

**PHOTOCATALYTIC DEGRADATION OF 4-CHLOROPHENOL USING Pd/Ag DOPED ON P25 DEGUSSA TiO<sub>2</sub> NANOPARTICLE WITH ULTRAVIOLET (UV) RADIATION**

\*<sup>1</sup>Omoniyi, K. I., <sup>1</sup>Aroh, A. O., <sup>1</sup>Gimba, C.E., <sup>1</sup>Abba H. and <sup>2</sup>Yilleng, M. T.

<sup>1</sup>Department of Chemistry, Ahmadu Bello University, Zaria-Nigeria.

<sup>2</sup>Department of Chemistry, Kaduna State University, Kaduna-Nigeria.

\*Correspondence author: israelflourish@yahoo.com

**ABSTRACT**

Photocatalysis is an established technique for pollutant degradation and hydrogen production. This study reported the photocatalytic degradation of 4-chlorophenol using Pd/Ag doped on P25 Degussa TiO<sub>2</sub>. The Pd/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> photocatalysts were prepared by sol immobilization method. A fabricated photo-reactor was used in the photocatalytic degradation of 4-chlorophenol and monitored using HPLC. The results indicated that Pd/TiO<sub>2</sub> has photodegradation efficiency of 78.44%, while Ag/TiO<sub>2</sub> has a photodegradation efficiency of 82.44% within 120 min of ultraviolet irradiation. There was significant difference in the photodegradation efficiency compared to that of pure TiO<sub>2</sub> nanoparticles. The dried catalysts were used again under the same experimental condition with freshly prepared 4-chlorophenol for four times. The re-used catalysts remained active up to four times of usage with minor reduction in activity, due to metal leaching. Ag-TiO<sub>2</sub> recorded higher rate constant than Pd-TiO<sub>2</sub>; the rate constant for the degradation followed first-order reaction kinetics. The use of heterogeneous photocatalysis for treating organic pollutants has found relevance in environmental purification and energy generation.

**Keywords:** 4-chlorophenol, degradation, doped, environmental, kinetics, Pd/Ag.

**INTRODUCTION**

The contamination due to chlorophenols in many lakes and rivers has resulted in serious environmental problems for many decades [1]. These compounds are highly toxic and are human carcinogenic even at low concentrations. This has triggered the search and improvement of many of its treatment techniques [2]. Chlorophenols are used in the manufacture of numerous products including pesticides, pharmaceuticals, plastics and dyes and are released into the environment during their production processes. Due to the resistance of chlorophenol and its derivatives to degradation, common treatments such as the use of biological systems and

physical method are slow or ineffective for the removal of these compounds from contaminated water systems. Other techniques were implemented to achieve the depuration degree needed to accomplish environmental regulations. Over several years, heterogeneous photocatalysis using TiO<sub>2</sub> as the photocatalyst have been proposed as an alternative for water and waste water treatment [3]. Photocatalysis involves the irradiation of suitable semiconductor particles with light energy greater than the band gap. Hydroxyl radicals (OH<sup>•</sup>) are generated from water when light is absorbed by the semiconductor catalyst [4], as photocatalytic degradation occurs by stimulating a reaction at the solid/solution interface.

TiO<sub>2</sub> in the anatase form is one of the best photocatalysts for pollutant degradation [5]. However, because of the relatively high intrinsic band gap of anatase TiO<sub>2</sub> (3.2eV), UV irradiation is required for its photoactivity, and thus only 4% of the sunlight (UV fraction of solar spectrum) can be utilized effectively [6]. Thus, pure TiO<sub>2</sub> based systems have been found to be inactive under sunlight. Application of UV lamps has serious disadvantages including high energy consumption and handling problems. Researchers have focused on developing TiO<sub>2</sub> based systems having decreased band gap so as to show photocatalytic activity in the visible region. This enables the use of sunlight for photocatalysis [7]. Several modification methods are available to shift the wavelength of absorption of TiO<sub>2</sub> from UV to visible region, among which, transition metals' doping play a major role.

The second main drawback associated with the photocatalytic activity of TiO<sub>2</sub> is that most of the activated charge carriers will undergo recombination before reaching the surface, preventing interaction with adsorbed molecules. About 90% of the charge carriers may be lost within a nanosecond of their generation leading to low photoactivity of TiO<sub>2</sub> [8]. So when transition metals such as Ag, Pd, V, Cr and Au are deposited over TiO<sub>2</sub>, they can act as electron traps [9].

Rijuta *et al* (2014) showed that the highest phenol degradation rate was obtained at pH 9.0, 60°C and TiO<sub>2</sub> dosage 2.0 g L<sup>-1</sup>. Under the optimized conditions the phenol removal efficiency was 98 % and 100 % for the TiO<sub>2</sub>/UV and TiO<sub>2</sub>/UV/H<sub>2</sub>O<sub>2</sub> system, respectively. The photodegradation of phenol followed first-order kinetics [10]. Also, the photodegradation kinetics of UV/TiO<sub>2</sub>-mediated 4-chlorophenol (4-CP) and 2, 6-dichlorophenol (2, 6-DCP) mixtures showed that the adsorption of 2, 6-DCP is considerably higher with respect to 4-CP in both TiO<sub>2</sub> particles, but this relation decreases in the mixture of these pollutants [11]. Choi *et al* (1994) also assessed the

effects of 21 different metal ion dopants on the photochemical activity of quantum sized TiO<sub>2</sub> [12].

The aim of this study is to degrade 4-chlorophenol in wastewater using palladium and silver doped on P25 Degussa TiO<sub>2</sub> nanoparticle with UV radiation, towards developing an efficient catalyst which can prevent the recombination of charge carriers.

## **MATERIALS AND METHODS**

### **Catalyst preparation**

The catalysts used were prepared using sol immobilisation method as reported by Moses (2014) [13], with a few modifications. Standard sol-immobilization method was utilised to prepare the Ag and Pd nanoparticles supported on TiO<sub>2</sub>. The supported silver and palladium colloids were prepared by using polyvinyl alcohol (PVA) as the protective ligand. Aqueous solutions of 0.005 mol/dm<sup>3</sup> PdCl<sub>2</sub> and 0.006 mol/dm<sup>3</sup> AgNO<sub>3</sub> were prepared. A 1.0 wt % aqueous PVA, (MW = 10000, 80% hydrolysed, obtained from Aldrich, USA) solution was freshly prepared just prior to the synthesis of the metal colloid.

A representative protocol for preparing a catalyst comprising Ag and Pd nano-particles with 1.0 wt% total metal loading on TiO<sub>2</sub> was carried out as follows: To an aqueous 0.005 mol/dm<sup>3</sup> PdCl<sub>2</sub> solution and 0.006 mol/dm<sup>3</sup> AgNO<sub>3</sub> solution, 100 cm<sup>3</sup> of PVA solution (1.0 wt %) was added (PVA/ (Ag and Pd) (w/w) = 1.2). A freshly prepared solution of NaBH<sub>4</sub> (0.1M NaBH<sub>4</sub>/ (Ag and Pd) (mol/mol) = 5) was then added to form a dark brown sol. After 30 min of sol-generation, the colloid was immobilised by adding TiO<sub>2</sub>, acidified to pH 1-2 by using tetraoxosulphate (VI) acid, with vigorous stirring using a glass rod. The amount of support material required was calculated to have a total final metal loading of 1.0 wt %. After 2 h, the slurry was filtered and the catalyst of each experimental set was washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C overnight in an oven.

Then a calibration curve of concentration against peak area was obtained for 4-chlorophenol using a Knauer HPLC instrument (p/n A24, Santa Clara CA, USA) with a reverse phase C18 column (Erouphere 250 x 4.6 mm), so as to get the initial concentration *C*<sub>0</sub> of 4-chlorophenol for the photodegradation experiment.

### Photocatalytic reaction experiments

The photocatalytic activity was evaluated by carrying out degradation experiments on 3-Chlorophenol. The reactors used were closed Pyrex reactors, each having an outer diameter of 42.0 mm and height 210 mm and thickness 4 mm. Into each reactor was added 100 cm<sup>3</sup> solution containing 1.0 M of 4-Chlorophenol in deionized water from Barnstead Nano pure diamond machine and 0.5% of Ag/TiO<sub>2</sub> or Pd/TiO<sub>2</sub> nanoparticles. This was also done using pure TiO<sub>2</sub> nanoparticles. The suspension was stirred magnetically using yellow line MST basic magnetic stirrer (H88, Italy) at 650 rpm at ambient temperature for 2 h in a dark room. Then 10 cm<sup>3</sup> of the suspension was withdrawn with a suction pipette, in order to analyze the equilibrium concentration of 4-chlorophenol in the solution.

The mixture was then exposed to UV light (300 nm) using a fabricated photoreactor. At 20 min time interval during the typical 2 h reaction, 5 cm<sup>3</sup> of the suspension was withdrawn with a suction pipette and filtered using an Acrodise CR 13 mm syringe filter with 0.45µm PTFE membrane, and then taken for HPLC analysis.

Then the rate constant ( $k_a$ ) for the degradation process was obtained from the relation

$$\ln c/c_0 = k_a t$$

Where:  $C_0$  = initial concentration;  $C$  = final concentration;  $K_a$  = rate constant;  $t$  = time

Then the order of the reaction was obtained.

The percentage of the pollutant degraded by each of the photocatalyst was then calculated as:

$$\frac{C_0 - C}{C}$$

The efficiency of reusing the Pd/TiO<sub>2</sub> nanoparticle for the photodegradation of 4-chlorophenol was tested by using the resulting solution obtained from the first time photocatalytic degradation of 4-chlorophenols. This was filtered, and the catalyst obtained was washed and air-dried. The dried catalyst (0.5%) was subsequently used the second, third and fourth time, applying the same experimental conditions as in the first time, but using fresh solution of 4-chlorophenol in each case.

### Statistical analysis

The photodegradation efficiency of Ag/TiO<sub>2</sub>, Pd/TiO<sub>2</sub> and pure TiO<sub>2</sub> was assessed using Students' t-test with significance taken at  $P < 0.05$ .

## RESULT AND DISCUSSION

### Photocatalytic degradation of 4-chlorophenol under 300 nm light using 0.5% Ag/TiO<sub>2</sub> or Pd/ TiO<sub>2</sub>

The calibration curve for 4-chlorophenol using HPLC in order to obtain its initial concentration in the photodegradation experiment is shown in Figure 1.

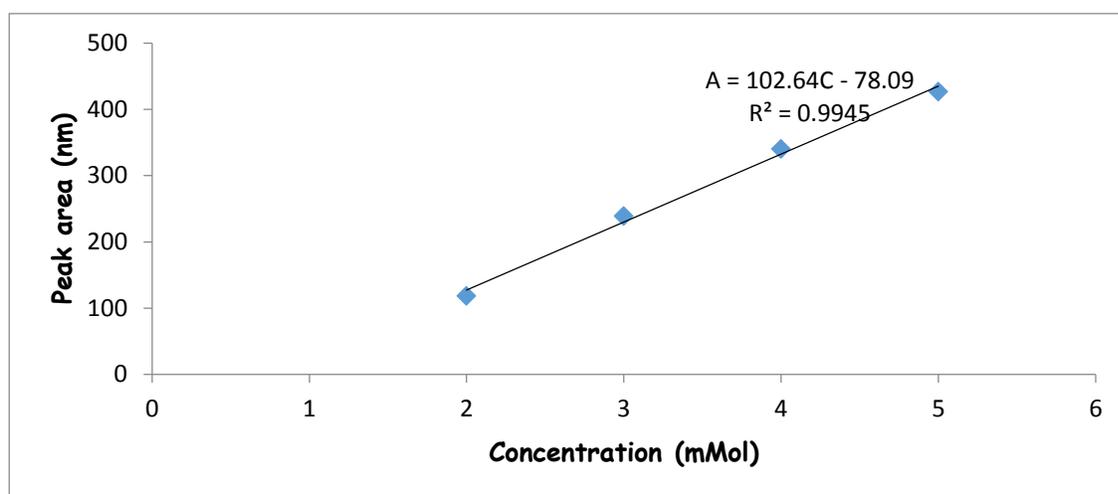


Figure 1: Calibration curve of 4-chlorophenol

The concentration of maximum peak area (426.8 nm) was 5 mmol; and was used as  $C_0$  (the best stock solution for the photodegradation experiment in the 5 cm<sup>3</sup> assessed by HPLC).

### Photo-degradation of 4-chlorophenol under 300 nm light using 0.5% Pd-TiO<sub>2</sub>

The equation obtained from Figure 1 with A representing the absorbance and C the concentration was used in calculating the absorbance and concentrations obtained in Table 1. From this the value of  $\ln(C/C_0)$  and  $k_a$  in the degradation process was obtained (Table 1).

Table 1: Photo-degradation of 4-chlorophenol using 0.5% Pd-TiO<sub>2</sub> catalyst

S/no	Time (min)	Absorbance (nm)	Concentration (mMol)	C/C <sub>0</sub>	$\ln(C/C_0)$	Rate constant, $k_a$ (s <sup>-1</sup> )
1	0	426.8	5.000	1.000	0	0

2	20	187	2.583	0.526	-0.642	-0.032
3	40	143.5	2.159	0.439	-0.823	-0.021
4	60	113.8	1.869	0.381	-0.965	-0.016
5	80	54.5	1.292	0.263	-1.335	-0.017
6	100	40.6	1.156	0.235	-1.448	-0.015
7	120	30.6	1.059	0.216	-1.532	-0.013

The use of 0.5% Pd-TiO<sub>2</sub> resulted in decrease in the concentration of 4-chlorophenol in the simulated wastewater from 5.0 mmol to 2.159 mmol in the first 40 min, and sharp decrease to 1.292 mmol at 80 min of the degradation process (Table 1). At 120 min the concentration was 1.059 mmol; the rate constant of the degradation by Pd-TiO<sub>2</sub> ranged from -0.032 to -0.0135 s<sup>-1</sup> (Figure 2).

However, the use of 0.5% Ag-TiO<sub>2</sub> for degradation of 4-chlorophenol in the 5.0 mmol aliquot decreased the concentration to 2.055 mmol at 40 min. There was a sharp decrease to 1.379 mmol at 80 min and to 0.989 mmol at the 120 min of the degradation. The rate constant for the degradation using Ag-TiO<sub>2</sub> ranged from -0.038 to -0.0160 s<sup>-1</sup> (Figure 3). The result indicated that Ag-TiO<sub>2</sub> recorded better degradation of 4-chlorophenol and slightly higher rate constant than Pd-TiO<sub>2</sub> (Figure 4).

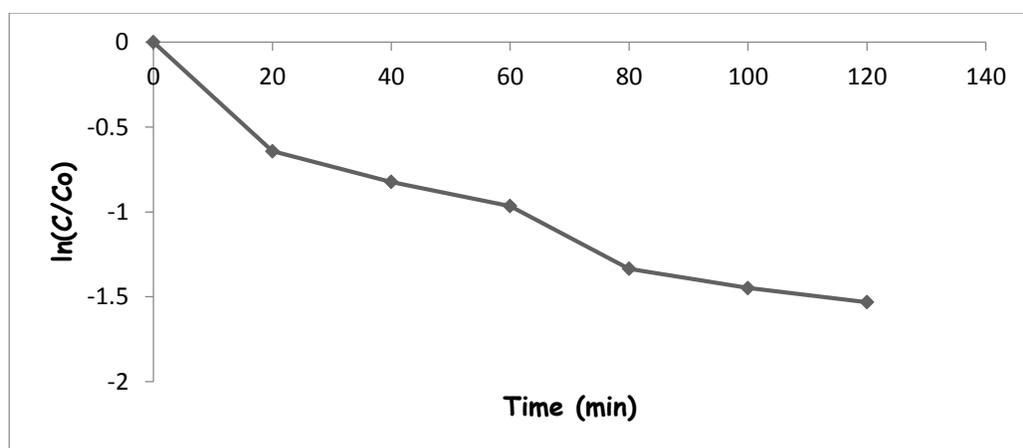


Figure 2: Photo-degradation of 4-chlorophenol under 300nm light using 0.5%Pd-TiO<sub>2</sub>

As presented in Table 2, Pd-TiO<sub>2</sub> has a photodegradation efficiency of 78.44% within the 120 min irradiation, while Ag-TiO<sub>2</sub> has a photodegradation efficiency of 82.44%. On the other hand,

pure TiO<sub>2</sub> led to the degradation of 56.00% of 4-chlorophenol. This conforms to the trend obtained by Grabowska *et al* (2010) in which the highest photoactivity for degrading phenol was observed for TiO<sub>2</sub> loaded with silver (91%), gold (49%) and Au (91%) after 60 min of irradiation under UV light [14].

This result can be attributed to the fact that the silver doped titanium dioxide particles exhibited enhanced visible light induced photocatalytic activity, which was as a result of the ability of the silver dopant in trapping excited electrons from TiO<sub>2</sub>, so leaving holes for the degradation reaction of 4-chlorophenol. On the other hand, Pd-TiO<sub>2</sub> has stronger interaction, so the Pd is evenly distributed in the TiO<sub>2</sub> particle thereby having less effect in the modification of the titanium dioxide [10].

Addition of Pd or Ag provoked the transference of photogenerated electrons from TiO<sub>2</sub> conduction band to the dopant conduction and the holes were accumulated in the TiO<sub>2</sub> valence band, so reducing electron-hole pair recombination, thus improving the photodegradation activity of the catalyst [5].

Table 2: Photodegradation of 4-chlorophenol using 0.5% Ag-TiO<sub>2</sub>, 0.5% Pd-TiO<sub>2</sub> and Pure-TiO<sub>2</sub>

S/No	Time (min)	Concentration(m Mole) Ag-TiO <sub>2</sub>	Percentage (%) Ag-TiO <sub>2</sub>	Concentration (mMole) Pd-TiO <sub>2</sub>	Percentage (%) Pd-TiO <sub>2</sub>	Percentage (%) Pure -TiO <sub>2</sub>
1	0	5.000	0.0	5.000	0.0	0.0
2	20	2.362	52.77	2.583	47.40	32.10
3	40	2.055	58.90	2.159	56.04	39.41
4	60	1.869	62.62	1.869	61.94	41.88
5	80	1.379	72.42	1.292	73.69	46.75
6	100	0.989	80.22	1.156	76.43	53.55
7	120	0.878	82.44	1.059	78.44	59.00

The result supports the findings of Sakthivel *et al.* (2004) in the investigation of the performance of TiO<sub>2</sub> after supplementing with platinum and palladium dopants. Pt acted as an electron trap in the formation of TiO<sub>2</sub>, while the generated electrons gravitated toward Pt that served as temporary electron trap preventing electron energized recombination [15]. Doping with palladium acts as electron traps thereby preventing the generated electron from falling back to the valence band. So the degradation was achieved for Pd- TiO<sub>2</sub> because doping solves the problem of excited electron recombination [8].

Table 3: Photo-degradation of 4-chlorophenol under 300nm light using 0.5%Ag-TiO<sub>2</sub> catalyst

S/No	Time (Min)	Absorbance, A (nm)	Concentration, (mMole)	C/C <sub>0</sub>	ln(C/C <sub>0</sub> )	Rate constant
1	0	426.8	5.000	1	0	0
2	20	164.3	2.362	0.473	-0.750	-0.038
3	40	132.8	2.055	0.411	-0.889	-0.022
4	60	113.8	1.869	0.374	-0.984	-0.016
5	80	63.4	1.379	0.276	-1.288	-0.016
6	100	23.4	0.989	0.198	-1.621	-0.016
7	120	12.0	0.878	0.176	-1.739	-0.014

The result of this study indicated that doping of TiO<sub>2</sub> nanoparticles with Ag resulted to higher photocatalytic degradation of 4-chlorophenol than with pure TiO<sub>2</sub>. This finding is similar to the report by Hassan *et al.* (2011) [16].

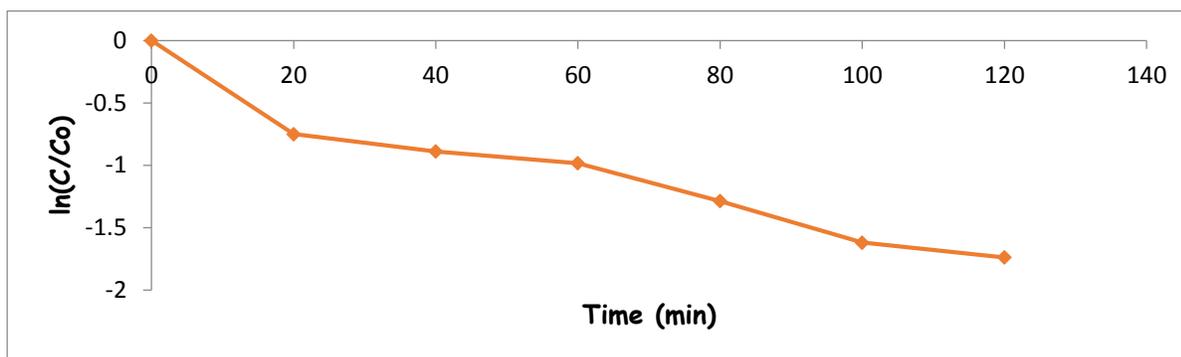


Figure 3: Photodegradation of 4-chlorophenol under 300 nm light using 0.5%Ag-TiO<sub>2</sub> catalyst

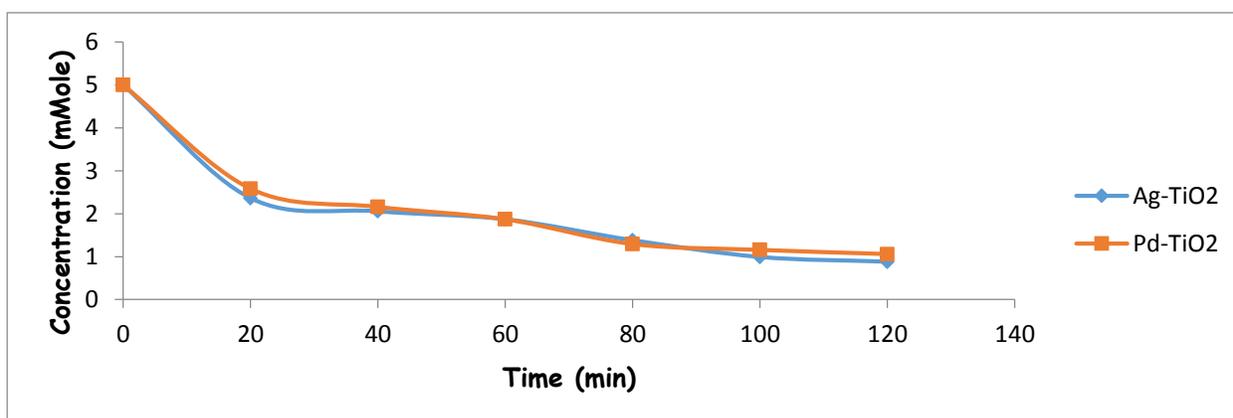


Figure 4: Photodegradation of 4-chlorophenol using 0.5%Ag-TiO<sub>2</sub>, 0.5%Pd-TiO<sub>2</sub>

The re-usability curves for the photodegradation of 4-chlorophenol using 0.5% Pd-TiO<sub>2</sub>, generally depicted a dramatic decrease in the concentration of 4-chlorophenol from 5.0 mmol with time for the first to the fourth re-use. At the first 20 min of the all the reuseability trials, except the fourth one, there was drastic decrease in the concentration of 4-chlorophenol (Figure 5). The trend obtained for the fourth re-use of Pd-TiO<sub>2</sub> can be attributed to the active sites of the Pd-TiO<sub>2</sub> blockage by preventing light penetration of the UV light by the photocatalyst materials, thereby reducing the rate of photodegradation.

However, between 20 and 40 min of UV irradiation, all the curves showed that the concentration of the organic compound had decreased considerably, except for the third re-use where the decrease was from 3.802 to 3.924 mmol (Figure 5).

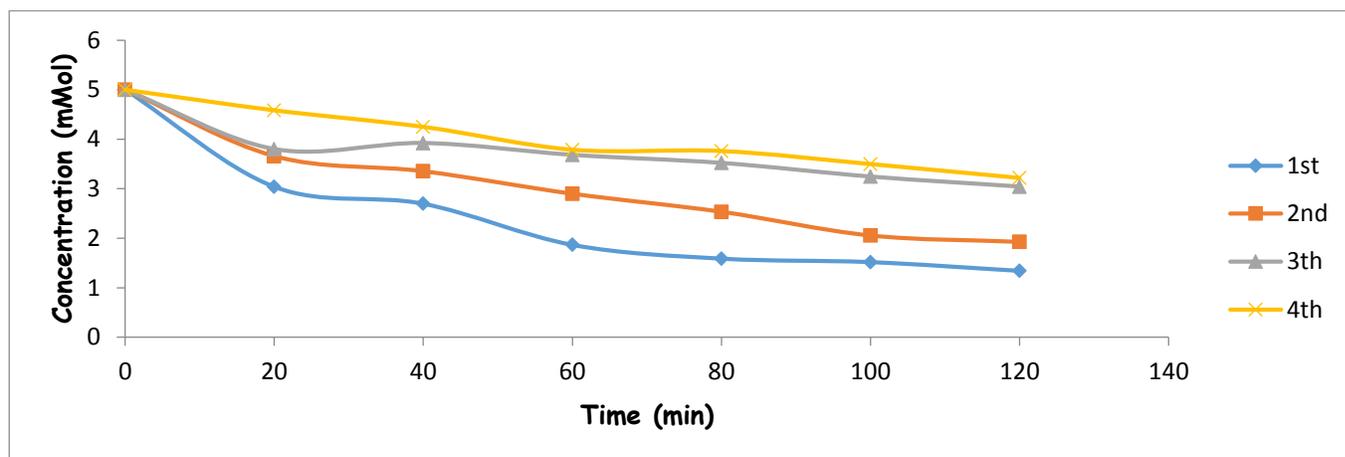


Figure 5: Reusability curve for photo-degradation of 4-chlorophenol using 0.5% Pd-TiO<sub>2</sub>

From the 60 - 120 min of the irradiation, there was a general increase in the rate of degradation of 4-chlorophenol with re-used Pd/TiO<sub>2</sub> photocatalyst. At the end of 120 min the use of fresh Pd/TiO<sub>2</sub> led to reduction in the concentration of 4-chlorophenol to 1.345 mmol. The second re-use led to concentration being reduced to 1.929 mmol. At the third re-use the concentration at 120 min was 3.043 mmol, and was reduced to 3.219 mmol by the re-use of Pd/TiO<sub>2</sub> the fourth time (Figure 5). Therefore, the re-use of Pd/TiO<sub>2</sub> for up to four times can serve efficiently in the photocatalytic degradation of 4-chlorophenol.

The slight decrease in the amount of reduced 4-chlorophenol with the number of re-use of Pd/TiO<sub>2</sub> can be attributed to deactivation of catalyst by deposition of the intermediates formed and as a result of the active metal leaching due to the loss of Pd<sup>2+</sup> ions into the reacting solution

as a result of dissolution of Pd ion. The results show that the 0.5%Pd-TiO<sub>2</sub> catalyst lost 48.9% activity after being reused four times. The loss of activity is attributed to the amount of intermediates deposited on the surface of the catalyst due to insufficient oxygen to support the photocatalytic process.

This report is similar to the work of Silija *et al* (2013), in which regenerated 2% Au/TiO<sub>2</sub> had the photocatalytic activity remaining intact even up to ten consecutive use for the degradation of a number of dye pollutants. Therefore, the finding in the present study is of enormous economic benefit in environmental control and management.

## CONCLUSION

Silver and palladium doped on P25 Degussa TiO<sub>2</sub> catalyst demonstrated improved photocatalytic degradation of 4-chlorophenol. In this result Ag modified TiO<sub>2</sub> nanoparticle showed high activity than Pd modified TiO<sub>2</sub>. There was significant difference in the photodegradation efficiency of Ag-TiO<sub>2</sub> and Pd-TiO<sub>2</sub> compared to that of pureTiO<sub>2</sub> nanoparticles. The re-used Pd-TiO<sub>2</sub> for up to four times proved effective and efficient for the photodegradation of 4-chlorophenol. The photocatalytic degradation of 4-chlorophenol followed the first order reaction which is described well in Langmuir – Hinshelwood model.

## REFERENCES

1. Oh, J. J. (2001). Destruction of 2-Chlorophenol from wastewater and investigation of by-products by ozonation. *Bulletin of Korean Chemical Society*, 232 (8), 851 – 855.
2. Raquel, C., Laura, H. R., Jorge, L. G., Juan, M. P. H. & Aracely, H. R. (2011). Photocatalytic degradation of phenolic compounds contained in the effluent of a dye manufacturing industry. *Sustainable Environmental Resources*, 21 (5), 307 – 312.
3. Gimeno, O. M., Carbajo, J. B., Beltrin & Rwas, F. J. (2005). Phenol and Substituted Phenols AOPS Remediation. *Journal of Hazardous Matter*, 119 (1-3), 99 – 108.
4. Fabbri, D. A., Bianco, P. & Pramauro, E. (2016). Effect of surfactant microstructures on photocatalytic degradation of phenol and chlorophenols. *Applied Catalysis B. Environment*, 63 (2), 21 – 27.
5. Bickley, R. I., Gonzalez-carreno, T., Lees, J.S., Palmisano, L. & Tilley, R. J. D. (1991). A structural investigation of Titanium dioxide photocatalysts. *Journal of Solid State*

- Chemistry*, 92 (1), 178-190.
6. Qin, H. L., Gu, G. B. & Liu, S. (2008). Preparation of nitrogen-doped titanium using sol-gel technique and its photocatalytic activity. *Material Chemistry and Physics*, 12(2), 346-352.
  7. Gandhe, A. R. C. & Fernandes, J. B. (2005). A Simple method to synthesize N-doped Rutile Titania with enhanced photocatalytic activity in sunlight. *Journal of Solid State Chemistry*, 178 (9), 2953-2957.
  8. Binitha, N. N., Yakob, Z. & Resmi, R. (2010). Influence of synthetic methods on zirconium doped titania photocatalysts. *Central European Journal of Chemistry*, 8(1), 182-187.
  9. Kamat, P. V. (1993). Photochemistry on non-reactive and reactive (semiconductor). *Surface Chemical Reviews*, 93 (1), 267-300.
  10. Rijuta, G. S., Hyun, S. N. , Ji, Y.S. & Dong, S.K. (2014). Influence of parameters on the photocatalytic degradation of phenolic contaminants in wastewater using TiO<sub>2</sub>/UV system. *Journal of Environmental Science and Health, Part A, Toxic/Hazardous Substances and Environmental Engineering*, 49(13),1542-1552.
  11. Pino, E. & Ecinas, E.V. (2012). Photocatalytic degradation of chlorophenols on TiO<sub>2</sub>-325 mesh and TiO<sub>2</sub>-P25. An extended kinetic study of photodegradation under competitive conditions. *Journal of Photochemistry and Photobiology A Chemistry*, 242, 20–27.
  12. Choi, W., Termin, A. & Hoffmann, M.R. (1994). Effect of 21 different metal ions dopants on photochemical activity of quantum sized TiO<sub>2</sub>. *Journal of Physics and Chemistry*, 98, 13669.
  13. Moses, T. Y. (2014). Strategies for photo chemical oxidation of phenol contaminated Waste water using TiO<sub>2</sub> based catalyst. A Ph.D. dissertation submitted to the School of Post Graduate Studies, Ahmadu Bello University, Zaria.
  14. Grabowska, E., Remita, H. & Zaleska, A. (2010). Photocatalytic activity of TiO<sub>2</sub> loaded with metal clusters, *Physicochemical Problems of Mineral Processing*, 45, 29-38.
  15. Li-chin, C., Hui, L.C. & Sing, W.H. (2010). Photocatalytic degradation of 4-chlorophenol using prepared TiO<sub>2</sub> catalysts. Department of Safety, Health and Environmental Engineering, Hung Kuan University, 61 – 72.

16. Hassan, I., Ishtiaq, A. Q., Wasim, A., Ali, M. A. & Zahir-Ud-Din, K. (2011). Photocatalytic degradation of nitro and chlorophenols using doped and undoped titanium dioxide nanoparticles, *Journal of Nanomaterials*, Article ID 589185.
17. Siliya, P. I., Binitha, N., Zahira, Y., Suraja, V. & Siti, M. T. (2013). Au/TiO<sub>2</sub> reusable photocatalysts for dye degradation. *International Journal of Photoenergy*, 10, 6505-752.