method was used to determine the pore size distribution of the samples and the results are presented in figures 4.

From the BJH plots it could be seen that the narrow pore size distributions centered at 9 and 8 nm for SGP and SGHP respectively, which according to Sing *et al*., [37] are classified as mesoporous (pore widths between 2 – 50 nm). figure 4 and 5 showed the N_2 adsorption-desorption isotherms and BET plots for the two samples. The isotherms depict the typical type IV curve accompanied by H4 hysteresis loop, which according to IUPAC classification indicates the presence of mesopores [37 – 39].

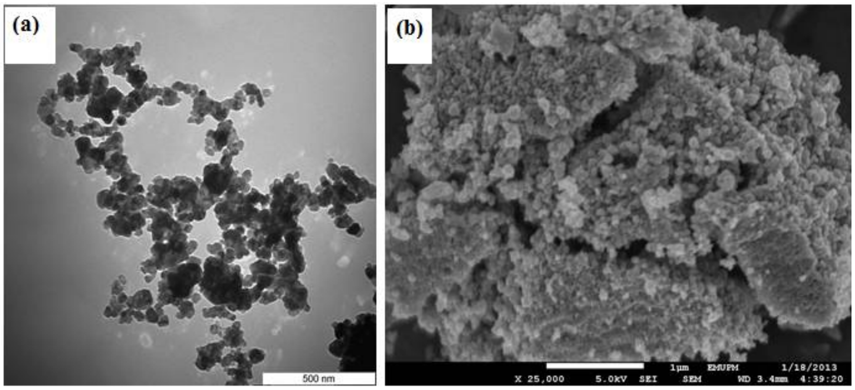

Figure 2. The (a) TEM and (b) FESEM images of ZnO prepared by sol-gel-hydrothermal method (SGHP)

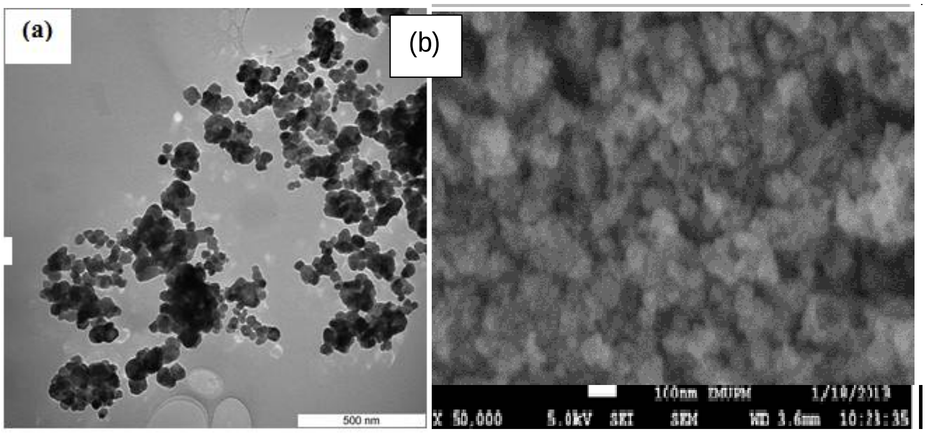

Figure 3. The (a) TEM and (b) FESEM images of ZnO prepared by sol-gel method (SGP)

From the BJH plots it could be seen that the narrow pore size distributions centered at 9 and 8 nm for SGP and SGHP respectively, which according to Sing et al. [37] are classified as mesoporous (pore widths between 2 – 50 nm). Figure 4 and 5 showed the N_2 adsorption-desorption isotherms and BET plots for the two samples. The isotherms depict the typical type IV curve accompanied by H4 hysteresis loop, which according to IUPAC classification indicates the presence of mesopores [37 – 39].

Table 2. BET surface area and pore size distribution for SGP and SGHP

Sample	BET surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (A)
SGP	9.0716	0.077	187.894
SGHP	12.631	0.089	163.060

CBand gap energy of the samples was measured by utilizing diffuse reflectance spectra of the modified ZnO for the two samples (SGP and SGHP) synthesized via two different methods. The diffuse reflectance spectra for the two samples are shown in figure 6. It can be seen that the strongest absorption is between 350 – 390 nm while above that the absorption is weak. The band gap energies are shown on table 4 and the band gap energy values were estimated through a plot of $(ahv)^2$ against photon energy (hv). The estimate was made by determining the intercept of tangent at x-axis and the results are shown in figure 7.

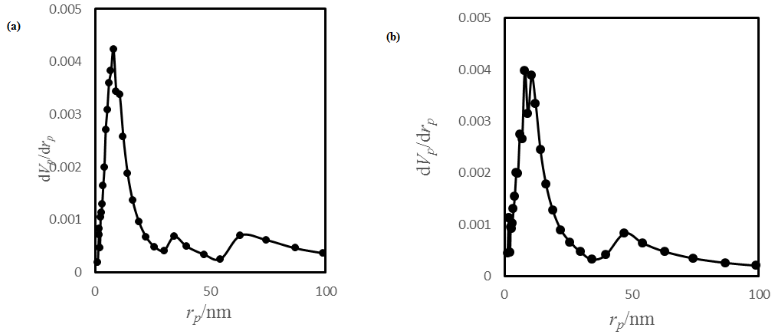

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Figure 4. Pore size distribution of (a) SGP and (b) SGHP

Table 3. Band gap energies for the SGP and SGHP

Sample	Band gap energy (eV)
SGP	3.24
SGHP	3.21

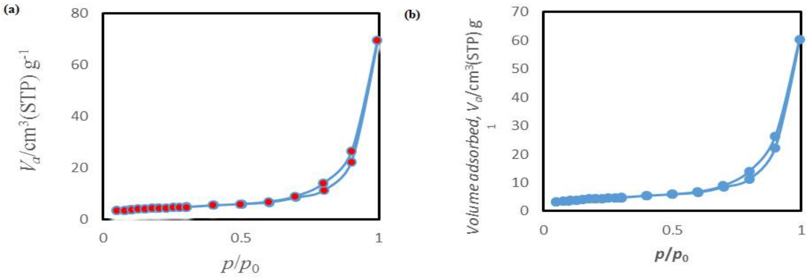

Figure 5. N2 adsorption-desorption isotherms for (a) SGP and (b) SGHP

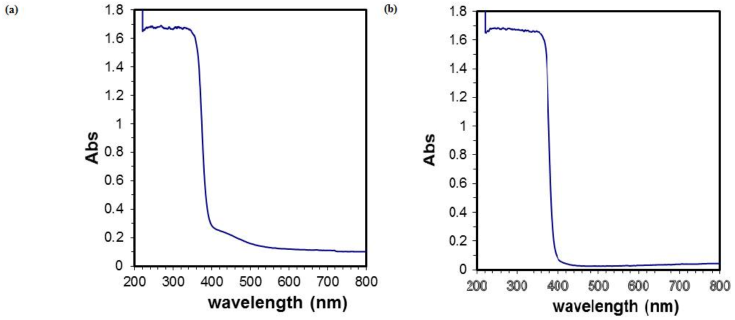

Figure 6. Diffuse reflectance spectra of (a) SGP1 and (b) SGHP

Photoactivity: The photoactivity of the samples prepared from the two different methods was studied and the results were illustrated in figures 8 and 9. It is clear from the result that SGHP has shown a better photoactivity than SGP1 even though the difference is not much. The result of the photodegradation studies conforms to the characterization results. The larger surface area of SGHP as compared to that of SGP gave it an advantage by providing much catalyst surface for adsorption to take place. Table 4 gives the rate constant as calculated using pseudo-first order rate. The rate is in agreement with photoactivity results, indicating a better performance by SGHP.

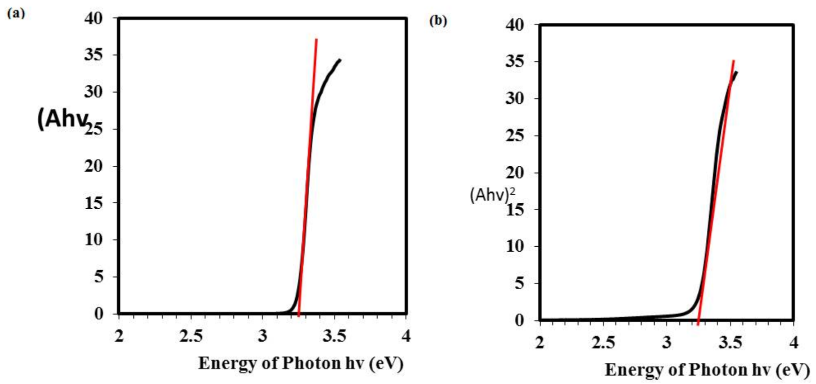

Figure 7. Band gap energy plot of (a) SGP1 and (b) SGHP

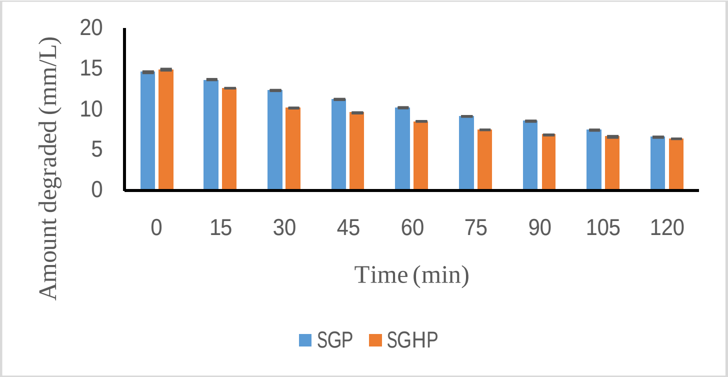

Figure 8. Degradation trend of NB by the ZnO samples synthesized using two different methods (Solgel and Solgel-Hydrothermal) for 2 h duration.

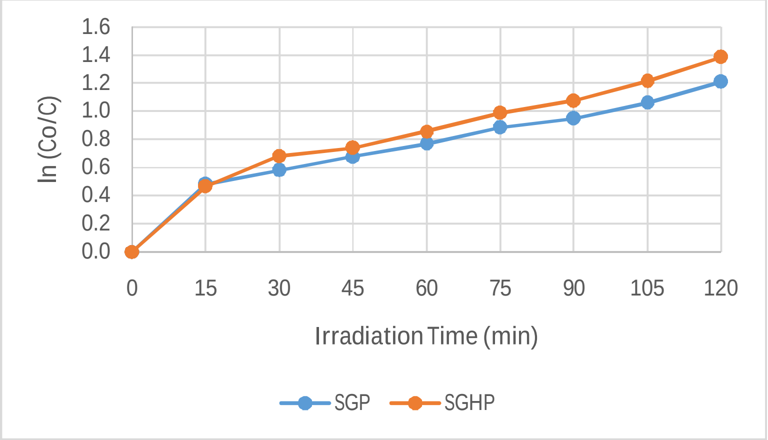

Figure 9. Kinetics of the degradation trend of NB by the ZnO samples synthesized using different methods

Table 4. First-order rate constant, K1 and R2 values of various samples synthesized using two different methods

Concentration (mg/L)	First-order	
	Rate constant, K_1 (x 10^{-3} mg L^{-1} min^{-1})	R^2
SGP	11.1	0.9780
SGHP	12.6	0.9882

APPLICATION

Zinc oxide photocatalyst was prepared via two different methods. The combined sol-gel and hydrothermal methods has shown an improvement on the photoactivity of zinc oxide on the removal of nitrobenzene. Therefore, the zinc oxide photocatalyst nanoparticle is applicable in the water treatment polluted by nitrobenzene.

CONCLUSIONS

In this study, ZnO nanoparticles were successfully synthesized via sol-gel and a combined sol-gel and hydrothermal methods. The characterization studies are in agreement with the photoactivity results of the ZnO samples against nitrobenzene. The optimum condition of NB removal was achieved at catalyst loading of 0.75 g, 20 ppm of NB and at neutral pH (pH = 7) under UV irradiation. The SGHP sample resulted in a better removal than the SGP sample under the study condition. Therefore, the combined sol-gel-hydrothermal method is a step forward towards the preparation of zinc oxide with enhanced activity.

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