# Photocatalytic degradation of pentachlorophenol by activated carbon-supported ZnO

Djihane Ayadi, Mostefa Belhakem, Hanane Belayachi, Nouredine Benderdouche*, Benaouda Bestani

_Laboratoire de Structure, Elaboration et Application des Matériaux Moléculaires (SEA2M), Faculté des Sciences et de la Technologie (FST), BP 188, Université Abdelhamid Ibn badis, Mostaganem, Algeria, emails: benderdouchen@yahoo.fr (N. Benderdouche), Djihanedo@gmail.com (D. Ayadi), mbelhakem@hotmail.com (M. Belhakem), belayachi.hanane@hotmail.fr (H. Belayachi), bestanib@yahoo.fr (B. Bestani)_

### ABSTRACT

Activated carbon (AC) was used to support zinc oxide to develop AC/ZnO system. ZnO was used as a photocatalyst to impregnate the carbonaceous material. The samples studied (AC, ZnO and AC/ZnO) were characterized by measuring iodine number, Methylene blue number, scanning electron microscopy, X-ray diffraction and FTIR spectroscopy. Equilibrium adsorption studies of pentachlorophenol (PCP) from aqueous solutions by the samples studied showed that the experimental data were well adapted to Langmuir and Freundlich models. Degradation kinetics of PCP was well described by the pseudo-first-order model of Langmuir–Hinshelwood. Photocatalytic activity of ZnO and the hybrid system AC/ZnO was evaluated by degradation of PCP in aqueous solution. A synergistic effect of AC and ZnO was observed where a complete photodegradation of PCP was reached within 90 min by AC/ZnO and about 65% using ZnO alone. Degradation of PCP was followed up by monitoring COD. The PCP molecules were adsorbed by the AC hybrid and then efficiently degraded by the ZnO particles supported on AC.

_Keywords:_ Powdered activated carbon; ZnO; Impregnation; Pentachlorophenol

## 1. Introduction

Pollution caused by the release of toxic organic compounds into aquatic resources is of increasing concern because water is essential for humans. Due to their toxicity, organochlorine pesticides are among organic pollutants of most concern. Pesticides are widely used to prevent, destroy or control pests in food and staple crops. The intensive use of pesticides in various agricultural, household and industrial activities has had adverse effects on the environment in soil, air and water, as pesticides are highly toxic and carcinogenic [1].

Activated carbon (AC) is a porous material often used to treat wastewater containing persistent organic pollutants that are refractory to other adsorbents [2–4]. The fact that these toxic substances are trapped in the pores does not make this process clean, since it is an ordinary pollution transfer from a liquid phase to a solid phase. The idea of degrading the adsorbed molecules in the pores of AC and consequently regenerating AC is, therefore, an interesting remedy to this problem. Modification of AC by nanostructured photocatalysts such as zinc oxide (ZnO) has been recently carried out by various authors [5–8], as for example: (i) loading ZnO on the surface of AC: El-Khouly et al. [5] prepared photocatalysts ZnO to AC through hydrothermal method at 200°C for 120 min and followed by calcination at 400°C for 180 min;

* Corresponding author.

(ii) activated carbon-supported ZnO: Muthirulan et al. [6] prepared a zinc oxide–carbon hybrid by infiltration of a commercial ZnO–ethanol suspension onto activated carbon in a rotary evaporator; (iii) carbon xerogel as a substrate for ZnO: FaragReham et al. [7] prepared samples by a sol–gel process using different solvents such as an ionic liquid or isopropanol; (iv) ZnO doped with carbon: Zhang et al. [8] prepared nanorods and nanospheres of carbon-doped ZnO with large surface area. These methods can lead to efficient degradation of organic pollutants in aqueous phase. However, they have two main disadvantages: (i) relatively high process cost, (ii) synthesis complexity and arduousness.

Pentachlorophenol (PCP) is a wood preservative and a restricted use organochlorine pesticide, also used as insecticide, fungicide formulations and as a pesticide and as a disinfectant. According to EPA [9], PCP is acutely and highly toxic to the human health and aquatic organisms classified as Group B2, a potential human carcinogen. It is a relatively volatile substance which evolves from solutions or treated products. Its olfactory threshold from water is 0.03 mg/L [10]. Various methods have been reported for the removal of PCP in the literature with varying success, including enzymatic oxidation, microwave in combination with hydrogen peroxide and sodium persulphate, biosorption [11–14].

In this work, commercial AC particles were impregnated with a zinc oxide semiconductor (ZnO) by a simple and suitable method for application on an industrial scale. To illustrate the high photocatalytic properties of this facile route synthesized material and demonstrate the synergistic effects between AC and ZnO, tests were performed on pentachlorophenol (PCP) chosen as an organic compound model.
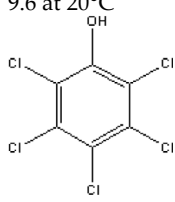
## 2. Experimental

### 2.1. Materials

Zinc oxide with a specific surface area of 220 $m^2/g$ supplied by Sigma-Aldrich was used as a photocatalyst without physical or chemical modification (Sigma-Aldrich, Saint-Quentin-Fallavier, France). The nanoparticles of ZnO of 25 nm in size were used. Acetone (99.5%) was purchased from BIOCHEM (France). All other chemical reagents used were of analytical grade. Pentachlorophenol was provided by Acros (Sigma-Aldrich, Saint-Quentin-Fallavier, France) with purity content greater than 86%. Aqueous solutions of PCP at various concentrations were prepared from a PCP stock solution of 400 mg/L in 160 mg/L of NaOH. Marouf et al. [15] showed that the solubility of PCP in water is only 86 ± 2 mg/L at 319.8 K. Working solutions were prepared by diluting the stock solution to the concentrations desired. Table 1 shows some properties of PCP.

### 2.2. Preparation of AC/ZnO hybrid

Riedel-de-Haën commercial activated carbon powder was used to support ZnO. AC/ZnO precursor solutions were prepared as follows: the AC/ZnO hybrid was prepared by stirring 4.0 g of AC in 40 mL of acetone (10% v/v) in which 1 g of ZnO was added. The mixture was mechanically stirred at room temperature for 8 h and then centrifuged at 4,000 rpm for 20 min using a Hettich ZENTRIFUGEN D-78532, Tuttlingen, 6,000 U/min centrifuge. The solid fraction was then washed with distilled water to neutral pH, filtered and

Table 1
Some properties of pentachlorophenol (PCP)

| Name | Pentachlorophenol (PCP) |
| --- | --- |
| Empirical formula | $C_6HCl_5O$ |
| Molecular weight (g/mol) | 266.34 |
| $\lambda_{max}$ (nm) | 320 |
| Pesticide type | Insecticide, herbicide, fungicide |
| Solubility (mg/L) | 9.6 at 20°C |
| Molecular structure | |



then dried overnight at 110°C. Finally, the hybrid material was heated in a muffle furnace at 400°C for 2 h with a heating ramp of 10°C/min.

### 2.3. Analytical methods

The FTIR spectra of the samples studied (AC, ZnO and AC/ZnO) were determined using the potassium bromide pellet method and an IRprestige-21 FTIR Shimadzu spectrometer (Shimadzu corporation, Japan). X-ray diffraction (XRD) was carried out using an Empyrion diffractometer, SEM micrographs of the microparticles were obtained with the help of a FEI quanta 200 scanning electron microscope. The mesoporous and the microporous surface areas were, respectively, estimated by Methylene blue adsorption and iodine number determinations. The concentration of PCP was measured using a Shimadzu UV/Visible spectrophotometer (Shimadzu corporation, Japan). PCP degradation was estimated by chemical oxygen demand (COD) analysis according to AFNOR NFT 90-040 and NFT 90-101 standard procedures, respectively.

### 2.4. Methods

#### 2.4.1. Adsorption

PCP batch adsorption experiments were carried out to study adsorption isotherms on AC, ZnO and the ZnO hybrid under magnetic stirring for initial concentration in the range of 100–1,000 mg/L in contact with AC powder at an adsorbent dose of 1,000 mg/L (solid/solution ratio) and a natural pH of 11. The suspensions were then stirred for a predetermined time at constant temperature (25°C) to reach equilibrium. The suspensions were centrifuged for 15 min at 4,000 rpm. Absorbance measurements were carried out on separate PCP solutions at 320 nm using a Shimadzu UV-VIS 1240 spectrophotometer for the equilibrium concentration (Shimadzu corporation, Japan).

The amount of the adsorbed substance ($q_t$) was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{W_s} \tag{1}$$

where $C_0$ is the initial PCP concentration and $C_t$ is the PCP concentration (mg/L) at time $t$, $V$ is the solution volume (L) and $W_s$ is the mass of adsorbent (g).

Each experiment was carried out in triplicate and the average values were presented with an average error not exceeding ± 3%.

### 2.4.2. Photocatalysis

The photoactivity of the samples was tested by degradation of PCP in water under UV irradiation at 365 nm by a 60 W ultraviolet lamp. The experiments were conducted inside a mirrored black box to ensure that the flasks were completely irradiated with UV light, fully isolated in the dark. PCP removal was also investigated in the reactor without catalyst to observe the photolysis effect on degradation. The solution was mixed with a magnetic stirrer during photocatalytic processing. PCP percentage removal was analyzed as follows:

$$PCP \text{ % removal} = \left( \frac{1 - C_t}{C_0} \right) \times 100\% \qquad (2)$$

where $C_t$ and $C_0$ are the pesticide concentrations at reaction times $t$ and 0, respectively.

## 3. Results and discussion

### 3.1. Sample characterization

#### 3.1.1. Iodine number, Methylene blue index and Methylene blue surface area

We followed the method described elsewhere by Nunes and Guerreiro [16] and Bestani et al. [17].

Table 2 shows the values of iodine number, Methylene blue index and the area available for Methylene blue.

It can be seen from Table 2 that iodine number for the AC/ZnO system is slightly lower than that of the pure AC but these values reflect the significant microporosity of both materials and consequently a high surface area and also a good liquid phase adsorption for low mass solutes. The Methylene blue index is affected accordingly by ZnO as shown by the values on the table. The decrease in the surface area can be accounted for by pore filling by ZnO but the appreciable surface area available for Methylene blue reflects the presence of mesoporosity on both systems, which promises good adsorption capacity.

#### 3.1.2. Optical properties

FT-IR spectra were recorded for the ZnO, AC and AC/ZnO hybrid. As shown in Fig. 1, the absorption spectra

of the AC/ZnO catalysts are due to the appearance of new functional groups induced by thermal activation (calcination) and by ZnO. The band around 3,400 cm⁻¹ corresponds to the O–H stretching vibration of the hydroxyl group (OH⁻) and the chemisorbed water. In the AC spectrum, the intensity of the absorption peak at 3,170 cm⁻¹ moves to higher wave numbers (from 3,170 to 3,393 cm⁻¹). On the surface of AC/ZnO system, which could be attributed to an increase of the positive charge on the OH groups adsorbed on the surface of ZnO and AC/ZnO hybrid. The same observation was reported by Connor et al. 1999 [18] (Figs. 1a and b). The transformation of the surface structure of AC/ZnO samples suggests that the high temperature treatment during catalyst preparation induced new functional groups. The band at 1,710 cm⁻¹ can be assigned to the C=O stretching vibration of the carbonyl group and indicates the presence of carboxylic acid or ester. In addition, two bands occur in the 800–1,600 cm⁻¹ wavenumber range, a band from 850 to 950 cm⁻¹ can be associated with the C–O–C structure on the surface of the AC/ZnO hybrid. The 1,555 cm⁻¹ band may be attributed to the stretching vibration C=C and indicates the presence of an aromatic ring. The latter two bands are structured in FTIR of AC/ZnO hybrid and in ZnO confirming the interaction between AC and ZnO [19,20]. The band at about 400–500 cm⁻¹ in Figs. 1b and c is associated with the stretching vibration of nanosized Zn–O [19,21].

For all samples obtained, the 1,020 cm⁻¹ band can be accounted for by the C–O stretching vibration and can be assigned to phenols, aromatic ethers, lactone groups and epoxide structures [19].

Morphology and microstructure of the prepared samples were examined by scanning electron microscopy (SEM) and XRD. Scanning electron micrographs are shown in Fig. 2. It can clearly be seen that the ZnO nanoparticles present a hexagonal-pyramid and the particles are agglomerated (Fig. 2a). The AC surface is very clean, irregular and porous (Fig. 2b). Small ZnO conglomerates (Figs. 2c and d) are scattered among large and small AC particles and many of them are not covered. The ZnO particles are surrounded by AC particles in an inhomogeneous and scattered manner, which may suggest that most part of ZnO particles is deposited inside the AC pores. This result is also corroborated by XRD analysis (Fig. 3).

Regardless of the location of ZnO, the photocatalytic process is favorable because ZnO particles can receive UV light enabling photodegradation of the pollutant [22].

Table 2
Iodine number values, Methylene blue index and MB surface area for AC, AC/ZnO, ZnO

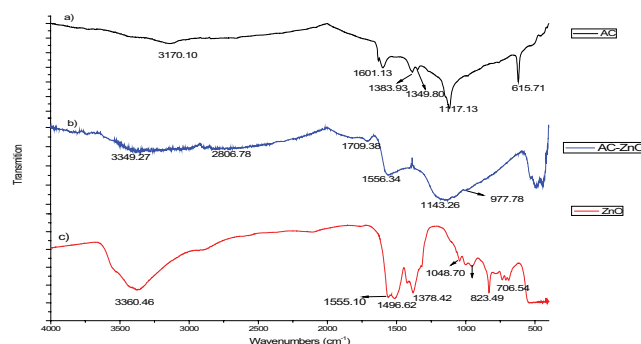| Material | Iodine number (mg/g) | MB index (mg/g) | $S_{(BM)}$ (m²/g) |
|---|---|---|---|
| AC | 948 | 211 | 546 |
| AC/ZnO | 816 | 135 | 457 |
| ZnO | 98 | 8 | 299 |



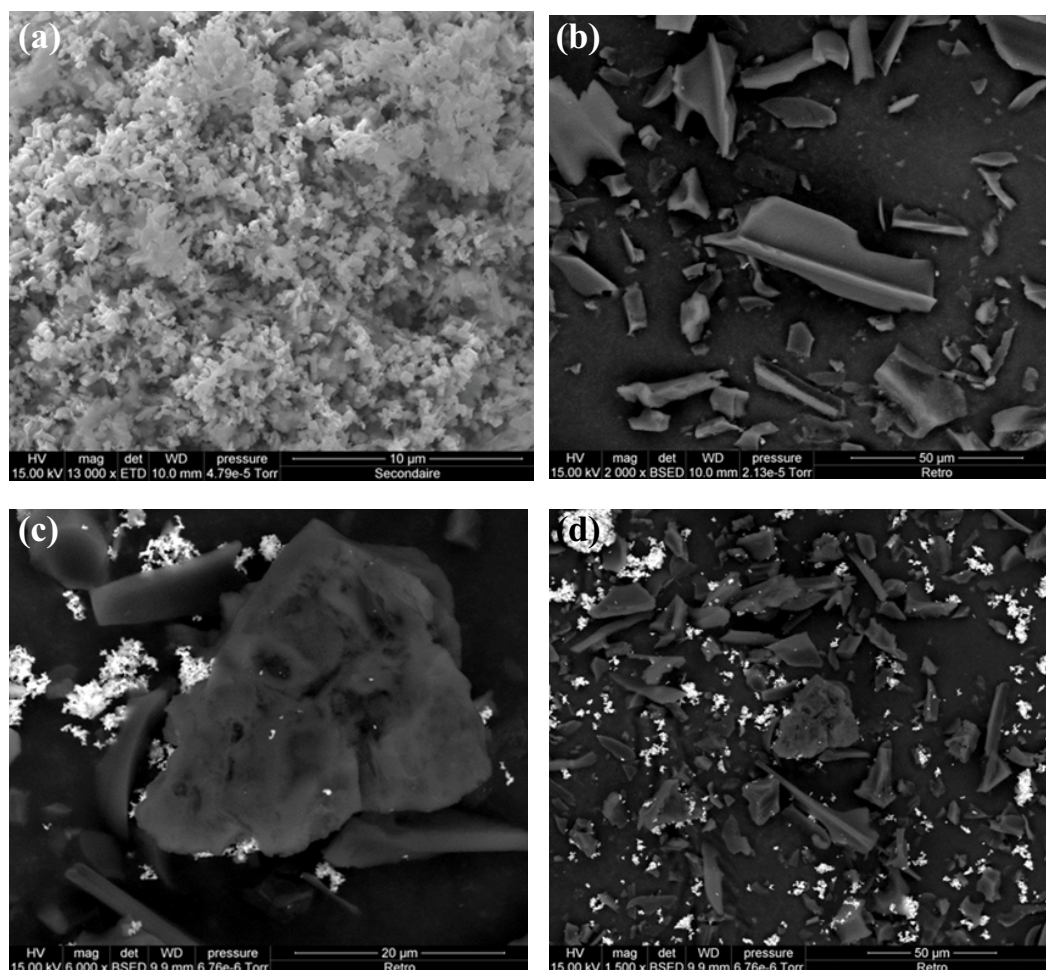Fig. 1. FTIR spectra for samples (a) AC, (b) AC/ZnO, and (c) ZnO.

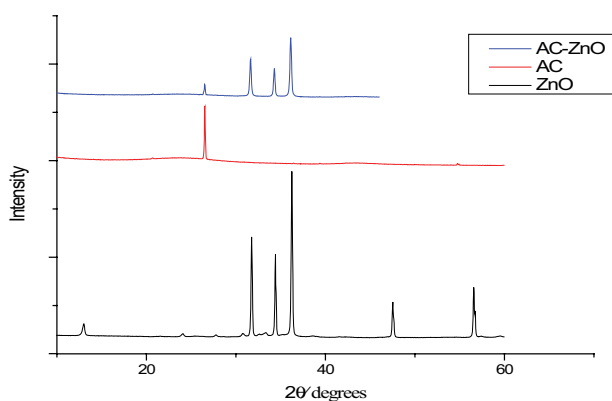Fig. 2. SEM images of (a) ZnO, (b) AC, and (c,d) AC/ZnO.



Fig. 3. XRD patterns of AC, ZnO and AC/ZnO.

XRD analysis of the AC/ZnO system (Fig. 3) shows the clear and well-defined peaks at 31.6°, 34.3°, 36.2°, 47.5° and 56.5° which are indexed as hexagonal wurtzite structure of ZnO and a peak at 26.62° could be characteristic of typical graphite carbons indicating that the AC/ZnO system was successfully synthesized without damaging the crystalline structure of ZnO in the coating process of carbon and zinc oxide [6,23].

## 3.2. Photocatalytic activity of PCP

### 3.2.1. Adsorption

#### 3.2.1.1. PCP adsorption kinetics

This study was carried out in order to determine the adsorbent–adsorbate contact time required to establish adsorption equilibrium and possibly the apparent order of the rate of removal.

Fig. 4 shows the amounts of PCP adsorbed by the materials studied as a function of time ($Q_t$ is the amount adsorbed at time $t$). The percentage of removal of PCP substance first increases with time and then stabilizes at equilibrium attained after 20 min for all materials. Fabre et al. [24] reported that adsorption of PCP by activated carbon reached equilibrium after 20 min contact time. Stirring of the mixture in the dark must be carried out for a period of at least 30 min before irradiating the mixture.

#### 3.2.1.2. Adsorption isotherms

Adsorption isotherms are important for the determination of the maximum adsorption capacity and the characterization of newly developed adsorbents [25]. Batch adsorption
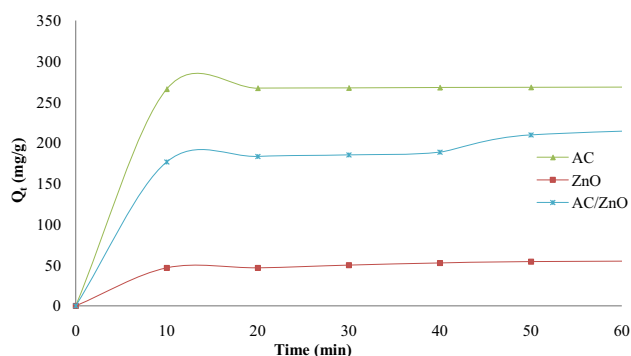
Fig. 4. Adsorption kinetics of PCP on AC, AC/ZnO, ZnO.

tests at constant temperature were carried out for the concentration range 26.63 to 372.88 mg/L (0.1 to 1.4 mmol/L). Fig. 5 depicts the adsorption isotherms for the systems studied.

The Langmuir model in its nonlinear form is expressed as:

$$Q_{ads} = \frac{K_L b \, C_{eq}}{\left(1 + K_L C_{eq}\right)} \qquad (3)$$

where $C_{eq}$ is the solute residual equilibrium concentration, $Q_{ads}$ is the amount of solute adsorbed per unit mass of adsorbent at equilibrium, $b$ is the maximum adsorption capacity of adsorbent, $K_L$ is the Langmuir constant, function of adsorption energy,

whereas the Freundlich model in its nonlinear form is given by Eq. (4) as:

$$Q_{ads} = K_F C_{eq}^{1/n} \qquad (4)$$

where $K_F$ is the Freundlich constant related to the amount adsorbed at equilibrium 1/$n$: the Freundlich constant related to adsorption intensity reflecting the degree of linearity of the isotherm. The value of $n$ is an indication of the favorability of adsorption [26].

The Langmuir model was fitted applied to the data AC and AC/ZnO systems whereas the Freundlich model to ZnO (inset) as depicted in Fig. 5. The results are summarized in Table 3.

The following conclusions can be drawn from PCP adsorption study on the materials investigated:

- PCP adsorption isotherms on AC and AC/ZnO systems are of Langmuirian type characteristic of monolayer coverage corroborating what has been reported elsewhere [27].
- The Freundlich model was found to describe correctly adsorption of PCP on the ZnO photocatalyst, applicable generally to non porous or macroporous materials. The value of $n$ being lower than 1 indicates that adsorption is unfavorable.
- In the case of AC, AC/ZnO, the Freundlich exponent $n$ being greater than 1 characterizes an S-type adsorption isotherm according to the classification proposed by Giles et al. [28], which suggests that PCP was favorably adsorbed by the materials studied. However, as the concentration of the solute increases, multilayer adsorption could occur.
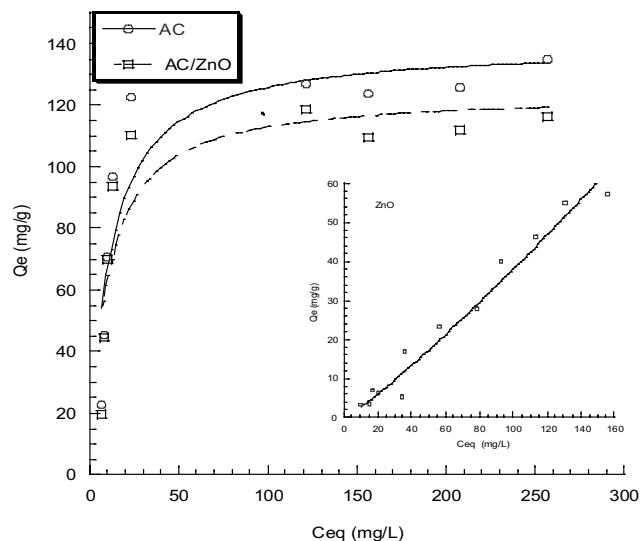


Fig. 5. PCP adsorption isotherms on AC, AC/ZnO, ZnO – Nonlinear Langmuir models applied to AC and AC/ZnO systems – Nonlinear Freundlich model to ZnO (inset).

Table 3
Langmuir and Freundlich constants for the adsorption of PCP on AC, AC/ZnO, ZnO

| Material | Langmuir constants | | | Freundlich constants | | |
|---|---|---|---|---|---|---|
| | $b$ (mg/g) | $a$ (L/g) | $R^2$ | $n$ | $K_F$ (mg$^{1-1/n}$ L$^{1/n}$ g$^{-1}$) | $R^2$ |
| AC | 139.48 | 0.091 | 0.90 | 3.62 | 36.96 | 0.48 |
| AC/ZnO | 123.7 | 0.105 | 0.98 | 3.3 | 28.37 | 0.49 |
| ZnO | 66.22 | 0.013 | 0.056 | 0.87 | 0.198 | 0.98 |

- The decrease in the adsorption of PCP on ZnO might be due to the reduced availability of adsorption sites.

### 3.2.2. Photodegradation studies

#### 3.2.2.1. Analysis of UV absorption spectra

To elucidate the photocatalytic degradation process of PCP on AC/ZnO, UV-Vis detection was performed during photoirradiation. The UV/Visible spectra used to identify the intermediates are shown in Figs. 6 and 7. Fig. 6 depicts the spectrum of PCP degraded by the UV method (without a catalyst). The spectrum of PCP shows two characteristic bands in the ultraviolet region stemming from the benzene ring at 220 and 250 nm, respectively, for PCP concentrations ranging from 10 to 100 mg/L and a large band at 320 nm for concentrations within the 100–1,000 mg/L range [29]. Fig. 6 shows that the absorbance of PCP at 320 nm decreases with an increase in the absorbance of phenol detected at 270 nm [30] under UV irradiation. Other bands appear between 200 and 240 nm confirming the photocatalytic dechlorination of PCP until all Cl atoms were separated from the benzene ring at the end of the process. Dechlorination resulted in the formation of phenol and other intermediary substances during
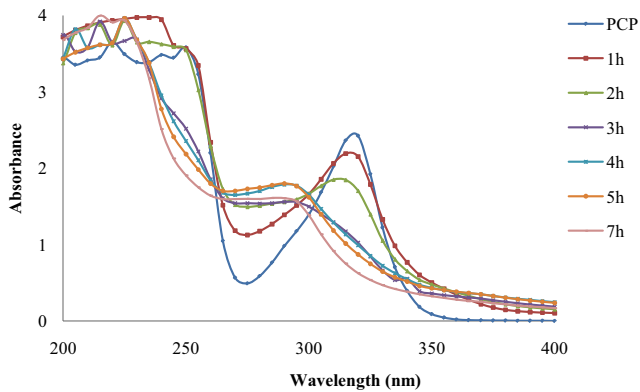
Fig. 6. Schematic illustration of PCP degradation by photolysis.

PCP photolysis. Unfortunately, the presence of highly toxic polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in the intermediates reveals that this photocatalytic degradation of PCP under UV alone was negligible. When the AC/ZnO hybrid used was as a photocatalyst (Fig. 7), the 320 nm absorption band decreased sharply after irradiation for 30 min, while the 270 nm bands disappeared. This indicates that the degradation of PCP did not end after dechlorination. The benzene ring continued to divide and transform into smaller molecular compounds. As the irradiation time increased, the PCP absorption bands between 200 and 240 nm were strongly weakened without no new band appearing, unlike photolysis process. This shows that intermediate aromatics were completely degraded to $CO_2$ and $H_2O$ as reported in several studies [31,32]. In addition, total degradation of PCP by AC/ZnO photocatalyst in 30 min is similar to that obtained in 120 min on ZnO only (Fig. 7). Moreover, it can be noted that a catalyst with a large surface area may offer more active adsorption sites.

### 3.2.2.2. Kinetics of degradation

The result of the photocatalytic degradation of PCP is shown in Fig. 8. It is first observed that direct photolysis can only reach 10% after a 60 min irradiation time because of the very low photon energy [30]. A dark adsorption period of 30 min was chosen to obtain the adsorption equilibrium. However, after 120 min irradiation time of the solution, PCP degradation was about 98% in the presence of pure ZnO. On the other hand, the AC/ZnO system completely degraded PCP within 90 min under UV irradiation. Obviously, the AC/ZnO sample exhibited much higher photocatalytic activity than commercial ZnO and UV alone, which can be attributed to the fact that there was more available surface area for pollutant adsorption and light [8,33,34].

The results of the photocatalytic degradation of PCP are illustrated in Fig. 9.

According to the published works [26,35–37], photodegradation kinetics of organic pollutants can be described by first order reaction whose rate is expressed by Eq. (5):

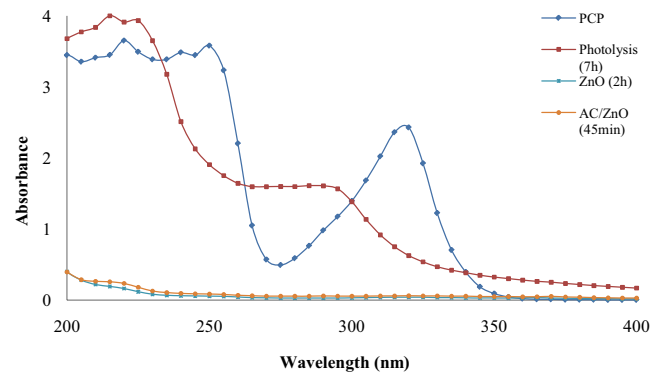$$r = -\frac{dC}{dt} = K_{app} \times C \qquad (5)$$



Fig. 7. Schematic illustration of PCP degradation by ZnO, AC/ZnO and photolysis at room temperature and concentration of 133.17 mg/L (0.5 mmol/L) and natural solution pH (10.5–11).
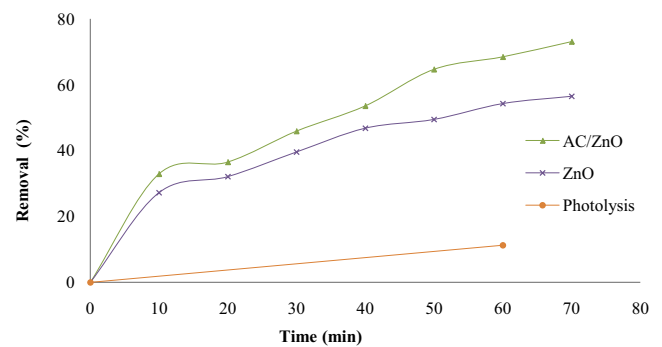


Fig. 8. Percentage removal of PCP vs. time for the conditions: UV irradiation alone, on AC/ZnO and ZnO, at room temperature and concentration of 186.44 mg/L (0.7 mmol/L) and natural solution pH (10.5–11).
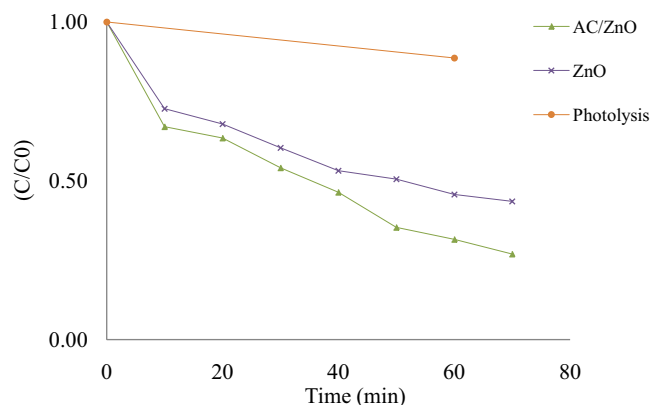


Fig. 9. Photodegradation of PCP in the presence of AC/ZnO, ZnO and UV alone, at room temperature and concentration of 186.44 mg/L (0.7 mmol/L) and natural solution pH (10.5–11).

where $r$: photocatalytic degradation rate (mg/L min); $K_{app}$: apparent degradation rate constant ($min^{-1}$); $C$: solute concentration (mg/L); $t$: irradiation time (min).

Integrating Eq. (5) yields:

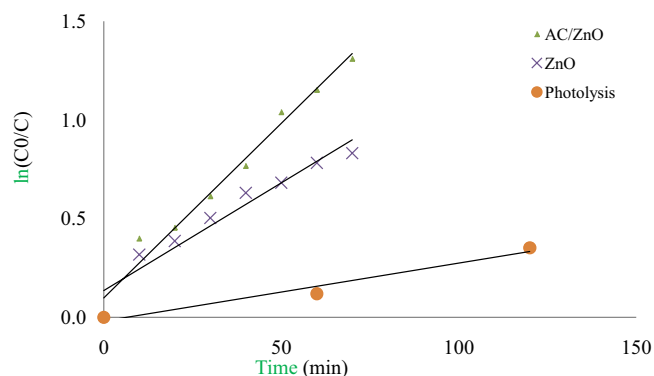$$\ln\frac{C_0}{C} = K_{app} \times t \qquad (6)$$

Fig. 10. Kinetics of PCP photodegradation using AC/ZnO, ZnO and UV alone.

Fig. 10 shows the Langmuir–Hinshelwood pseudo-do-first-order model applied to photodegradation of PCP under $UV_{365}$ irradiation and in the presence of AC/ZnO and ZnO materials is illustrated in Fig. 11. It can be seen that the curves are linear with a determination coefficient close to unity, representing a good linear fit. Thus, the catalytic photodegradation of PCP follows pseudo-first-order kinetics in agreement with the Langmuir-Hinshelwood theory [26]. The concentration of PCP under direct photolysis alone decreased only slightly which proved inefficient and can be ignored. The pseudo-first-order constants of PCP photodegradation are 0.0177 ($R^2 = 0.977$) for AC/ZnO and 0.0109 ($R^2 = 0.935$) for ZnO alone, with a removal percentage of 97% and 65% after 90 min of irradiation for the AC/ZnO and ZnO alone, respectively. Obviously, the AC-ZnO system has much higher photocatalytic activity than pure ZnO, which is mainly due to the synergistic effect of carbon and ZnO in the aqueous suspension. Amorphous carbon is known to have a low work function (3.5–4.0 eV), which is the minimum amount of energy required by an electron to escape from a solid surface [34]. The AC/ZnO system showed good adsorption capacity for PCP. After irradiation, pentachlorophenol-free water was obtained with this system, indicating that PCP can, therefore, be concentrated on the surface of photoactive AC/ZnO, where it is photochemically degraded.

### 3.2.3. Degradation follow-up by COD measurements

Degradation was followed up by COD which reflects the degree of mineralization of an oxidizable substance [38]. In the case of total mineralization of the PCP solution, carbon dioxide and hydrogen chloride would be obtained according to the following reaction [39,40]:

$$C_6H_5Cl + 7O_2 \xrightarrow{h\nu} 6CO_2 + HCl + 2H_2O \quad (7)$$

Figs. 11 and 12 depict the COD removal and $\ln(COD_0/COD)$ evolution as a function of time.

It can be observed that the system AC/ZnO was more efficient in terms of COD abatement than ZnO alone as 93% of initial COD was removed as compared with 40% obtained after 60 min irradiation time using ZnO alone. These results are in agreement with those monitored by UV-Vis spectroscopy. Mineralization using ZnO was slow as after 3-h
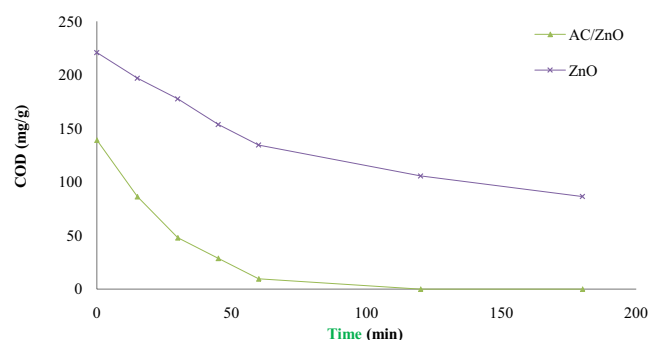


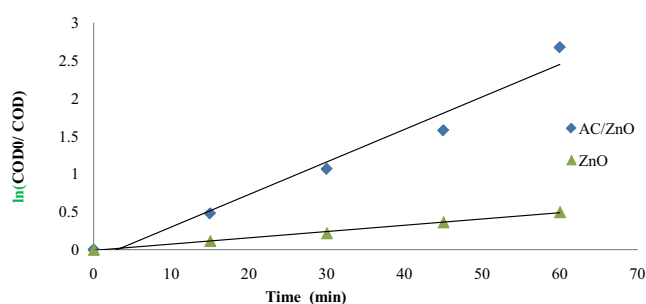Fig. 11. cod removal vs. time on ZnO alone and AC/ZnO system.



Fig. 12. ln ($COD_0/COD$) as a function of time on ZnO and AC/ZnO system.

irradiation time, only 60% of COD was removed. This is one of the drawbacks of heterogeneous catalysis [41]. Mohamed [42] reported that COD remained high even after complete decomposition of phenol. This can be accounted for by the presence of intermediates such as hydroquinone, catechol and hydroxyhydroquinone. The combined process was much more interesting since all pollutants present in the solution could be eliminated after 1 h of treatment. Small residual COD using the hybrid system as compared with that with the photocatalyst alone may be explained by the existence of more intermediates in solution for the second. This seems difficult to explain without considering that in the case of hybrid a higher amount of PCP would have turned into oligomers [43], which preferentially adsorbed on AC/ZnO to be later degraded and not contributing any further to pollution in solution. The hybrid system gives better results for conversion of pentachlorophenol or reaction intermediates.

## 4. Conclusion

This work aimed at studying the degradation of pentachlorophenol by carbon-doped ZnO in the presence of UV radiation. It was observed that the complete photodegradation of PCP with AC/ZnO only required 90 min to be compared with the 65% photodegradation using pure ZnO. The AC/ZnO system approximately showed 1.5 times higher photocatalytic activity than pure ZnO. These observations can be attributed to a strong absorption of visible light, a high surface area compared with undoped ZnO and the fact that a large-area photocatalyst can offer more active adsorption

sites. Moreover, activated carbon doping may prevent aggregation and coalescence of ZnO nanoparticles at high temperature, photocorrosion of ZnO under UV irradiation and recombination of photogenerated charges. The absence of toxic polychlorinated dioxins and furans in the intermediates reveals favorably that this photocatalytic degradation of PCP on the AC/ZnO material is an efficient and environmentally friendly method for removing highly toxic halogenated aromatic compounds.

In perspective, to reduce the costs associated with wastewater treatment, sunlight should be considered as a free energy source for photocatalysis processes.

**References**

[1] Y. Li, X. Li, J. Li, J. Yin, Photocatalytic degradation of methyl orange by $TiO_2$-coated activated carbon and kinetic study, Water Res., 40 (2006) 1119–1126.

[2] R. Leary, A. Westwood, Carbonaceous nanomaterials for the enhancement of $TiO_2$ photocatalysis, Carbon, 49 (2011) 741–772.

[3] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, Process Biochem., 40 (2005) 997–1026.

[4] J.M. Dias, M.C. Alvim-Ferraz, M.F. Almeida, J. Rivera-Utrilla, M. Sanchez-Polo, Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review, J. Environ. Manage., 85 (2007) 833–846.

[5] S.M. El-Khouly, G.M. Mohamed, N.A. Fathy, G.A. Fagal, Effect of nanosized $CeO_2$ or ZnO loading on adsorption and catalytic properties of activated carbon, Adsorpt. Sci. Technol., 35 (2017) 774–788.

[6] P. Muthirulan, M. Meenakshisundararam, N. Kannan, Beneficial role of ZnO photocatalyst supported with porous activated carbon for the mineralization of alizarin cyanin green dye in aqueous solution, J. Adv. Res., 4 (2013) 479–484.

[7] H.K. FaragReham, M.M. Aboelenin, N.A. Fathy, Photodegradation of methyl orange dye by ZnO loaded onto carbon xerogels composites, Asia-Pac. J. Chem. Eng., 12 (2017) 4–12.

[8] X. Zhang, J. Qin, R. Hao, L. Wang, X. Shen, R. Yu, S. Limpanart, M. Ma, R. Liu, Carbon-doped ZnO nanostructures: facile synthesis and visible light photocatalytic applications, J. Phys. Chem., C119 (2015) 20544–20554.

[9] EPA, 198b, Wood Preservative Pesticides: Creosote, Pentachlorophenol, Inorganic Arsenicals, Position document 4, U.S. Environmental Protection Agency, Office of Pesticide and Toxic Substances, Washington, DC.

[10] U.S. Environmental Protection Agency, Office of Drinking Water, Pentachlorophenol, Health Advisory, Draft Report, March 1987.

[11] E.Y. Kim, H.J. Chae, K.H. Chu, Enzymatic oxidation of aqueous pentachlorophenol, J. Environ. Sci., 19 (2007) 1032–1036

[12] G. Asgari, A.M. Seidmohammadi, A. Chavoshani, A.R. Rahmani, Microwave/$H_2O_2$ efficiency in pentachlorophenol removal from aqueous solutions, J. Res Health Sci., 14 (2014) 36–39.

[13] H. Movahedyan, A.M. Seidmohammadi, Comparison of different advanced oxidation process degradation P-chlorophenol in aqueous solutions, J. Environ Health, 6 (2009) 153–160.

[14] R. Shokoohi, S. Azizi, S. A. Ghiasian, A. Poormohammadi, Biosorption of pentachlorophenol from aqueous solutions by *Aspergillus niger* biomass, J. Toxicol., 10 (2016) 33–39.

[15] R. Marouf, N. Khelifa, K.M. Khelifa, J. Schott, A. Khelifa, Removal of pentachlorophenol from aqueous solutions by dolomitic sorbents, Colloid Interface Sci., 297 (2006) 45–53.

[16] C.A. Nunes; M.C. Guerreiro, Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers, J. Quím. Nova, 34 (2011) 472–476.

[17] B. Bestani, N. Benderdouche, B. Benstaali, M. Belhakem, A. Addou, Methylene blue and iodine adsorption onto an activated desert plant, Bioresour. Technol., 99 (2008) 8441–8444.

[18] P.A. Connor, K.D. Dobson, J.A. McQuillan, Infrared spectroscopy of the $TiO_2$/aqueous solution interface, Langmuir, 15 (1999) 2402–2408.

[19] J. Chen, X. Wen, X. Shi, R. Pan, Synthesis of zinc oxide/activated carbon nano-composites and photodegradation of Rhodamine B, Environ. Eng. Sci., 29 (2012) 392–398.

[20] H. Belayachi, B. Bestani, N. Benderdouche, M. Belhakem, The use of $TiO_2$ immobilized into grape marc-based activated carbon for RB-5 Azo dye photocatalytic degradation, Arab. J. Chem., (2015), doi.org/10.1016/j.arabjc.2015.06.040.

[21] L. Zhang, H. Cheng, R. Zong, Y. Zhu, Photocorrosion suppression of ZnO nanoparticles via hybridization with graphite-like carbon and enhanced photocatalytic activity, J. Phys. Chem. C, 113 (2009) 2368–2374.

[22] J. Xu, Y. Ao, M. Chen, D. Fu, C. Yuan, Photocatalytic activity of vanadium-doped titania–activated carbon composite film under visible light, Thin Solid Films, 518 (2010) 4170–4174.

[23] N. Sobana, M. Muruganandam, M. Swaminathan, Characterization of AC–ZnO catalyst and its photocatalytic activity on 4-acetylphenol degradation, Catal. Commun., 9 (2008) 262–268.

[24] B. Fabre, J. Ayele, M. Mazet, P. Lafrance, Adsorption of pentachlorophenol on various materials: influence of organiccoadsorbants (humic substances andlindane), Water Sci., 3 (1990) 277–292.

[25] L. Naidja, Removal of Orange II Dye in Aqueous Solution by Photochemistry and Adsorption, Master Thesis, University of Mentouri de Constantine, Algeria, 2010.

[26] H. Belayachi, Preparation of Carbon Porous Supports by Impregnation, Doctoral Thesis, Abdelhamid ibn Badis University, Mostaganem, 2016.

[27] N. Bouziane, Removal of 2-Mercaptobenzothiazole by Photochemistry and Adorption on Bentonite and Powedered Active Carbon, Master Thesis, University Mentouri of Constantine, Algeria, 2007.

[28] C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, Studies in adsorption. Part XI. A System of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, J. Chem. Soc., 786 (1960) 3973–3993.

[29] M.M.G. HernándezOrta, J.M. Barrón, R.M.G. Coronado, R.L. Ramos, Adsorción de pentaclorofenol en soluciónacuosa sobre carbones activadoscomerciales, Rev. Int. Contam. Ambient., 19 (2003) 137–144.

[30] Z. Zhou, Y. Zhang, H. Wang, T. Chen, W. Lu, The comparative photodegradation activities of pentachlorophenol (PCP) and polychlorinated biphenyls (PCBs) using UV alone and $TiO_2$-derived photocatalysts in methanol soil washing solution, PLoS One, 9 (2014) e108765.

[31] M.M. Ba-Abbad, A.A.H. Kadhum, A.A. Al-Amiery, A.B. Mohamad, M.S. Takriff, Toxicity evaluation for low concentration of chlorophenols under solar radiation using zinc oxide (ZnO) nanoparticles, Phys. Sci., 7 (2012) 48–52.

[32] M.M. Ba-Abbad, M.S. Takriff, M. Said, A. Benamor, M.S. Nasser, A.W. Mohammad, Photocatalytic degradation of pentachlorophenol using ZnO nanoparticles: study of intermediates and toxicity, Int. J. Environ. Res., 11 (2017) 461–473.

[33] M.M. Ba-Abbad, M.S. Takriff, A.W. Mohammad, Enhancement of 2-chlorophenol photocatalytic degradation in the presence $Co^{2+}$-doped ZnO nanoparticles under direct solar radiation, Res. Chem. Intermed., 42 (2016) 5219–5236.

[34] Y. Guo, H. Wang, C. He, L. Qiu, X. Cao, Uniform carbon-coated ZnO nanorods: microwave-assisted preparation, cytotoxicity and photocatalytic activity, Langmuir, 25 (2009) 4678–4684.

[35] A.A. Initha, Photocatalytic Degradation of Carbamazepine Using Graphene-$TiO_2$ Nanocomposites, Doctoral Thesis, University of Singapore, 2015.

[36] R. Djellabi, Contribution of Photo-catalysis to the Elimination of Industrial Pollutants, Doctoral Thesis, University of Annaba, Algeria, 2014.

[37] H. Bessaha, Syntheses, Characterizations and Applications of Anionic Clays of the Hydrotalcite Type to the Depollution of Waters, Doctoral Thesis, University of Mostaganem, Algeria, 2017.

[38] E. Weiss, Kinetic Study of the Electrochemical Degradation of Organic Compounds on the Boron Doped Diamond Anode: Application to the Depollution of Aqueous Effluents, Doctoral Thesis, University of Paul Sabatier, France, 2006.

[39] F. Sabin, Th. Tiirk, A. Vogler, Photo-oxidation of organic compounds in the presence of titanium dioxide: determination of the efficiency, J. Photochem. Photobiol. A Chem., 63 (1992) 99–106.

[40] R.W. Matthews, Purification of water with near-u.v. illuminated suspensions of titanium dioxide, Water Res., 24 (1990) 653–660.

[41] G.P. Atheba, Water Treatment by the Combined Action of Solar Photocatalysis and Adsorption on Activated Carbon: Design and Implementation of the Process, Doctoral Thesis, University of Paul Verlaine, Metz, France, 2009.

[42] E.F. Mohamed, Removal of Organic Compounds from Water by Adsorption and Photocatalytic Oxidation, Doctoral Thesis, University of Toulouse, France, 2011.

[43] L. Benhamed, Improvement by Adding a Transition Metal of the In Situ Regeneration of an Activated Carbon by Catalytic Oxidation, Doctoral Thesis, University of Toulouse, France, 2015.