

Photocatalytic Degradation of Resorcinol by ZnO/SiCnanocomposites under Visible Light Irradiation

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ABSTRACT: Resorcinol is widely used as a chemical intermediate in chemical, rubber and pharmaceutical industries. Wastewater containing resorcinol released from these industries contaminates the aquatic and can cause adverse effects to the environment and human health. Hence, it should be removed from the wastewater before it released into the different environmental compartments. The investigation focused on the photocatalytic degradation of resorcinol in aqueous solution was carried out in visible reactor with a novel photocatalyst i.e., ZnO nanorod/SiC nanocomposites prepared by simple sol-gel method. The prepared photocatalyst were characterized by XRD, UV-DRS, FT-IR, AFM, FE-SEM, EDAX, HR-TEM and SAED analyses. The analytical results proved that the prepared photo catalyst were highly crystalline, nanosized and possesses absorption in the visible region. The UV-DRS results suggested that the band gap energy was 3.019 eV for the prepared photo catalyst. The effect of various experimental parameters such as pH, catalyst dosage, variation of concentration and effect of electrolyte addition were investigated in detail to optimize the efficient degradation of resorcinol. It is observed that neutral pH was found to be optimum for the effective degradation of the resorcinol molecules. Catalyst dosage of 10mg/10ml resulted in higher percentage of degradation and the addition of sodium bicarbonate electrolyte showed a maximum interference in the photo degradation process. The photo degradation process followed a pseudo first order kinetics and was continuously monitored by UV-Visible absorbance measurement and COD. The experimental results clearly showed that the photocatalytic degradation efficiency of resorcinol was above 90% under visible light irradiation employing ZnO/SiC nanocomposite photocatalyst.

KEYWORDS: Photocatalyst; nanocomposite; resorcinol; sol-gel; visible light

I. INTRODUCTION

The release of phenolic compounds like resorcinol into the environment are from a number of anthropogenic sources, including production, processing, and consumer uses, especially from hair dyes and pharmaceuticals. Resorcinol from these sources may result in widespread contamination of the aquatic ecosystem due to their hazardous and carcinogenic properties [1]. Heterogeneous semiconductor photocatalysis is currently being considered as a promising technique for water purification in comparison to other conventional methods [2-3]. This is based on the generation of highly reactive hydroxyl radicals by semiconductor materials under UV and visible light irradiation and utilized to degrade organic compound into carbon dioxide and water [4-5]. In recent years, TiO₂, ZnO, WO₃ have been employed as active semiconductor photocatalysts. Among these photocatalyst, ZnO is a well known n-type semiconductor with a wide band gap of 3.2eV, low cost, environmentally friendly nature [6-9] and also showed good photocatalytic activity [10]. However, a major drawback of ZnO is the recombination of photogenerated electron-hole pair and thereby reduced photocatalytic efficiency. Therefore, it is essential to increase its visible-light activity and also reduce the recombination of photogenerated electron-hole pair.

Combination of two semiconductors has been proven to reduce the recombination of photogenerated electrons and holes through increasing the charge separation [11-12]. Silicon carbide (SiC) possesses a band gap of ~3 eV and exhibits attractive properties that are quite similar to ZnO; combination of both these materials may show promising photocatalytic activity. In the present work, ZnO/SiC nanocomposites had been synthesized by simple sol-gel method.

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The prepared material was tested for its photocatalytic efficiency for the degradation of a model pollutant such as resorcinol, under visible light irradiation. The highly visible active hybrid catalyst was characterized by XRD, UV-DRS, FT-IR, AFM, FE-SEM, EDAX, HR-TEM and SAED techniques. The extent of photodegradation was evaluated by UV-Visible spectroscopy and chemical oxygen demand (COD) analyses.

II. MATERIALS AND METHODS

Resorcinol, and zinc acetate ($\text{Zn}(\text{OAc})_2$) were obtained from S. D. Fine Chemicals Ltd., India. The other chemicals used in these studies are Sodium hydroxide, Hydrochloric acid, Sulphuric acid (Merck), Potassium dichromate (Extra pure AR, SRL), Ferrous solution (AR, SD Fine Chemicals Ltd), Ferrous ammonium sulphate (Extrapure AR, SRL), Silver sulfate (Merck). All the solutions were prepared by using deionised water.

The nanorod ZnO/SiC nanocomposite was synthesized from its precursor through a simple sol-gel method. Prepared photo catalyst was characterized by XRD, FT-IR, UV-DRS, AFM, HR-TEM, SAED, FESEM and EDAX techniques. The efficacy of the photo catalyst was tested for the degradation of resorcinol. In order to optimize the degradation of resorcinol, the following experimental parameters were studied viz. the effects of pH, dye concentrations, mass of catalyst, kinetics and addition of electrolytes. The extent of degradation was evaluated using UV-Vis spectroscopy (Shimadzu UV 2101PC) and also in terms of reduction in chemical oxygen demands (COD).

Nanorod ZnO/SiC nanocomposite (ZnO/SiC) was prepared from its acetate precursor by a sol-gel technique. In a typical synthesis, required amount of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in deionised water and then 25% w/w NH_4OH was added slowly until the solution attained pH 8, the white precipitate $\text{Zn}(\text{OH})_2$ thus formed were separated from the supernatant by filtration and further washed with double-distilled water repeatedly. Appropriate quantity of surface cleaned SiC was added into $\text{Zn}(\text{OH})_2$. Then the whole content was heated at 65°C until the excess ammonia evaporates completely. The resulting grey coloured ZnO/SiC precipitate was filtered and dried in a hot air oven at 150°C for 1 hour. The powder was calcined at 300°C for 30 min in a tubular furnace under atmospheric conditions.

III. RESULTS & DISCUSSION

A. XRD Analysis

The XRD pattern of the ZnO and ZnO/SiC shown in Fig.1 (i (a and b)) respectively. XRD patterns indicated all the peaks of ZnO with the hexagonal wurtzite structure [13]. No other impurity phases were observed. Six major diffraction peaks were observed at 2θ values of 31.7, 34.6, 36.2, 47.6, 56.5, 62.9 and 68.0, marked by their miller indices (100), (002), (101), (102), (110), (103) and (112) indicating that the phase of ZnO hexagonal wurtzite (Fig. i(a)). In addition, three peaks observed at 35.5, 41.3 and 59.72 which is due to the diffraction from (111), (200) and (220) planes of SiC respectively [14], were observed in the prepared nanocomposite (Fig. i(b)). These results proved that surface reaction occurred between ZnO and SiC, resulting in the formation of ZnO/SiC nanocomposites. The average particle sizes (36-59 nm) of ZnO/SiC were calculated using Scherer's equation (1):

$$d = 0.94\lambda / \beta \cos \theta \quad (1)$$

Where λ denotes the wavelength of the radiation equal to 0.154 nm, β is the full width at half maximum and θ is the half diffraction angle. These results confirmed that the prepared ZnO/SiC were highly crystalline and nano sized.

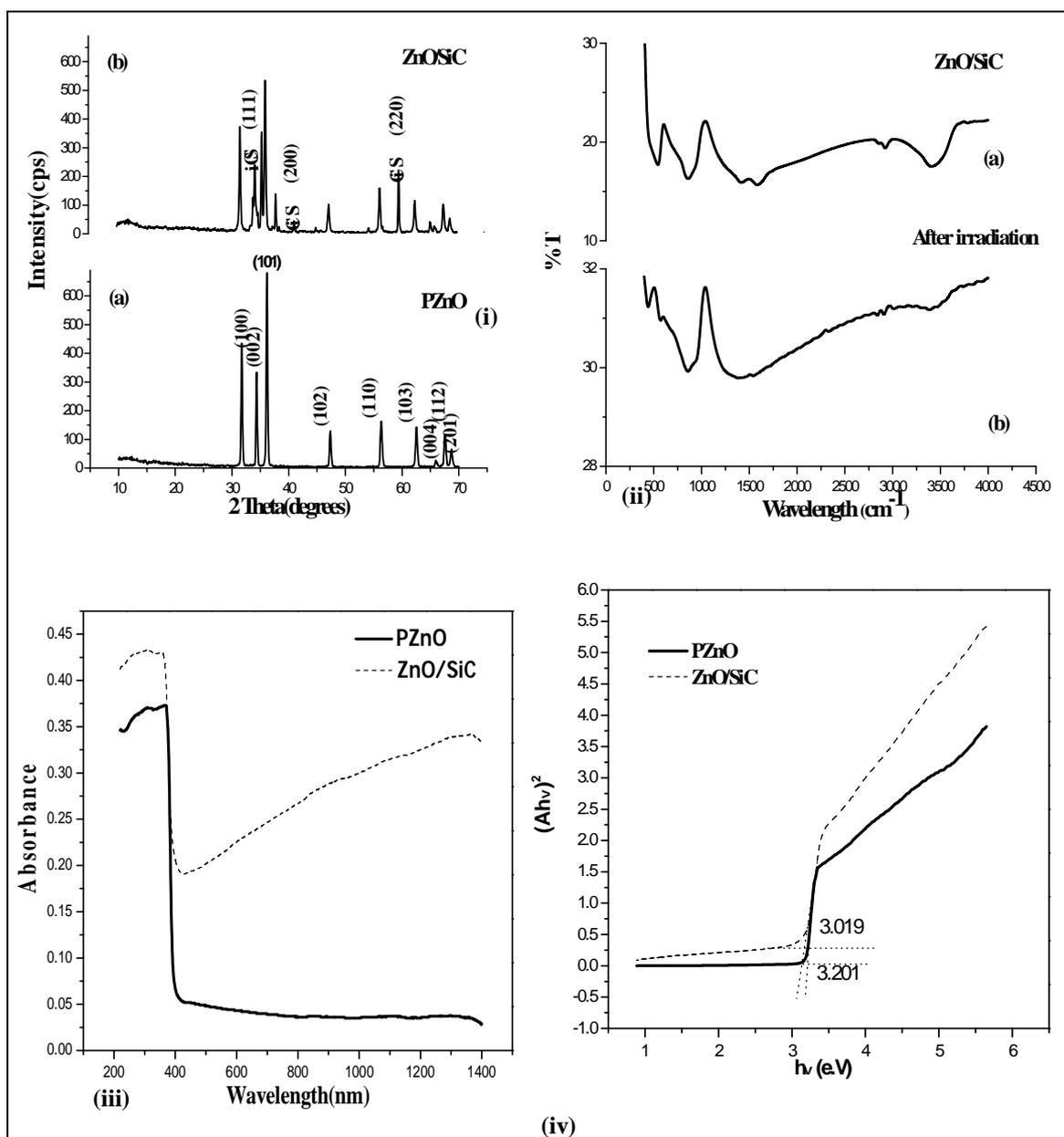


Fig.1. XRD patterns of (i) ZnO/SiC (ii) FTIR spectrum of ZnO/SiC (iii) UV-DRS spectrum of ZnO/SiC and (iv) shows a plot of $(Ahv)^2$ vs $h\nu$ for the determination of band gap of ZnO/SiC

B. FT-IR analysis

FT-IR spectrum of ZnO/SiC shown in Fig.1(ii). The absorption band at 537 cm^{-1} corresponds to the Zn-O stretching mode[15], while those at $2,900\text{ cm}^{-1}$ correspond to C-H mode, the peaks between $1,400$ and $1,600\text{ cm}^{-1}$ are represents the C=O stretching mode and the band at 3385 cm^{-1} corresponds to the stretching vibration of OH bond. The peak at 860.50 cm^{-1} which is attributed to the Si-C stretching vibration [16] present in ZnO/SiC nanocomposite. These

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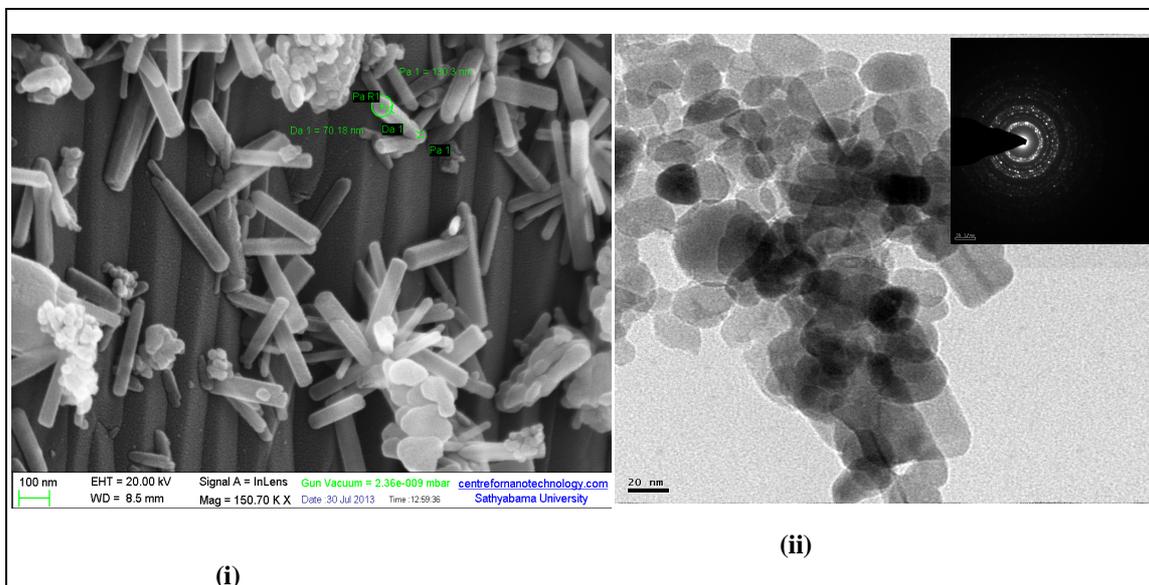
stretching vibrations indicated that the presence of water molecule on the surface of sample. The FT-IR spectrum of before and after irradiation of ZnO/SiC formed similar peaks.

C. Band gap energy

The direct band gap energy of the ZnO/SiC was calculated using diffuse reflectance spectra were shown in Fig .1(iii). The results showed an increase in the absorbance in the visible light region with the combination of SiC. The values of E_g for the prepared photocatalyst can be derived from the spectra by plotting $(Ah\nu)^2$ against $h\nu$ as shown in Fig .1(iv). The results revealed that the calculated values of E_g for ZnO and ZnO/SiC were 3.2 and 3.019 eV respectively. This indicates shifting the spectra of the ZnO/SiC nanocomposite to the visible light area. This narrow band gap (3.019 eV) indicates a shift in the spectrum of ZnO/SiC nanocomposite towards the visible region, which confirms that the material could act in the visible region [17]. This band-gap energy of ZnO/SiC resists the recombination of electron-hole pairs and could enhance the photocatalytic activity.

D. FE-SEM and HR-TEM analysis

The Field emission-Scanning electron microscopy images of ZnO/SiC were shown in Fig.2 (i). The FE-SEM morphology revealed that ZnO was formed as a uniform nanorod with a hexagonal wurtzite structure composite with SiC substrate. These results proved the ZnO/SiC formed as a nanocomposites. The size of the ZnO nanorod in ZnO/SiC was in the range of 30 to 40 nm. The surface morphology of the catalysts were also analysed by HR-TEM and the results were shown in Fig.2 (ii). It is observed that the prepared ZnO/SiC photocatalyst is arranged as a rod like structure with particle size of 20 nm.



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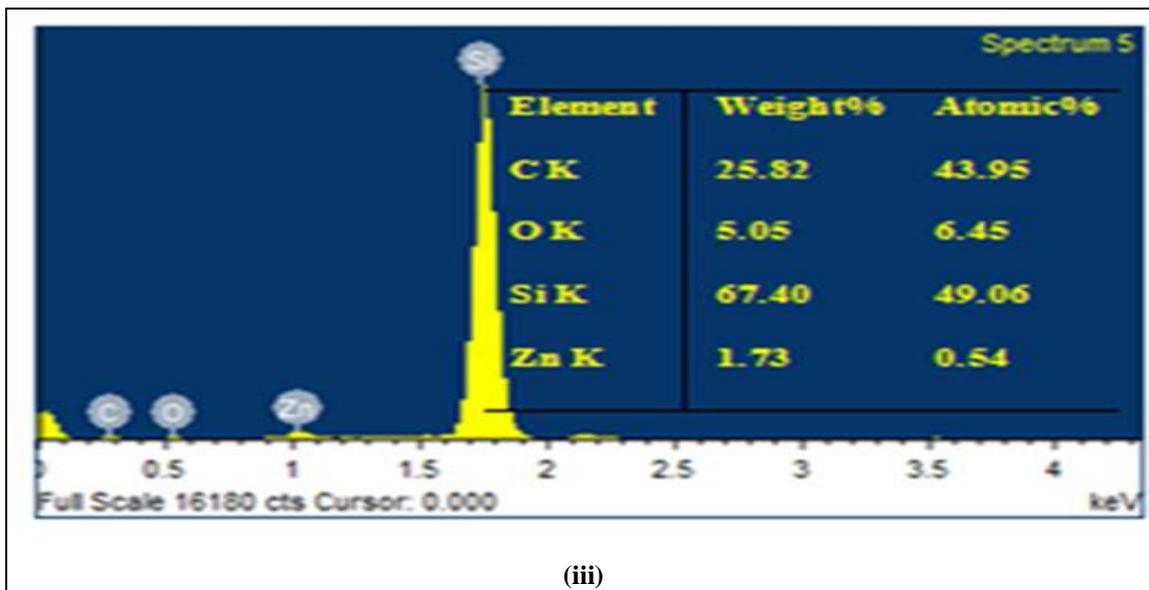
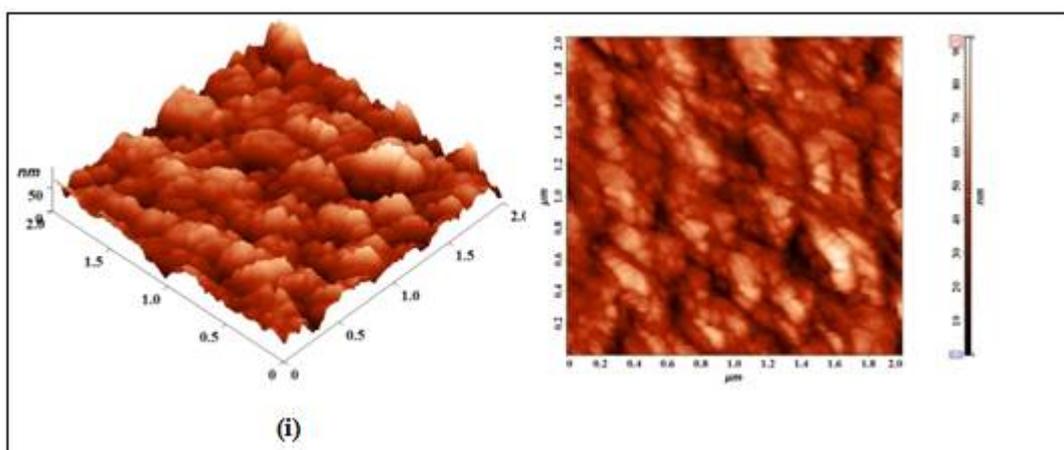


Fig.2. (i) shows the FESEM images of ZnO/SiC, (ii) shows the HR-TEM images of ZnO/SiC, The inset of (ii) shows the SAED pattern of the prepared ZnO/SiC and (iii) EDAX spectrum of ZnO/SiC.

The SAED pattern also suggested that the prepared ZnO/SiC catalyst is in polycrystalline nature. Fig.2 (iii) shows the EDAX spectrum of ZnO/SiC and this result confirmed that the presence of Si, Zn and O

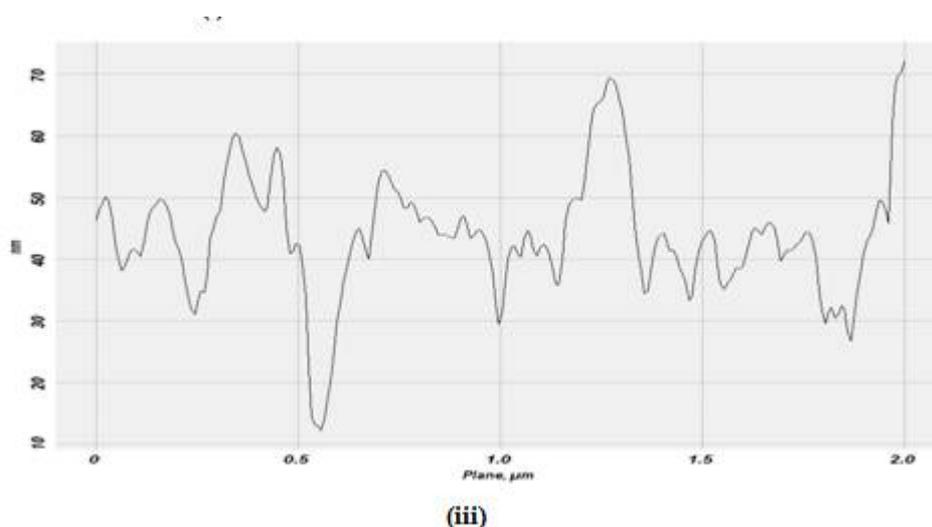
D.AFM analysis



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AFM images are shown in Fig.3 (i) and (ii). These results showed that the prepared ZnO/SiC was nano sized and possessed high surface roughness and porosity which may be

Fig.3. AFM images (i), (ii) and roughness profile (iii) of prepared ZnO/SiC.

depends up on their higher photocatalytic efficiency. The average roughness of ZnO/SiC was found to be 35.55 nm. The surface roughness profile of the photocatalyst is also shown in Fig.3 (iii). The high roughness of ZnO/SiC increases the adsorption of organic moieties on the surface of photocatalyst and increases the degradation efficiency.

IV. PHOTOCATALYTIC ACTIVITY

The photocatalytic activity of ZnO/SiC was tested by the photodegradation of resorcinol under visible light irradiation. The effect of pH on the degradation of resorcinol was studied in the pH range from 2-12 with 10 ppm concentration with 1 g/L catalyst dosage. Neutral pH was found to be optimum for the degradation of resorcinol (Fig.4. (i)). The effect of catalyst dosage on the degradation of resorcinol were shown in Fig.4(ii). A catalyst dosage of 10 mg ZnO/SiC produced >90 % photodegradation of resorcinol. Further increase in the amount of photocatalysts showed a decreasing the photodegradation, due to an increase in turbidity of the suspension with high loading of photocatalyst, there is a decrease in the penetration of light into the solution and hence photodegradation decreases [18]. The photocatalytic degradation of resorcinol at initial concentrations (10, 15, 20 and 25) for a catalyst dosage of 1g/L at neutral pH under visible light irradiation is shown in Fig.4 (iii). The extent of degradation decreased with increase the concentration of resorcinol. The reason for this is the resorcinol molecules act as a shield that affects the light penetration and thus leading to a decrease in the catalytic activities of ZnO/SiC photocatalysts.

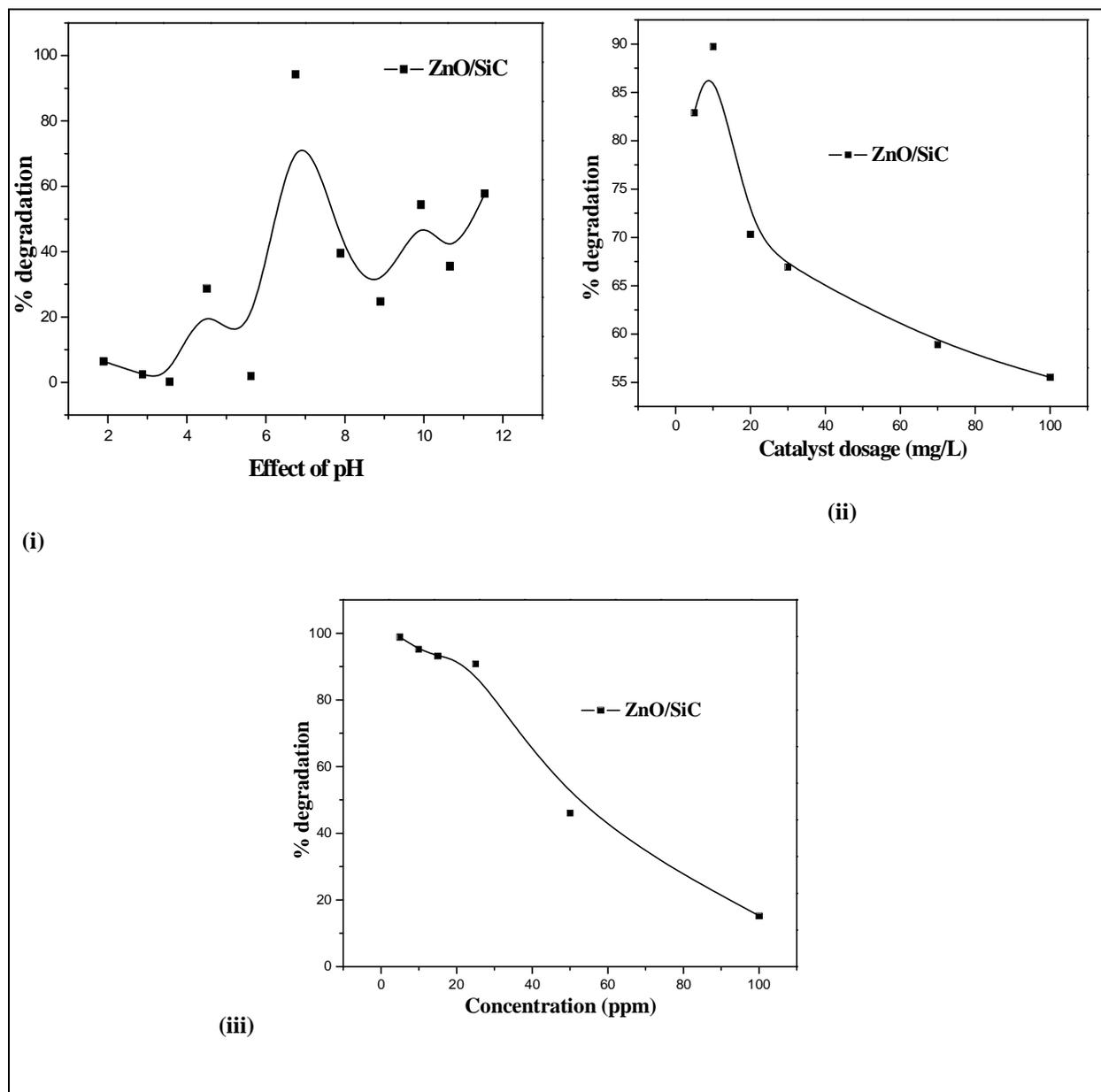


Fig.4. (i) shows a visible irradiation studies on the effect of pH on Resorcinol degradation. (ii) and (iii) shows the effect of catalyst dosage (5-50 mg/L) and concentration on Resorcinol degradation by the prepared ZnO/SiC photocatalyst.

A. Kinetic studies of resorcinol degradation

The kinetics of photodegradation of various concentration of resorcinol in visible light were illustrated in Fig.5 (i). The photodegradation of resorcinol by visible light employing ZnO/SiC as the photocatalyst followed a pseudo-first order kinetics (Fig.5(ii)) with respect to the initial concentration of resorcinol. The kinetics of photodegradation of resorcinol could be represented by the equation (2)

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$$\ln(C_0/C_e) = k_{obs}t \quad (2)$$

where, C_0 and C_e are the initial and final concentrations of resorcinol molecules with respect to time “ t ”, and k_{obs} is the observed pseudo-first order rate constant.

The values of k_{obs} were determined using least square regression analysis and the calculated periods of half life $t_{1/2}$ ($t_{1/2} = 0.693/k$). The values of k_{obs} were determined using least square regression analysis and the calculated periods of half-life $t_{1/2}$ ($t_{1/2} = 0.693/k$) are given in Tab.1. The COD is an effective technique to measure the strength of organic moieties present in waste water. Fig.5 (i) represents the reduction in COD of the resorcinol at various concentrations and also shows that the results of COD removal increased with degradation of the resorcinol increases [19-20]. It could be observed that the reduction in COD values of the treated resorcinol solution indicated complete degradation of resorcinol molecules.

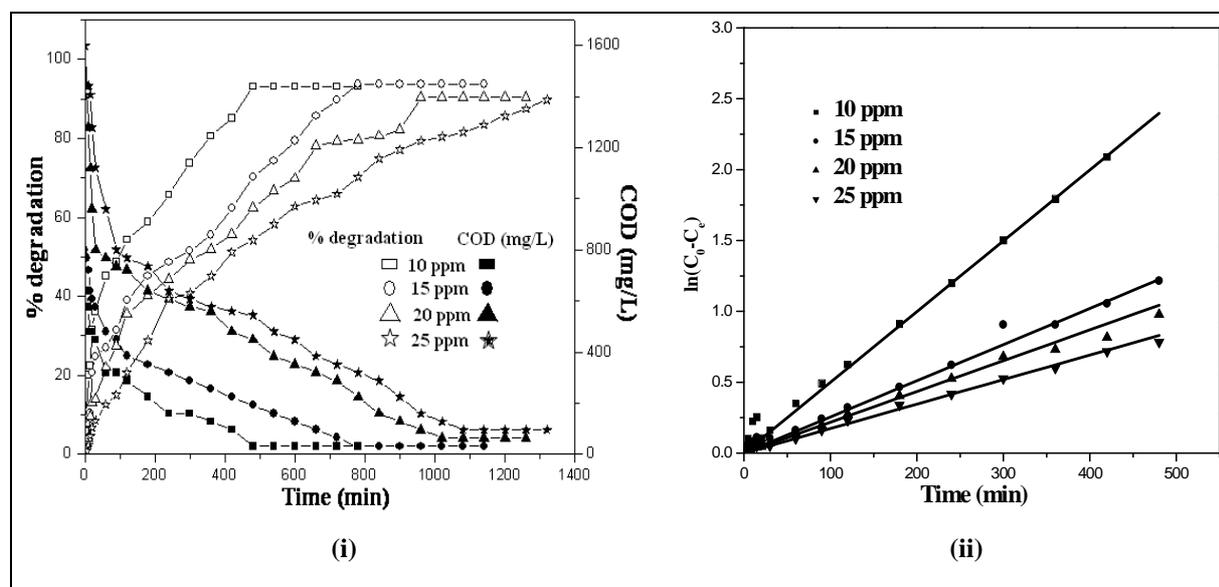


Fig.5. (i) shows the kinetics and COD plot, (ii) shows the plot of rate constants.

Tab.1. shows the parameters obtained from the pseudo-first order rate equation.

Initial Resorcinol concentration (ppm)	ZnO/SiC		
	$k_{obs} \times 10^{-3}$ (min^{-1})	$t_{1/2}$	R^2
10	4.99	138.87	0.97754
15	2.55	271.76	0.97827
20	2.13	325.53	0.98765
25	1.73	400.57	0.99521

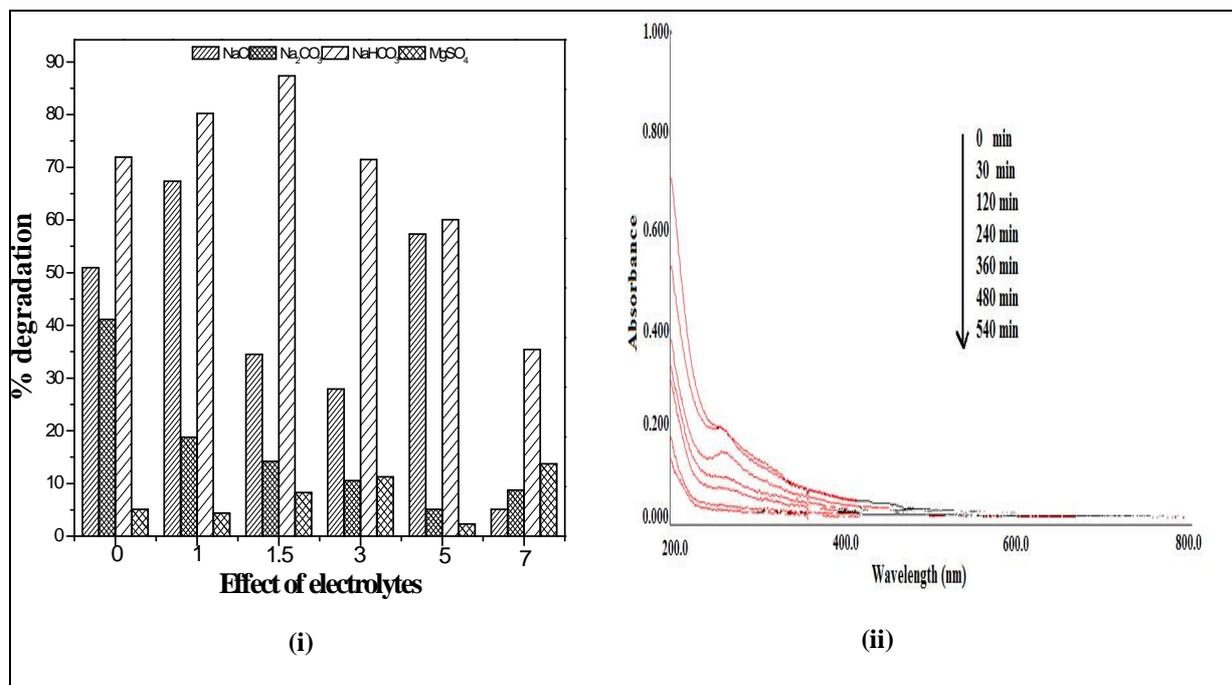
B. Effect of electrolyte addition

The effect of added electrolytes on photodegradation of resorcinol molecules have also been studied in the presence of NaCl, Na_2CO_3 , NaHCO_3 , and MgSO_4 for ZnO/SiC photocatalysts. The results are shown in Fig. 6 (i). The concentrations of electrolytes were varied from 0 to 7 wt%. It is observed that the percentage of resorcinol degradation was altered with an increase in the wt% of electrolytes in all photocatalytic experiments. In addition, 1.0 % NaCl, and

1.5 % of NaHCO_3 as electrolytes with 1g/L of ZnO/SiC and 0.5 g/L of resorcinol produced more than 60 and 90% degradation respectively which was a very high photocatalytic activity under visible light irradiation. On the other hand, the addition of MgSO_4 and Na_2CO_3 retarded the photodegradation with an increase in the concentration of electrolytes. This is because of the presence of carbonates and sulphates ions in the aqueous phase which act as a radical scavenger [21] thus leading to a decrease in the percentage of photodegradation.

C. Absorption spectra of resorcinol degradation

Fig.6 (ii) shows the UV-VIS spectrum for 10 ppm resorcinol solution under visible light irradiated for different time intervals. The absorption peaks of photodegradation process showed a decrease with an increase in irradiation time. The results showed the absorption peaks reduced gradually and completely disappeared after 540 min. The results indicated that ZnO/SiC showed high photocatalytic activity since 100% resorcinol removals were observed at 540 min



for 10 ppm concentration of resorcinol.

Fig.6. (i) shows the effect of different electrolytes on the degradation of Resorcinol by the prepared photocatalyst, (ii) shows a full length absorption spectrum (200 – 800 nm) for the photocatalytically degraded 10 ppm Resorcinol samples collected at different time intervals.

V. CONCLUSIONS

The ZnO/SiC was prepared by simple sol-gel method. The prepared photocatalysts were characterized by XRD, UV-DRS, FT-IR, FESEM, EDAX, HR-TEM and AFM analysis. ZnO/SiC photo catalyst was employed as the catalyst for the degradation of resorcinol in the presence of visible light radiation. Resorcinol solutions of lower concentration were completely degraded by using ZnO/SiC under visible light irradiation. The photo degradation of resorcinol was applicable in neutral pH. The band gap energy was 3.019eV for ZnO/SiC was calculated from UV-DRS spectra. AFM analysis showed that the ZnO/SiC possesses high roughness and porosity. The photodegradation of resorcinol followed the pseudo first order kinetics. Photo degradation of resorcinol confirmed through chemical oxygen demand of the aqueous phase solutions before and after irradiation of resorcinol solutions. It is confirmed that the lower

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resorcinol concentration produced minimum amount of COD. It proves that resorcinol could be easily degraded with ZnO/SiC photocatalysts.

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