

# Synergistic Effects of Activated Carbon on ZnO for Improved Photocatalytic Degradation of p-Nitrophenol

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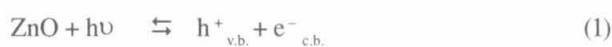
Here, we report the synergistic effect of heterogeneous photocatalysis by combining ZnO and activated carbon (AC) composite (ZnO/AC) towards the remediation of water polluted with hazardous organic pollutant. ZnO/AC composites were prepared by simple and non-toxic method, without use of organic solvents. The prepared composite was characterized by XRD, SEM and BET. The photocatalytic activity was tested with photodegradation of p-Nitrophenol (PNP) under UV irradiation. The present investigation showed enhanced photocatalytic degradation efficiency of ZnO/AC over ZnO. Different operational parameters like initial concentration of PNP, composite concentration, optimization of ratio of ZnO and AC, comparison of composite prepared by mechanical and physical mixing, and the effect of H<sub>2</sub>O<sub>2</sub> have also been studied. The optimized concentration of ZnO/AC composite was found to be 40 mg/100mL for photodegradation of PNP. Maximum degradation of PNP was achieved for the initial concentration of 2.5 x 10<sup>-4</sup>mol/L. Ratios of ZnO and AC in the composite were optimized and found to be 5:1 respectively. It was observed that photocatalytic degradation by ZnO/AC composite was more effective and faster mode of removing PNP from aqueous solutions than the ZnO alone due to the synergistic effect.

**Key words:** ZnO/AC composites, photodegradation, PNP, synergistic effect

## Introduction

With increasing stresses of water shortages due to deteriorating water quality, urbanization, and climate change, wastewater reclamation and reuse is becoming a widely endorsed strategy for augmenting freshwater resources. The frequent occurrence of pesticides and phenolic compounds in wastewater and associated environmental hazards has heightened concerns over public health due to their high toxicity and bio-recalcitrant nature<sup>1</sup>. These substances cause a high toxicity, provoking serious health problems: blood dyscrasia, eyes and skin irritations, neurotoxicity, carcinogenesis, effects on reproduction and cell development particularly in the early stages of life<sup>2</sup>. Advanced oxidation processes (AOPs) such as UV/H<sub>2</sub>O<sub>2</sub><sup>3</sup>, Ozonation<sup>4</sup>, photo Fenton<sup>5</sup>, sonolysis<sup>6</sup>, and photocatalysis<sup>7,8</sup> have been widely and extensively explored to mitigate a great variety of pollutants present in various environmental media. Among the different semiconductors reported in the literature, TiO<sub>2</sub> is the most stable, efficient and promising material widely used as a photocatalyst for generating charge carriers because of biological and chemical stability, low cost, non poisonous and long life span<sup>9,10</sup>. However, widespread use of TiO<sub>2</sub> catalyst is uneconomic for large-scale water treatment operations. ZnO appears to be a suitable alternative to TiO<sub>2</sub><sup>11, 12</sup> since its

photodegradation mechanism has been proven to be similar to that of TiO<sub>2</sub><sup>13, 14</sup>. ZnO is a wide band gap n-type semiconductor (3.37eV) with large exciton binding energy of 60meV at room temperature. This property has made ZnO as one of the most attractive photocatalyst in the treatment of wastes and pollutants present in air and water by photodegradation mechanism. ZnO has been reported<sup>13</sup>, sometimes, to be more efficient than TiO<sub>2</sub>. Its efficiency has been reported to be particularly noticeable in the advanced oxidation of pulp mill bleaching wastewater, the photooxidation of 2-phenylphenol and photocatalysed oxidation of phenol<sup>15,16</sup>. When ZnO is irradiated with the UV, an electron jumps from valance band to conduction band leaving hole behind.



Electrons from conduction band react with oxygen forming superoxide ions (O<sub>2</sub><sup>·-</sup>) in equation (2) and the hole react with adsorbed water on surface of ZnO (or hydroxide anions) to generate the hydroxyl radical which is shown in equation (3) and (4) depicted in **Fig.1**.

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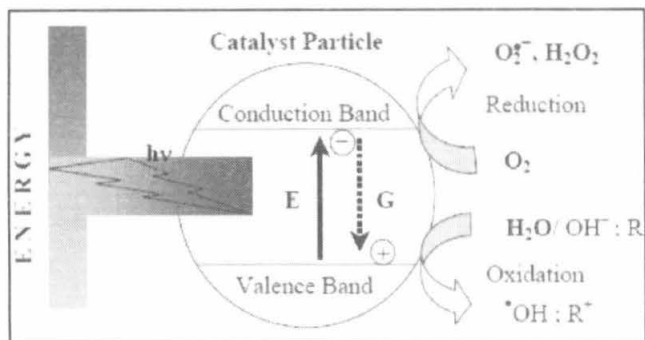


Fig. 1: Mechanism of ZnO photocatalysis

However, problems with the use of ZnO powders are also well recognized: specifically, (a) the difficulty in separating the powder from the solution after reaction is complete, (b) aggregation of particles in suspension, especially at high loadings, and (c) difficulty in application to continuous flow systems<sup>17</sup>. For these problems, various methods of photocatalyst particle support have been investigated such as alumina, zeolite, silica gel, fiber optic cable, glass beads, quartz, stainless steels, clays and activated carbon<sup>18,19</sup>. In particular, activated carbon (AC) has been extensively researched as a support for heterogeneous catalysis because of large specific surface area and a well developed porous structure, resulting in an attractive force toward organic molecules<sup>20,21</sup>.

### Materials and methods

Analytical Grade (A.R.) reagents were used throughout the present studies. The following chemicals were purchased from various companies and used without further purification. AC was procured from Lurgi Aktivkohle GmbH Germany, ZnO was purchased from Merck Pvt. Ltd, Germany. It was used for the preparation of ZnO/AC composites. PNP was purchased from Sisco Research Laboratory, Pvt. Ltd, India.

AC was available in granular form. It was washed with distilled water several times and then dried at 110 °C for 2 hrs in an oven. Dried granules of AC were crushed in a mortar into fine powder and the obtained powder was calcinated at 200 °C for 2 hrs to remove moisture and was kept into desiccators until further use. AC was used for the preparation of composite.

### Synthesis of ZnO/AC composite

Composite was synthesized by two methods : (1) Physical mixing – Definite amounts of ZnO and AC were dispersed in distilled water and magnetically stirred for 3 hrs. The composite was filtered and dried at room temperature. (2) Mechanical mixing – Definite amounts of ZnO and AC were grinded in mortar pestle and calcinated at 200 °C for 2 hrs.

ZnO and AC were mixed in different proportions such as 1:1, 5:1 and 10:1. They were named as ZnO/AC (1:1), ZnO/AC (5:1), and ZnO/AC (10:1) respectively. AC has high surface area than ZnO, hence amount of AC was kept constant and amount of ZnO was varied while preparing the composites. As prepared composites were then used as photocatalysts and studied for their photocatalytic degradation efficiencies for the degradation of PNP as a target pollutant.

### Photoreactor

Photocatalytic experiments were carried out with 100 mL,  $2.5 \times 10^{-4}$  M PNP aqueous solution using 40 mg ZnO/AC composite as photocatalyst under exposure to UV irradiation in a multilamp photoreactor constituting four 8W low pressure mercury vapor lamps at  $30 \pm 1^\circ\text{C}$ . Air was bubbled through the reaction solution from the bottom using aerator with constant speed. The whole reactor assembly was mounted on magnetic stirrer for mixing the aqueous solution during the reaction in order to ensure that the solution was well-mixed and the catalysts did not settle down inside the container as depicted in Fig. 2.

## Results and discussion

### Characterization

To confirm the formation of ZnO/AC composite, XRD pattern has been observed for composite with 5:1 ratio

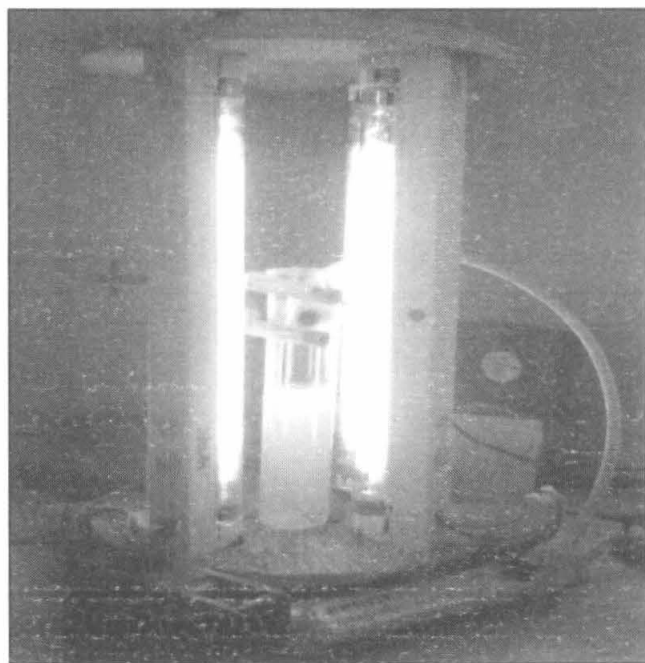


Fig. 2: Experimental set-up of photoreactor

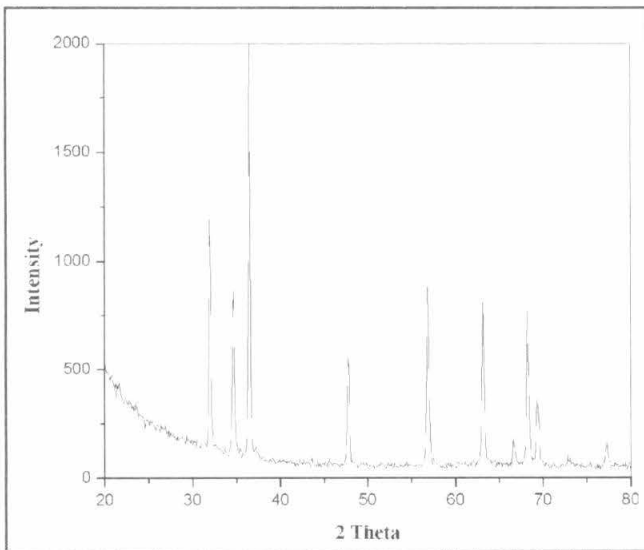
of ZnO/AC mixture (**Fig. 3**). The clear and well-defined peaks at  $31.6^\circ$ ,  $34.2^\circ$ ,  $36.2^\circ$ ,  $47.4^\circ$  and  $56.6^\circ$  (D8-Advance Bruker axis) appeared in the nanocomposites which confirm the typical hexagonal wurtzite structure of ZnO particles in the XRD pattern of ZnO/AC mixture. Besides there was no AC peak in the XRD pattern of ZnO/AC mixture, this suggests that the crystal structure of ZnO particles has not modified due to the presence of AC<sup>22,23</sup>. The SEM image of ZnO/AC composite is depicted in **Fig.4**, which reveals that pores of AC particles are uniformly covered by ZnO particles. The BET surface area of ZnO and the synthesized composite ZnO/AC were measured by using the BET surface area Analyzer (Thermo Scientific Surfer) using nitrogen as the

adsorbate and were found to be  $15 \text{ m}^2/\text{g}$  and  $71.24 \text{ m}^2/\text{g}$  respectively. Increased surface area of the composite as compared to ZnO causes increased rate of photocatalytic degradation of PNP.

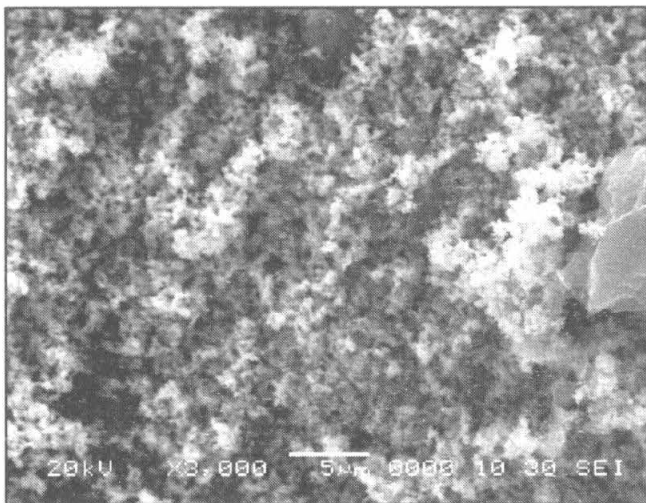
*Effect of addition of AC and optimization of ratio of ZnO and AC*

ZnO and AC were mixed with each other with different ratios such as 1:1, 5:1 and 10:1 and were named as ZnO/AC (1:1), ZnO/AC (5:1) and ZnO/AC (10:1) respectively. ZnO/AC (5:1) showed better degradation than ZnO/AC (1:1) and ZnO/AC (10:1) as shown in the **Fig. 5**. Since amount of AC and ZnO is in same proportion in the composite ZnO/AC (1:1), AC absorb the maximum UV in the system due to its black characteristics resulting in very less availability of UV light for ZnO activation. The system thus shows mainly the adsorption of organic pollutant on ZnO/AC (1:1) due to the good adsorbent capacity and high surface area of AC.

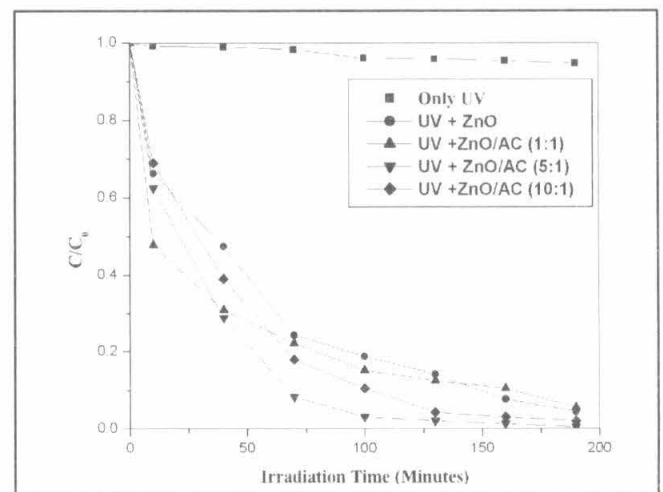
Composite ZnO/AC (5:1) showed very good degradation rate of PNP in presence of UV, which is shown in the **Fig. 5**. In the presence of UV light, adsorbed ZnO on the AC in the composite gets activated and  $\cdot\text{OH}$  radicals are generated on ZnO surface. Also due to high surface area of AC, PNP gets easily adsorbed on it and generated  $\cdot\text{OH}$  radicals come closer to play their role effectively. The overall effect is the optimum utilization of  $\cdot\text{OH}$  radicals giving enhanced rate of PNP degradation. Hence, in presence of UV, both ZnO as well as AC play important role for the maximum degradation of



**Fig. 3 :** XRD pattern of ZnO/AC (5:1) composite



**Fig. 4 :** SEM image of ZnO/AC (5:1) composite



**Fig. 5 :** Effect of addition of AC and optimization of ratio of ZnO/AC composite

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PNP. Hence synergistic effect due to presence of optimum proportion of ZnO and AC in the composite ZnO/AC (5:1) is observed.

### Optimization of dose of composite ZnO/AC

Effect of catalyst dose was studied by varying the amounts of composite ZnO/AC (5:1) ranging from 30-50 mg/100mL, in order to obtain an optimum catalyst dose for the maximum photodegradation, which could save unnecessary use of excess of photocatalyst. From Fig. 6, 40 mg dose of the

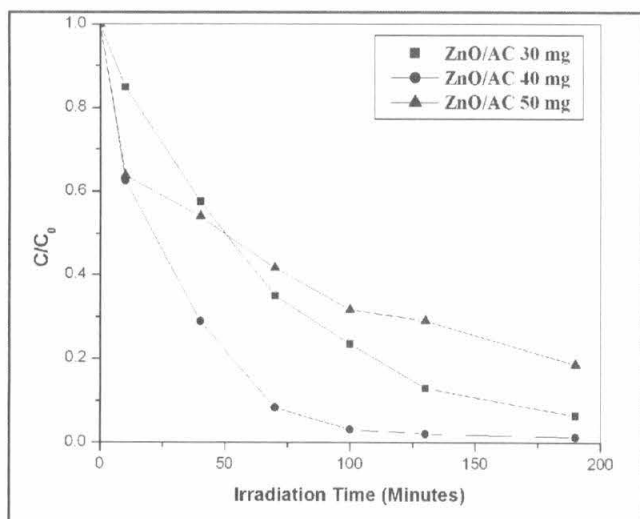


Fig. 6 : Optimization of composite dose

catalyst ZnO/AC (5:1) showed the better result for the degradation of the  $2.5 \times 10^{-4}$  M PNP. Beyond this dose the substrate molecules available are not sufficient for adsorption by the increased amount of composite ZnO/AC (5:1) in the solution. Hence the additional amount of catalyst is not involved in catalyst activities and the rate does not increase with an increase in the amount of catalyst<sup>20</sup>. Also at high composite ZnO/AC (5:1) dose, particles aggregate which reduces the interfacial area between the reaction solution and the photocatalyst, thereby decreasing the number of active sites on the catalyst surface. Hence the catalyst dose for the degradation of PNP has been optimized and found to 40mg/100 mL of aqueous solution of PNP.

### Optimization of initial concentration of PNP

Using the above optimized dose of catalyst, studies were carried out for the optimization of initial PNP concentration. For this, concentration of PNP was varied for  $2.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  M. The rate of degradation of PNP was

found to be less for concentration  $5 \times 10^{-4}$  M. At the higher concentration, the number of collisions between molecules increased whereas the number of collisions between molecules and OH radical decreased. Consequently, the rate of reaction was retarded<sup>23</sup>. Therefore, the degradation of  $2.5 \times 10^{-4}$  M showed better result than  $5 \times 10^{-4}$  M PNP as shown in the Fig.7. Hence in the present investigation the optimized initial concentration of PNP was found to be  $2.5 \times 10^{-4}$  M.

### Effect of grinding ZnO and AC

AC and ZnO were taken in required ratio and carefully ground in a mortar with the aim of favoring an intimate mixture

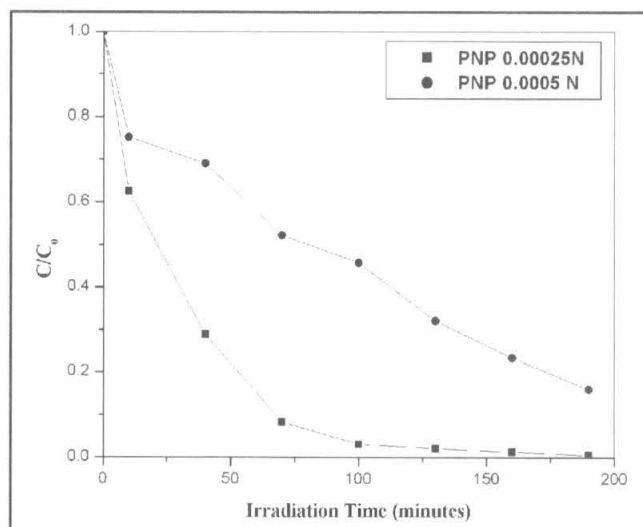


Fig. 7 : Optimization of initial concentration of PNP

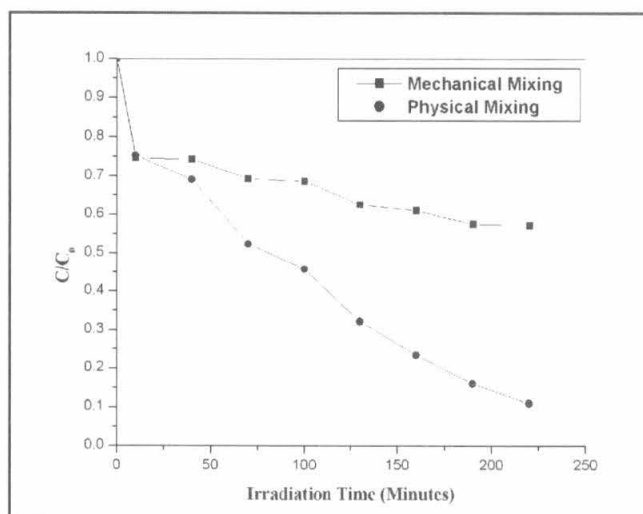


Fig. 8 : Comparison of composite prepared by mechanical and physical mixing

of both solid phases. The effect of grinding was then studied for photocatalytic degradation of PNP. It is clear from Fig.8. that grinding of ZnO and AC results in decrease in degradation rate. In mechanical mixing, crystallinity is affected, the adsorption and synergistic effect are reduced. Grinding had practically negative effect on degradation of PNP because of introduction of some crystal defects in the ZnO crystal lattice.

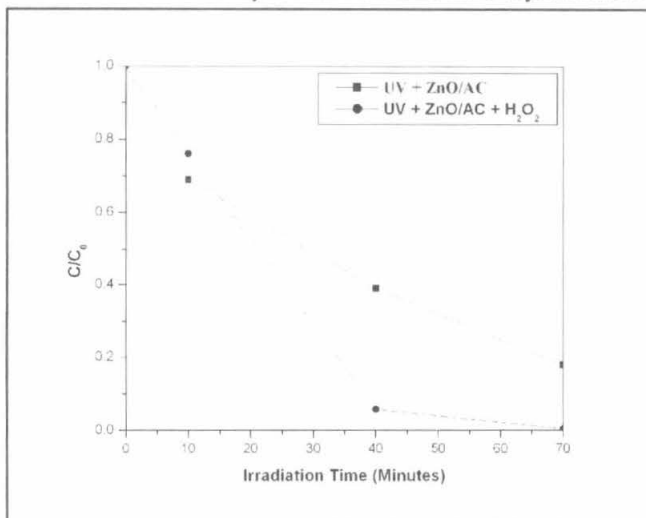


Fig. 9 : Effect of addition of H<sub>2</sub>O<sub>2</sub> to PNP+UV+ZnO/AC system

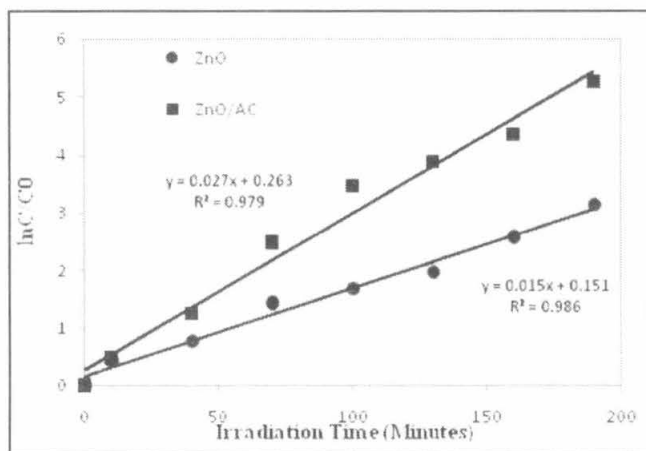


Fig. 10 : Kinetic plot of degradation of PNP by ZnO and ZnO/AC composite

This affects the crystalline structure of the catalyst. In this process, the increased activity of ZnO/AC catalyst is found to be due to increased adsorption and synergistic effect. If the crystallinity is affected, the adsorption and synergistic

effect are reduced. Thus the grinding decreases the photocatalytic activity of the catalyst<sup>24</sup>.

#### Effect of addition of H<sub>2</sub>O<sub>2</sub>

The addition of H<sub>2</sub>O<sub>2</sub> to the heterogeneous system increases the concentration of OH radicals<sup>25</sup>. The experimental

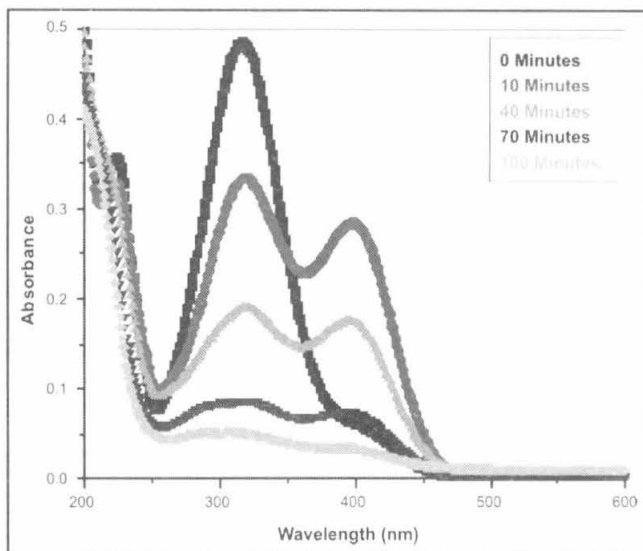


Fig. 11 : Changes in the UV-visible spectra during photodegradation of PNP by ZnO/AC composite

results for the UV + ZnO/AC + H<sub>2</sub>O<sub>2</sub> system are depicted in Fig.9. A drastic increase in the rate of degradation of PNP was found due to the increased concentration of OH radicals. As an electron acceptor, H<sub>2</sub>O<sub>2</sub> does not only generate OH radicals but inhibits the electron-hole recombination process<sup>26</sup> at the same time, which is one of the most important practical problems in using ZnO as photocatalyst<sup>27</sup>. Hydrogen peroxide can also absorb light at 254 nm and decompose to produce ·OH radicals, which would lead to increased rate of PNP degradation<sup>28</sup>.

#### Synergy effect

The mechanism of semiconductor photocatalysis has been well established. As discussed in literature<sup>29</sup> the photocatalytic degradation of organic substrate occurs mainly by the attack of hydroxyl radicals. The addition of activated carbon to ZnO increases the efficiency of degradation. The synergy factor has been estimated quantitatively using Eq. (1) as reported for AC-TiO<sub>2</sub><sup>24</sup>. The synergistic effect of ZnO/



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AC is shown by the synergy factor of 1.8, is depicted in **Fig.10**. The ZnO/AC system showed significant improvement in photoreactivity compared to bare ZnO due to the synergistic effect of ZnO and AC.

$$R = k_{app}(\text{ZnO/AC}) / k_{app}(\text{ZnO}) \quad (5)$$

### Chemical Oxygen Demand (COD)

The degradation and mineralization of the targeted pollutant (PNP) was confirmed by chemical oxygen demand (COD) analysis. The PNP solution was oxidized by excess amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  in presence of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{Ag}_2\text{SO}_4$  at  $150^\circ\text{C}$  for 2 hrs using COD digester (Spectralab COD digester 2015M). The excess amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  was evaluated by carrying out titration with Ferrous ammonium sulfate using COD titrator (Spectralab COD titrator CT-15). The dichromate consumed gives the amount of  $\text{O}_2$  required for the oxidation of the organic matter. The results are calculated in ppm using the following formula

$$\text{COD (mg/L)} = (A-B) \times \text{normality Fe (NH}_4)_2(\text{SO}_4)_2 \times 8 \times 1000 / \text{quantity of sample (mL)}$$

Where:

A = Quantity of  $\text{Fe (NH}_4)_2(\text{SO}_4)_2$  (0.1 N) added for blank

B = Quantity of  $\text{Fe (NH}_4)_2(\text{SO}_4)_2$  (0.1 N) added for the sample

Photocatalyst	COD (ppm)	
	Initial	Final
ZnO	460	180
ZnO/AC	460	92

The % reduction in COD was found to be 80% for the degradation of PNP by ZnO/AC composite in contrast with 61% by ZnO as photocatalyst. COD data reveals that there is substantial degradation and mineralisation for PNP when ZnO/AC composite was used as a photocatalyst.

### Method of estimation of PNP

During photocatalytic experiment, the slurry containing aqueous PNP solution and composite was

magnetically stirred for 10 minutes in dark to attain adsorption desorption equilibrium between PNP molecule and catalyst, then it was irradiated and aliquot (1mL) was withdrawn at specific time intervals and filtered to separate the catalyst through  $0.2\mu\text{m}$ , 13mm diameter millipore disc. Changes in absorption spectra were recorded at  $\lambda_{\text{max}}$  using Shimadzu (UV-1800) UV-Visible spectrophotometer. The results are given in **Fig. 11**, which show the UV-visible absorption spectra of PNP which were studied at different times of irradiation. The disappearance of the band at 318 nm reveals that PNP is eliminated in the presence of ZnO/AC composite.

### Conclusions

Composite of ZnO/AC was prepared by very simple and non-toxic method without use of organic solvents. Ratios of ZnO and AC in the composite were optimized and found to be 5:1. The optimized initial concentration of PNP and dose of the composite were found to be  $2.5 \times 10^{-4}$  M and 40 mg respectively. This ratio of the composite showed synergistic effect since each component preserved its individual surface property resulting in increased rate of photocatalytic degradation. The present investigation showed enhanced photocatalytic degradation efficiency of ZnO/AC (5:1) over ZnO. Photocatalytic degradation efficiency increased due to the synergistic effect which is present in the ZnO/AC (5:1) and absent in ZnO. This study could be extended from lab scale to industrial scale since it is cost-effective. Study of this composite could be useful for the degradation of industrial effluents since AC has good adsorption capacity.

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