International Journal of the Physical Sciences Vol. 7(1), pp. 48 - 52, 2 January, 2012
Available online at http://www.academicjournals.org/IJPS
DOI: 10.5897/IJPS11.1684
ISSN 1992-1950 ©2012 Academic Journals

Full Length Research Paper

Toxicity evaluation for low concentration of chlorophenols under solar radiation using zinc oxide (ZnO) nanoparticles

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Accepted 12 December, 2011

Photo catalytic degradation of chlorophenols in aqueous solution by ZnO nanoparticles under sunlight was investigated. The toxicity of chlorophenols was evaluated by agar plates technique with paper discs in the presence of *Escherichia coli*. The relative toxicity data of chlorophenols, before and after degradation, was used in comparing between them. The degree of toxicity was estimated by clear zone around each paper disc of chlorophenols. Results show toxicity of chlorophenols as PCP>TeCP>2,4,6-TCP>2,4-DCP>2-CP before photocatalytic degradation. After degradation, no more toxicity was observed by clear zone around each paper disc. The toxicity test indicates that higher degradation of chlorophenols occurred by ZnO nanoparticles under sunlight as alternative method for treatment.

Key words: Chlorophenoles, degradation, toxicity, zinc oxide (ZnO) nanoparticles.

INTRODUCTION

The chlorinated compound such as chlorophenols can cause serious environmental problems. In particular, these compounds were introduced into the environment in the waste streams of several industrial operations, such as, pulp bleaching with chlorine, water disinfection or even waste incineration. The general purpose of chlorophenols has been reported as disinfectants (Bollag et al., 1986). Because of their toxic effects, phenol and chlorophenols tend to accumulate and in some cases they can contaminate the soil and water in concern (Keither and Tellard, 1979; Moos et al., 1983). 2-chlorophenol and 2, 4-dichlorophenol are two typical phenolic substances that had been used as an intermediate in making insecticides, herbicides, preservatives, antiseptics, disinfectants and other organic compounds. 2,4,6-trichlorophenol is particularly of environmental interest owing to its mutagenicity and carcinogenicity (Lewis, 2002). Many microorganisms are found to be capable of degrading phenol, especially bacteria (Jiang et al., 2007; Yang and Lee, 2007; Wei et al., 2007) and some yeasts (Bergauer et al., 2005; Yan et al., 2006; Pouretedal and Keshavarz, 2011; Nwanya et al., 2011). But the use of fungi for degradation of phenol is relatively an untouched area. The wide band gap ZnO nanoparticle excites by UV light to generate electron-hole pairs for $^{\bullet}OH$ and $^{\bullet}O^{2-}$ radicals formation. The measurement of the chemical toxicity is very important and effective for pollutants in the environment. The inhibition of growth rate of bacteria was used to measure the chemical toxicity (Narkis and Zur, 1979; Rashed and El-Amin, 2007) and colony formation on agar plate (Anderson and Abdelghani, 1980). The toxicity of halogenated phenolic compounds has been evaluated by growth rate of *Escherichia coli* (Cenci et al., 1987). The main objective of this paper is to describe chlorophenols toxicity before and after degradation under solar radiation in presence the zinc oxide (ZnO) nanoparticle. The agar plate technique with *E. coli* was used in this study.

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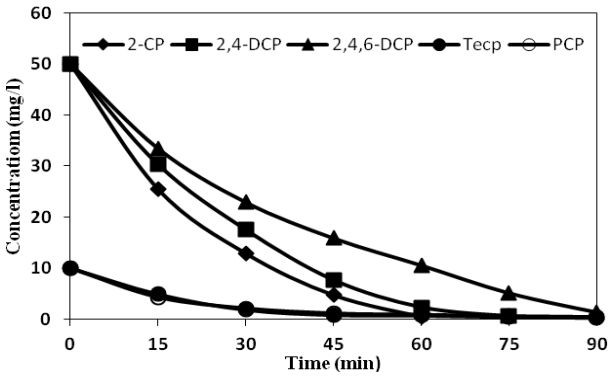


Figure 1. Photocatalytic degradation of chlorophenols under solar radiation presence optimum loading of ZnO nanoparticles.

MATERIALS AND METHODS

Chemicals

2-chlorophenol (2-CP) and 2,4,6-trichlorophenol (2,4,6-TCP) were obtained from Merck, 2,4-dichlorophenol (2,4-DCP) from Sigma-Aldrich, 2,3,4,5-tetarchlorophenol (2,3,4,5-TeCP) and pentachlorophenol (PCP) were obtained from Supelco Company. All chlorophenols were of the highest purity available, and were made to 50 mg/L for 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and 10 mg/L for 2,3,4,5-tetarchlorophenol (TeCP), pentachlorophenol (PCP). De-ionized water was used for preparing all standard solutions. A Whatman filter paper of 9 cm diameter was used and ZnO nanoparticle was prepared by sol gel method and the procedures were reported (Ba-Abbad et al., 2010).

Media and culture conditions

The growth of *E. coli* medium was 13 g/L concentration nutrient broth (Oxoid Company). Nutrient agar (Oxoid Company) at concentration of 28 g/L was used to prepare plate test. All the mediums were sterilization by autoclaved at 121°C for 20 min before use. To prepare agar plates, approximately 15 ml was used in plastic petri dish. The plates of agar were solidified under room temperature before use for the adsorption of the liquid containing chlorophenols before and after degradation. One colony of *E. coli* bacteria was used to growth it in 10 ml medium of 13 g/L concentration nutrient broth. After 24 h under aerobic condition, growth on agitation shaking (150 rpm) at 37°C, 10^7 colony formed unit (CFU) of culture was transferred into the petri dish containing nutrient agar and was distributed by L-loop. A 30 to 60 min time leaving before toxicity test was considered (Kadhum et al., 2011a; Al-Amiery et al., 2009, 2011; Kadhum et al., 2011b).

Photocatalytic degradation of chlorophenols and analysis

Photocatalytic experiments were conducted using a cylindrical batch reactor. All of the experiments were carried out under similar conditions on sunny days at times between 11.00 a.m. and 2.30 p.m. A 100 ml solution containing certain concentration of chlorophenols was mixed with optimum ZnO catalyst loading, magnetically stirred in the dark for 60 min, and then irradiated under direct sunlight. The irradiated solutions were drawn every 15 min and filtered through a 0.2 µm filter for measurement of the residual of chlorophenols using high performance liquid chromatography (HPLC, Agilent 1200). A Johnes LC-18 (250 mm × 4.6 mm × 5 µm) column with wavelength UV detector and acetonitrile: phosphoric acid (H_3PO_4), solution (20:80:0.01 M) was used as a mobile phase with a flow rate of 1.0 ml/min. The photocatalytic degradation was calculated according to Equation 1:

$$\text{Degradation\% of PCP} = \left(\frac{Co - C}{Co}\right) \times 100 \quad (1)$$

where C_o is the initial concentration and C is the concentration of chlorophenols at intervals of the irradiation time.

Toxicity testing

The agar plate technique was designed to be simple and rapid method was used for toxicity measurement of chlorophenols. To perform the toxicity measurement, 5 discs of filter paper with diameter of 6.2 mm was used to determine the inhibition zone of *E. coli* growth for chlorophenols before degradation and 5 discs after degradation. A 1 ml of chlorophenols before and after degradation was placed separately in 5 ml tube using micropipette. Filter paper discs were placed in the tube and were left for 20 min for the absorption of chlorophenols liquid before and after degradation. After 20 min, the filter paper discs were placed on surface of agar plate. Usually, 50 mg/L for 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol and 10 mg/L for 2,3,4,5-tetarchlorophenol, pentachlorophenol and one control (De-ionized water) were prepared. All agar plates were incubated at 37°C for 48 h to evaluate the toxicity by the inhibition zone of *E. coli* bacteria. The inhibition zone can indicate by clear spot around each disc on agar plate in which *E. coli* bacteria had failed to grow.

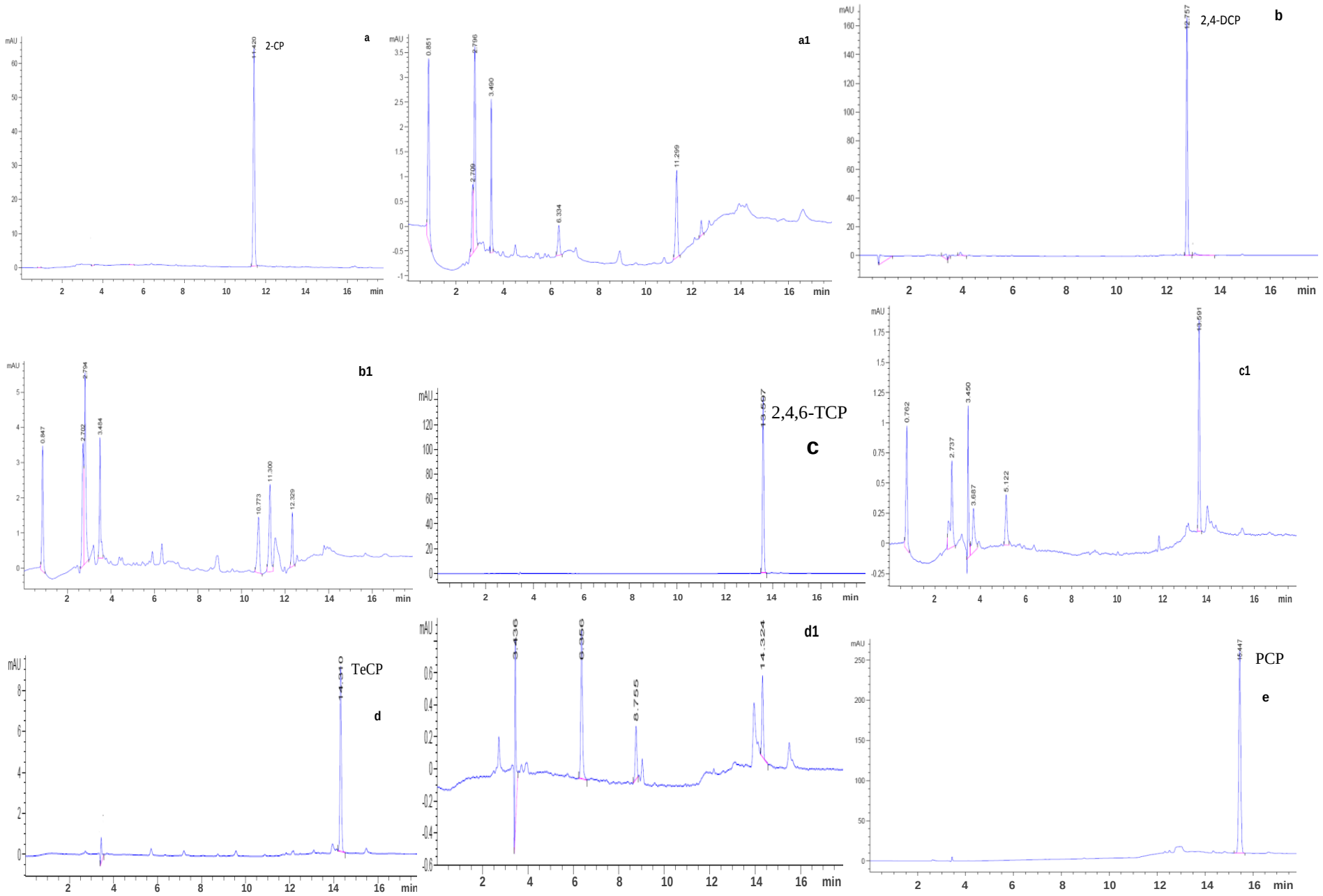
RESULTS AND DISCUSSION

Photocatalytic degradation of chlorophenols

Figure 1 shows the photocatalytic degradation of various chlorophenol irradiated under sunlight in the presence of ZnO nanoparticles. The ZnO loading was investigated as a very important factor for degradation process. The optimal loading was found to decrease as 2, 1.5 and 1 g/L when chlorophenol gradient for (2-CP 2,4-DCP and 2,4,6-TCP), (TeCP) and PCP, respectively.

Higher efficiency of degradation was found within 90 min irradiation time using optimum loading of catalyst. A 99.7% degradation of 2-CP and 2,4-DCP was obtained within 90 min irradiation time. The degradation of 98, 97 and 96% were achieved for 2,4,6-TCP, TeCP and PCP, respectively. At the same time, the high performance liquid chromatography (HPLC) analysis of chlorophenols before and after photocatalytic degradation were measured as shown in Figure 2.

The retention time of single pecks of 2-CP, 2,4-DCP, 2,4,6-TCP, TeCP and PCP were 11.40, 12.75, 13.56, 14.31 and 15.44 min, respectively before degradation. After 90 min of radiation time with ZnO nanoparticles, the main peaks were almost decreased and other peaks were increased, which confirmed that chlorophenols converts to intimidates compound. However, the toxicity


a
2-CP
11.420
a1
0.851
2.796
3.490
2.709
6.334
11.299
b
2,4-DCP
12.757
b1
0.847
2.794
2.702
3.484
10.773
11.300
12.329
c
2,4,6-TCP
13.597
c1
0.762
3.450
2.737
3.687
5.122
13.591
d
TeCP
14.310
d1
8.436
6.356
8.755
14.324
e
PCP
15.447
mAU
min

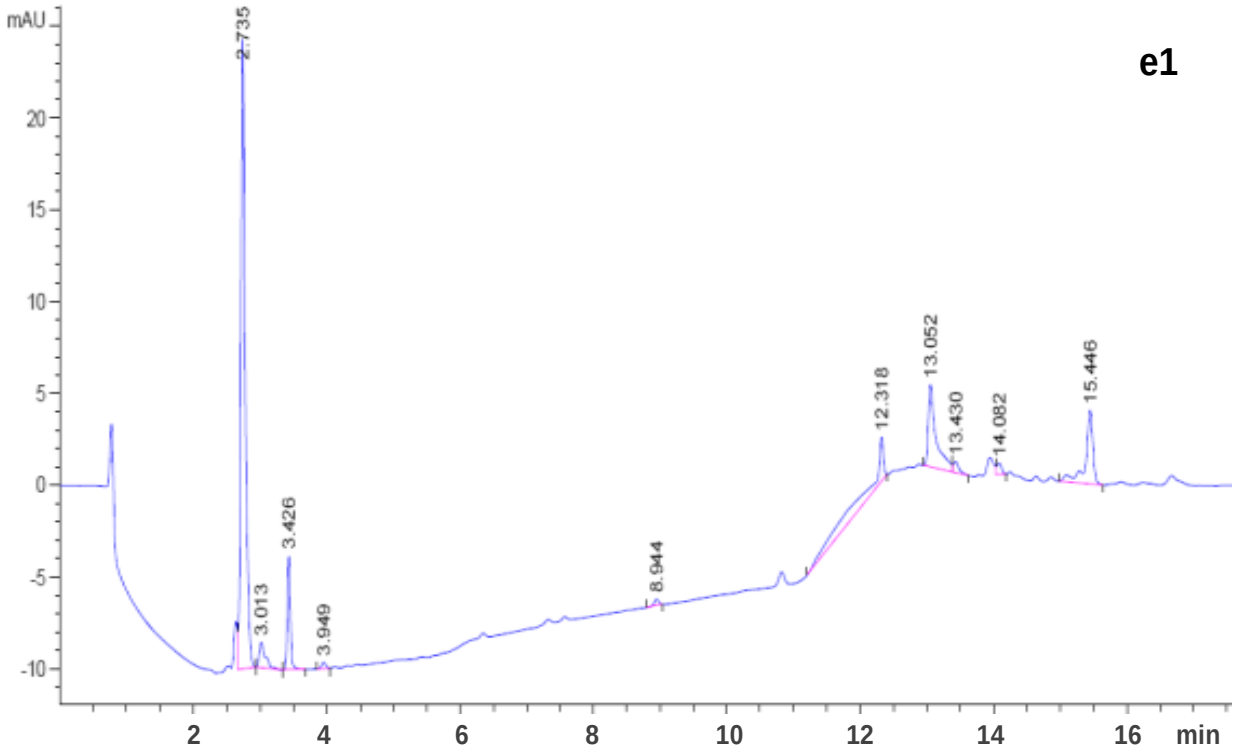


Figure 2. HPLC analysis of chlorophenols (a, b, c, d and e) before and (a1, b1, c1, d1 and e1) after photocatalytic degradation.

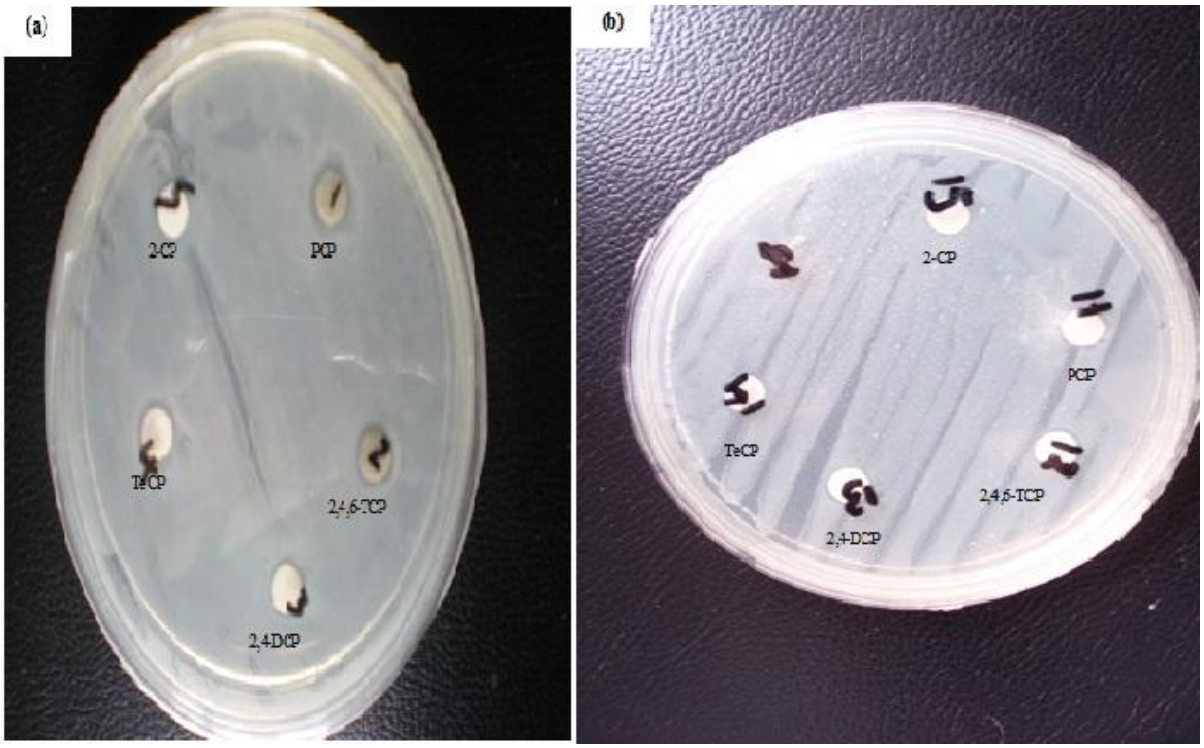


Figure 3. Agar plates and paper discs with various chlorophenols: (a) before photocatalytic degradation and (b) after photocatalytic degradation.

of chlorophenols before and after photocatalytic degradation was discussed in the toxicity test previously.

Toxicity test of chlorophenols before and after photocatalytic degradation

All experiments were run using paper discs absorbed by chlorophenols, and clear zone around all the discs were observed. The clear zone indicates the degree of bacterial inhibition growth under the incubation condition. Figure 3 shows the results of inhibition zones of chlorophenols on plate agar using paper discs before and after degradation.

Chlorophenols toxicity before degradation was evaluated at 50 mg/L for 2-CP, 2,4-DCP and 2,4,6-TCP and 10 mg/L for TeCP and PCP. 2-CP shows very small inhibition zone of toxicity in the test paper disc. This observation for lower effects of 2-CP due to the retention of the toxicant by paper and diminished the toxicity effect. However, the toxicity of chlorophenols in this study did not compare quantitative toxicities, but relative toxicities with 2-CP as a reference. The toxicity of chlorophenols was obtained as PCP>TeCP>2,4,6-TCP>2,4-DCP>2-CP before photocatalytic degradation reaction in the presence of ZnO nanoparticles as shown in Figure 3a. The gradient level of chlorophenols toxicity has been reported by a previous study done by Milner and Goulder (1986). At the same time, after photocatalytic degradation process, the clear inhibition zones were reduced or did not appear, which was attributed to be no or low toxicity of the final products. These results were observed to be very close with the efficiency of photocatalytic degradation, and it indicated higher chlorophenols treatment.

Conclusion

Nanoparticles of ZnO under sunlight were effective for toxicity removal of water polluted by chlorophenols, such as 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,5-tetarchlorophenol and pentachlorophenol. The agar plate technique succeeds the determination of chlorophenols toxicity before and after degradation process. Non toxic products after chlorophenols degradation were observed, which indicates no clear zone around each paper disc after degradation. This study provides a versatile approach for highly efficiency method for the degradation of toxic compounds of poly chlorinated phenol under solar radiation in the presence of nano-ZnO photocatalyst.

ACKNOWLEDGEMENTS

The authors are grateful to the Solar Energy Research Institute (SERI), the University Kebangsaan Malaysia for the support under grant and the Hadhramout University of Science and Technology, Yemen for their financial support.

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