

# Comparison of Photocatalytic Degradation of 4-Chlorophenol and 3-Chlorophenol Using Silver/Palladium Nanoparticles Doped On TiO<sub>2</sub>

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## Abstract:

Photocatalytic degradation of 4-chlorophenol and 3-chlorophenol was studied using Ag and Pd doped on P25 Degussa TiO<sub>2</sub>. The Ag/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> photocatalysts were prepared by sol immobilization method. The prepared photocatalysts were used in photocatalytic degradation of 4-chlorophenol and 3-chlorophenol respectively and monitored using HPLC. The resulting solution from the photocatalytic degradation of 4-chlorophenol and 3-chlorophenol were filtered and the catalyst washed and dried. The dried catalysts were subsequently used again under the same experimental condition with a fresh 4-chlorophenol and 3-chlorophenol respectively. The re-usability curve of the 4-chlorophenol and 3-chlorophenol photodegradation using 0.5% Pd/TiO<sub>2</sub> and 0.5% Ag/TiO<sub>2</sub> were obtained. The comparison of the result obtained indicates that Pd/TiO<sub>2</sub> has a photodegradation efficiency of 78.44% within 120 minutes' irradiation while Ag-TiO<sub>2</sub> has a

**IJARBAS**

Accepted 11 August 2019  
Published 13 August 2019  
DOI: 10.5281/zenodo.3367512

photodegradation efficiency of 82.44%. The result indicates that the photodegradation of 4-chlorophenol is smoother than 3-chlorophenol because of inductive and mesomeric effect on ortho-para and meta-position. The re-usability curve indicates that the 0.5% Pd/ TiO<sub>2</sub> and Ag/ TiO<sub>2</sub> used for 4 times in photo-degradation gives reduction in concentration of chlorophenol except for the fourth usage which is attributed to catalyst leaching. The calculation of rate constant indicates that the photo-degradation of 4-chlorophenol and 3-chlorophenol follows pseudo-first order reaction kinetics. These indicate that the use of dopants increases the photocatalytic efficiency titanium dioxide.

**Keywords:** 4-chlorophenol, 3-chlorophenol, degradation, kinetics, Ag/Pd-dopant, photocatalysis, inductive and mesomeric effect, photodegradation,

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## Introduction

Increasing demand and shortage of water sources due to the rapid development of industrialization, population growth and long term droughts have become an issue worldwide with this growing demand, there is a need to increase new water and waste water treatment processes to reduce negative effect on water bodies (Assadiet al., 2014).

Among the methods considered, heterogeneous photocatalytic oxidation systems can efficiently eliminate persistent organic pollutants at a low cost energy (Catrinescuet al., 2011). Photocatalytic oxidation processes concerned with photo-activated metal oxides as semiconductors to remove contaminants in aqueous environment (Lo et al., 2004). In the photocatalytic systems, the UV irradiation of metal oxides upon incidence of photon with an energy higher than its band gap energy result in the formation of electron (e-) in the conduction band and positive holes (h<sup>+</sup>) in the valence band. The hole can either oxidize a compound directly or react with electron donors like water to form OH radicals, which react with pollutants and mineralize them to CO<sub>2</sub> and H<sub>2</sub>O (Goelet al., 2010).

Chlorophenol are hazardous chemicals and generally categorized as non biodegradable pollutants. Continuous consumption of drinking water contaminated with chlorophenols can affect human health. A representative of this class of compounds is 4-chlorophenol (4-cp) and 3-chlorophenol (3-cp). Sources of this compound include industrial effluents, such as petroleum refining, and production of pesticides paint, plastic, resin, textile, iron, solvent, pharmaceuticals and wood preserving chemicals and named as one of the priority pollutants by the US environmental protection Agency (EPA) and the European Union (EU).

The permissible limit of 4-chlorophenol in drinking water supply is 0.5mg/< (Neppolianet al., 2011). Due to 4-cp and 3-cp high toxicity and persistence in environment, attention has been focused on its removal from the aqueous media.

Titaniumdioxide (TiO<sub>2</sub>) has received the greatest interest in research of photocatalytic process due to chemical and thermal stability or resistance to chemical breakdown, low cost and their strong mechanical properties have promoted its wide application in photocatalytic water treatment (Gaya et al., 2009). The main pitfall of TiO<sub>2</sub> include its poor response to visible natural solar light and the recombination of photogenerated charge carriers.

Therefore, doping helps to overcome the limitation of TiO<sub>2</sub> in its use for photocatalytic degradation of organic pollutant. Doping is the practice of using metal, non-metal, transition metal semiconductors and dyes to improve the morphology of TiO<sub>2</sub> (Manojet al., 2012). The principles of doping is to modify the electronic structure of Nano-TiO<sub>2</sub> to broaden its effective range of light sensitivity for photocatalysis from the UV region to visible region.

In this work, Ag/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> dopants were used in photo-degradation of 4-cp and 3-cp. The result obtained were used in comparism of photocatalyticdegradation efficiency of Ag/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> in the removal of 4-cp and 3-cp in wastewater.

## Experimental

### Catalyst Preparation

The catalysts used were prepared using sol immobilisation method as reported by Moses (2014), with a few modifications. Standard sol-immobilization method was utilised to prepare the Ag, Pd, Ag-Pd nano particles supported on TiO<sub>2</sub>. The supported silver and silver-palladium colloids were prepared by using Poly vinyl alcohol (PVA) as 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 wt % aqueous PVA, (Aldrich, MW = 10000, 80% hydrolysed) solution was freshly prepared just prior to synthesis of the metal colloid.

A representative protocol for preparing a catalyst comprising Ag-Pd nano-particles with 1 wt% total metal loading on a TiO<sub>2</sub> was carried out as follows: to an aqueous 0.005 mol/dm<sup>3</sup> PdCl<sub>2</sub> and 0.006 mol/dm<sup>3</sup> AgNO<sub>3</sub> solution, 100 cm<sup>3</sup> of PVA solution (1 wt %) was added (PVA/ (Ag and Pd)(w/w) = 1.2); a freshly prepared solution of NaBH<sub>4</sub> (0.1 M, NaBH<sub>4</sub>/ (Ag and Pd)(mol/mol) = 5) was then added to form a dark brown sol. After 30 minutes 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 with a glass rod. The amount of support material required was calculated to have a total final metal loading of 1 wt %. After 2 hours, the slurry was filtered and the catalyst 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  $C_0$  of 4-chlorophenol for the photodegradation experiment.

### Photocatalytic Reaction Experiments

Photocatalytic activity was evaluated using Chlorophenol degradation experiments. The reactors used were closed Pyrex reactors with an outer diameter of 42.0mm and a height of 210 mm and thickness of 4mm, to 100 cm<sup>3</sup> of a solution containing 0.001M of Chlorophenol in deionized water from Barnstead Nano pure diamond machine and 0.2 g of the catalyst was added to the reactor. The pH of the aqueous Chlorophenol solution was monitored during the reaction using the Jenway 3010 pH meter. The suspension was stirred magnetically using yellow line MST basic magnetic stirrer at 650 rpm at ambient temperature for 2 hours in the dark, and a small amount of the suspension was withdrawn to analyze equilibrium concentration of Chlorophenol in the solution.

The mixture was then exposed to UV light using a fabricated photoreactor. At selected time intervals of approximately 20 minutes over a typical 2 hours reaction, 5 mL of the suspension was withdrawn and filtered using Acrodisc CR 13 mm syringe filter with 0.45 $\mu$ m PTFE membrane 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;

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

The efficiency of reusing the Pd /TiO<sub>2</sub> nanoparticle for the photodegradation of 4-chlorophenol and 3-chlorophenol was tested by using the resulting solution obtained from the first time photocatalytic degradation of 4-chlorophenols and 3-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

condition as in the first time, but using fresh solution of 4-chlorophenol and 3-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.

### Results and Discussion

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

The calibration curve of 4-cp and 3-cp using HPLC in order to obtain the best stock solution for photo-degradation experiment is shown in Figure 1 and 2 respectively. Table 1 and 2 were used to obtain the calibration curve. The equation obtained from figures 1 and 2, A represents the absorbance, while C is the concentration and the equation is used in calculation of concentration of 4-Cp and 3-Cp during photo-degradation reaction as shown in tables 3 and 4 respectively.

From table 3 and 4, the loss of 4-Cp and 3-Cp was observed as function of irradiation time and data fitted to a first order rate model according to following equation with an apparent rate constant (k).

$$\ln C_0 / C = kt$$

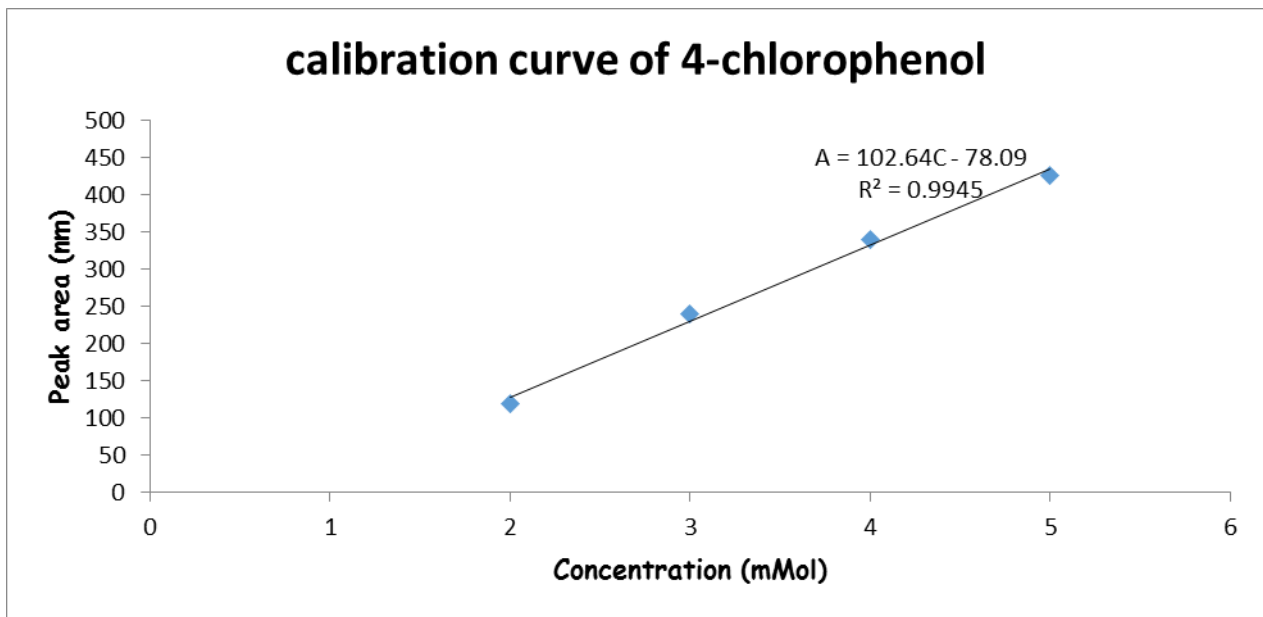
Where C<sub>0</sub>=Initial Concentration, C= Final concentration, k=Rate constant and t=Time

#### Calibration of 4-chlorophenol standards

**Table 1: calibration curve of 4-chlorophenol standards and their absorbance**

**Figure 1: calibration curve of 4-chlorophenol standards and their absorbance.**

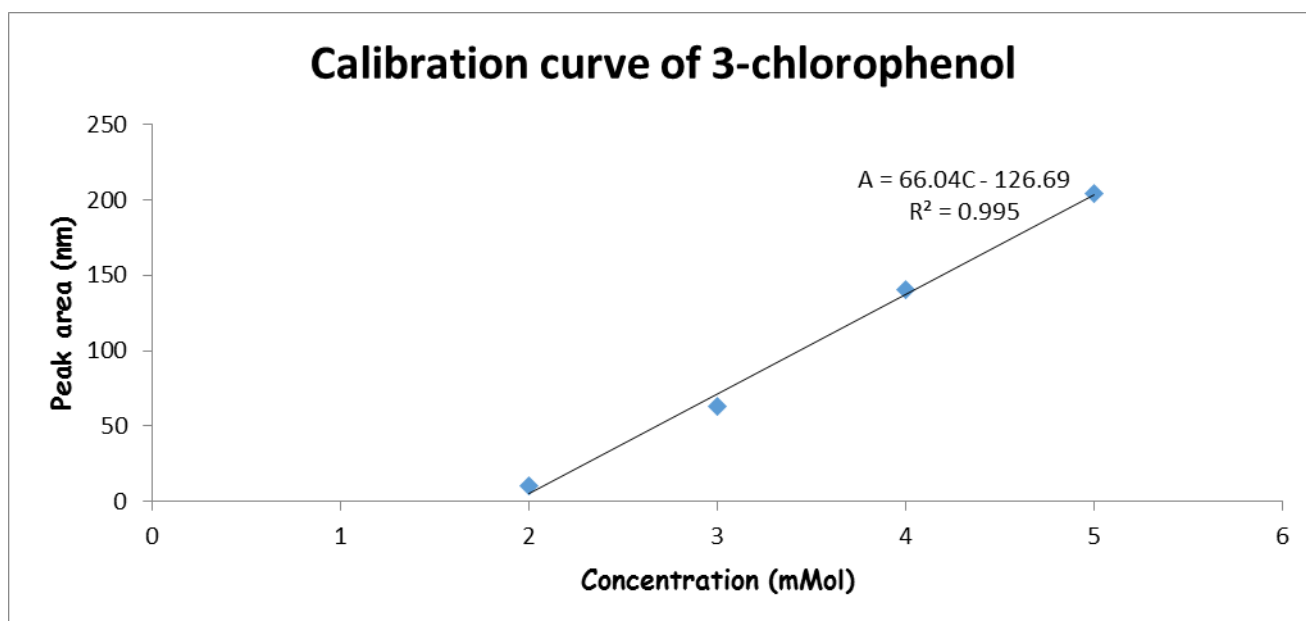
S/NO	Concentration (mMol)	Peak area (nm)
1	2	118.4
2	3	239.1
3	4	340.3
4	5	426.8



### Calibration of 3-chlorophenol standards

**Table 2: Calibration curve of 3-chlorophenol standards and their absorbance**

S/NO	Concentration (mMol)	Peak area (nm)
1	2	10.2
2	3	62.7
3	4	140.5
4	5	204.4



**Figure 2: Calibration curve of 3-chlorophenol standards and their absorbance**

The concentration of maximum peak area (426.8 and 204.4) was 5 mmol; and was used as  $C_0$  (the best stock solution for the photodegradation experiment in the 5 ml assessed by HPLC for 4-cp and 3-cp respectively (table 1 and 2). The equation obtained from figure 1 and 2 respectively with A representing the absorbance and C the concentration was used in calculating the concentrations,  $\ln C/C_0$ , and rate constant K in the degradation process was obtained in table 3 and 4 respectively.

**Table 3: 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 <sub>0</sub> )	Rate constant
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

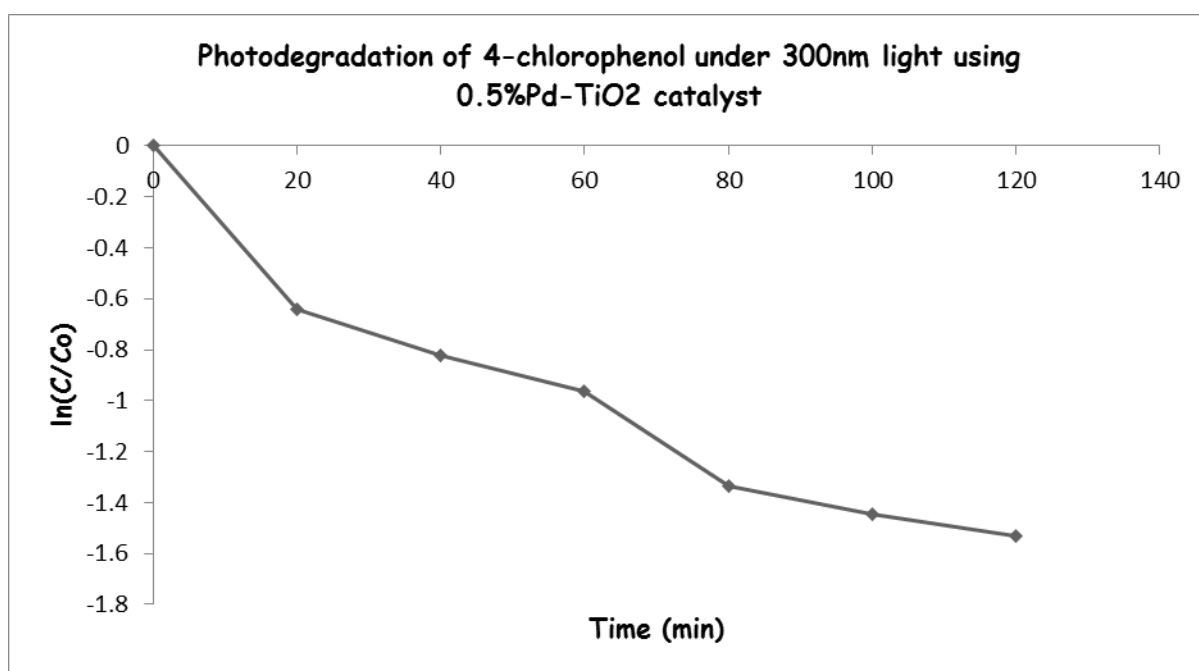
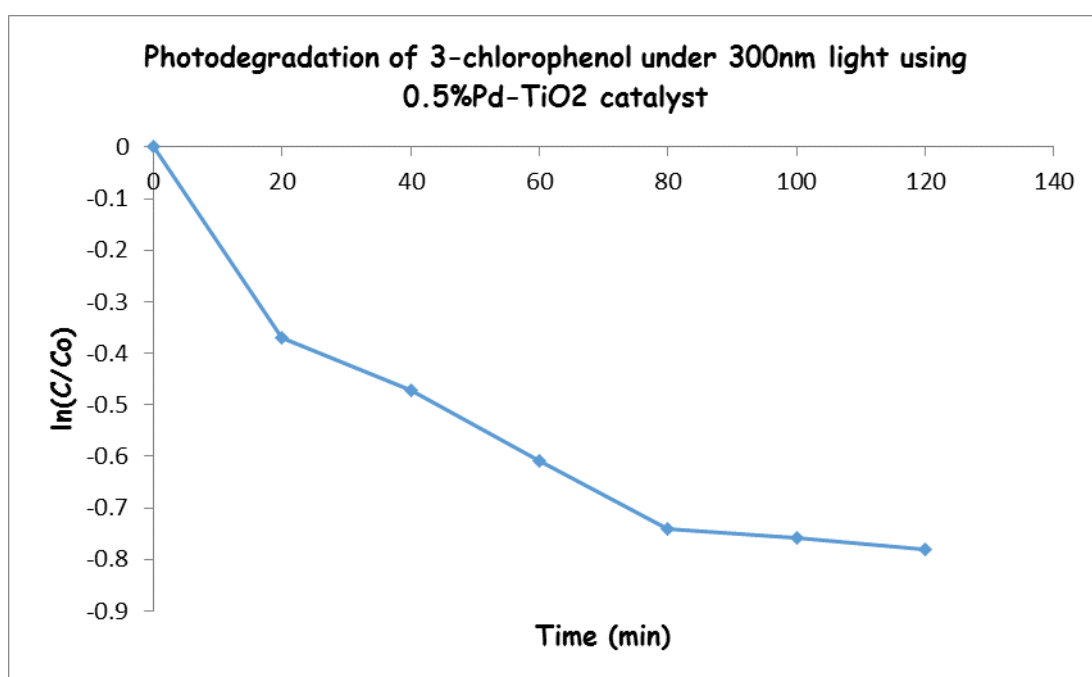


Figure 3: Photo-degradation of 4-chlorophenol under 300nm light using 0.5%Pd-TiO<sub>2</sub>

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

S/NO	time (min)	Absorbance, A (nm)	Concentration, C (mMole)	C/Co	ln(C/Co)	Rate constant
1	0	204.4	5.000	1	0	0

2	20	101.2	3.451	0.690	-0.371	-0.019
3	40	79.5	3.122	0.624	-0.471	-0.012
4	60	52.8	2.718	0.544	-0.609	-0.010
5	80	30.8	2.385	0.477	-0.740	-0.009
6	100	28.0	2.342	0.468	-0.758	-0.008
7	120	24.8	2.294	0.459	-0.78	-0.0006



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

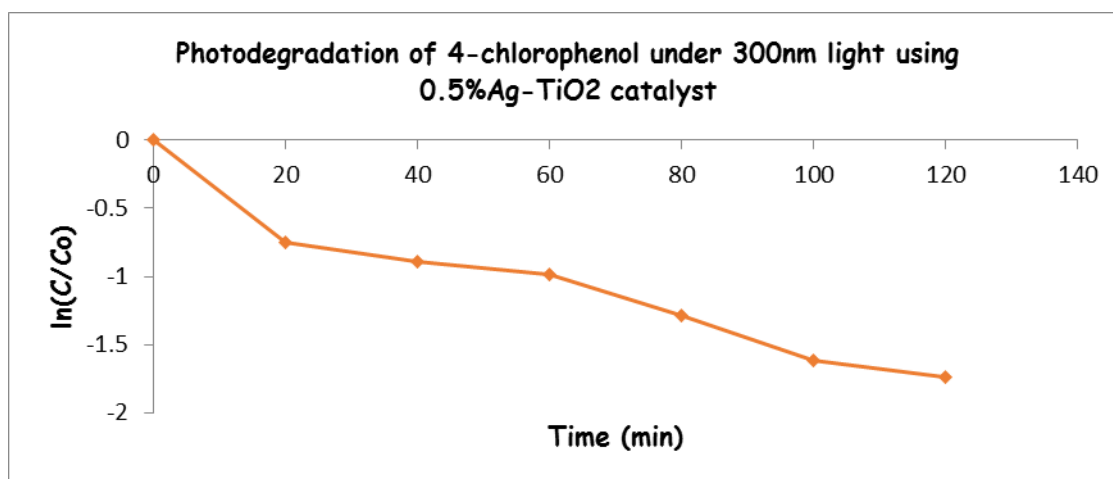
The use of 0.5% Pd-TiO<sub>2</sub> resulted in the concentration of 4-chlorophenol in the simulated wastewater from 5.0 mmol to 2.159 mmol in the first 40 min, and sharp decrease to 1.292 mmol at 80 min of the degradation process (Table 3). At 120 min the concentration was 1.059 mmol; the rate constant of the degradation by Pd-TiO<sub>2</sub> ranged from -0.032 to -0.0135 s<sup>-1</sup>

(Figure 3). For 3-cp the concentration decreases from 5 mmol to 3.122 mmol at 40 min interval, 2.385 mmol at 80 min and finally to 2.294 at 120 min interval of the degradation interval (table 4). The rate constant of the degradation of 3-cp ranges from -0.019 to  $0.006\text{s}^{-1}$  (figure 4).

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  $0.0169\text{ s}^{-1}$  (Figure 5). 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 5).

**Table 5:** 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, C (mMole)	C/Co	ln(C/Co)	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



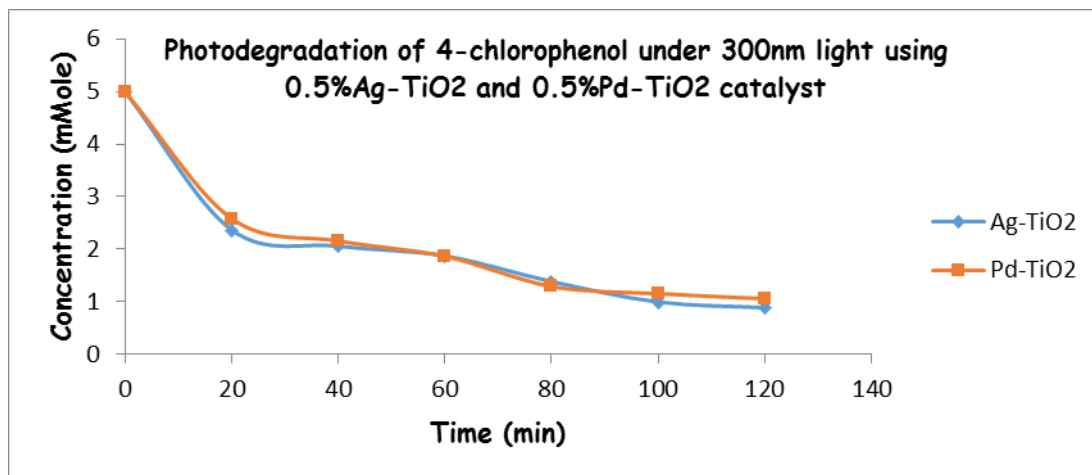
**photodegradation of 4-chlorophenol under 300nm light using 0.5%Ag-TiO<sub>2</sub> catalyst**

S/NO	TIME (min)	Concentration( mMole) 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
	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	46.75
5	80	1.379	72.42	1.292	73.69	53.55
6	100	0.989	80.22	1.156	76.43	59.00
7	120	0.878	82.44	1.059	78.44	

**Table 6: Photodegradation of 4-chlorophenol using 0.5%Ag-TiO<sub>2</sub>, 0.5%Pd-TiO<sub>2</sub>**

As presented in table 6, Pd/TiO<sub>2</sub> has a photodegradation efficiency of 78.44% within 120 min irradiation, while Ag/TiO<sub>2</sub> has a photodegradation efficiency of 82.44% on the other

hand, pure  $\text{TiO}_2$  led to the degradation of 56.00% of 4-cp. This conform to the trend obtained by Grabowska et al., (2010) in which the highest photoactivity for degrading phenol was observed for  $\text{TiO}_2$  loaded with silver (91%), gold (49%) and Au (91%) after 60 min of irradiation under UV light.



**Figure 6: photodegradation of 4-chlorophenol using 0.5%Ag-TiO<sub>2</sub>, 0.5%Pd-TiO<sub>2</sub>**

The photocatalytic activity of  $\text{pd}/\text{TiO}_2$  on photo-catalytic degradation of 4-Cp and 3-Cp follows the first order kinetics according to a Langmuir-Hinshelwood mechanism (Yu et al., 2002). Figures 3 and 4 shows the plot of  $\ln C/C_0$  versus time which gives the rate of degradation of 4-Cp and 3-Cp over time respectively.

Using  $\text{pd}/\text{TiO}_2$  catalyst comparing the result, it shows that 4-Cp has a progressive degradation within the 120 minutes irradiation than 3-Cp because chlorine, (Halogen) is ortho-para directing in this reaction. In 3-Cp, there is deactivation on the benzene ring because of meta-position of chlorine. The 4-Cp has smooth degradation because inductive and mesomeric effect is more in ortho-para position than ortho-meta position.

Many researchers indicates the importance of the chlorine position on chlorophenol isomers in the kinetics of chlorophenol degradation. Akai et al., (2001) and Ahnet al., (2003) described the molecular structure of phenol chloroderivatives and their complexes with water. They indicated that the structure of compounds, especially of a position of the chlorine atom relative to the hydroxyl group determines the reactivity of chlorophenol in direct photolysis. The chlorine atom is photo reactive more in ortho and para position than in meta position.

**Photo-degradation of 4-chlorophenol using 0.5% Ag/ TiO<sub>2</sub>, and 0.5% pd/TiO<sub>2</sub>**, Table 5 and 6 shows the photo degradation of 4-cp under 300 nm light using 0.5% Ag/ TiO<sub>2</sub> catalyst and photo-degradation of 4-cp using 0.5% Ag/TiO<sub>2</sub> and 0.5% pd/TiO<sub>2</sub> respectively. The photo-degradation curve is shown on figures 5 and 6 respectively. The curve of the photo-degradation of 4-cp using two different catalysts generally showed a decrease in the concentration of the 4-cp with time. There was a dramatic decrease in the rate of degradation of 4-cp using the pd/TiO<sub>2</sub> within the first 20 minutes with respect to that of Ag/TiO<sub>2</sub>. Ag-TiO<sub>2</sub> showed a very high photo-degradation efficiency than pd/TiO<sub>2</sub> because Ag/TiO<sub>2</sub> particles exhibited enhanced visible light induced photocatalytic activity which was as a result of the Ag/TiO<sub>2</sub> ability in trapping excited electrons from TiO<sub>2</sub> and leaves the hole for the degradation reaction of 4-Cp organic compound while pd/TiO<sub>2</sub> also traps the excited electron but not as active as Ag/TiO<sub>2</sub>. The doping of Ag/pd-TiO<sub>2</sub> provoked the transference of photo generated electrons from TiO<sub>2</sub> conduction band to the dopant conduction band and the holes were accumulated in the TiO<sub>2</sub> valence band reducing electron pair recombination thereby increasing the photocatalytic degradation of Ag/Pd-TiO<sub>2</sub> dopants. Pd/TiO<sub>2</sub> have the photo-degradation efficiency of 78.44% within 120 minutes irradiation while Ag-TiO<sub>2</sub> has a photo degradation efficiency of 82.44% as shown from calculations on table 6.

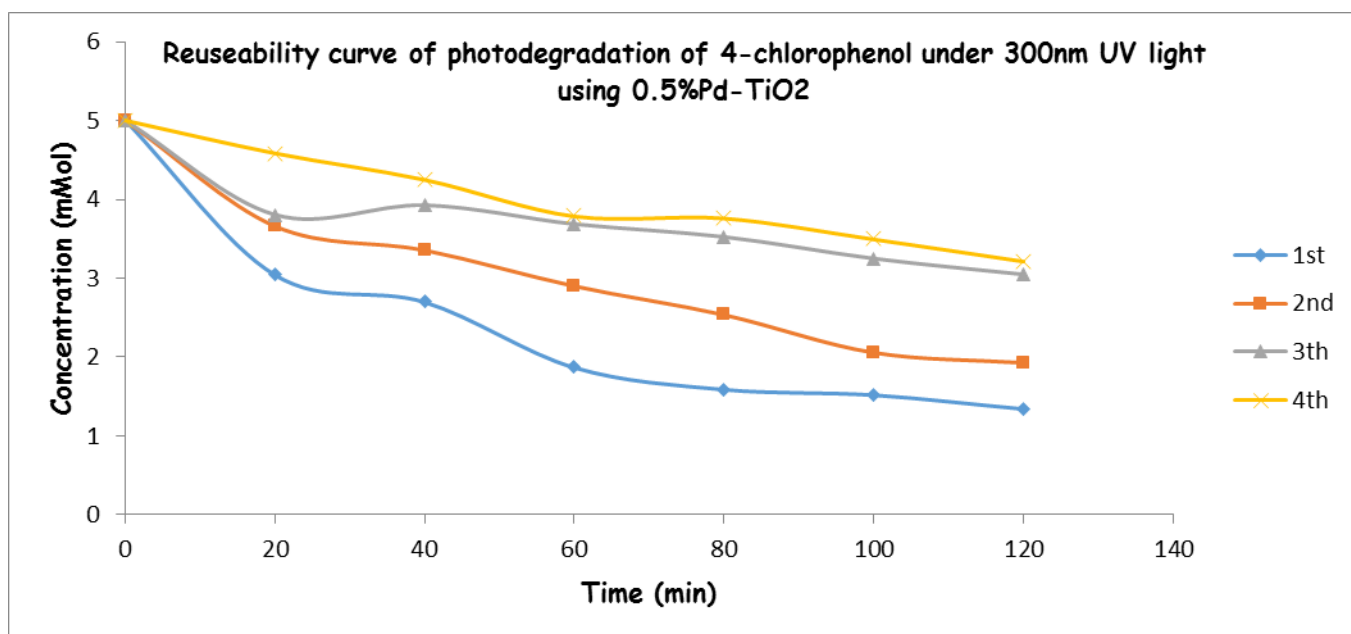
This is similar to work done by Young et al., (2011) in which he reported that Fe<sup>3+</sup> ion doped on TiO<sub>2</sub>, act as a shallow charge traps in the lattice of TiO<sub>2</sub> and this accounts for its high photocatalytic activity. This is explained by the conduction band edge of TiO<sub>2</sub> being above the energy level for Fe<sup>3+</sup>/Fe<sup>2+</sup>, where as the valence band edge of TiO<sub>2</sub> is below the energy level for Fe<sup>3+</sup>/Fe<sup>4+</sup>. Hence, Fe<sup>3+</sup> can react easily with the photo-generated electron (from conduction band of TiO<sub>2</sub>) and the hole (from valence band of TiO<sub>2</sub>) to form Fe<sup>2+</sup> and Fe<sup>4+</sup> ion. In this manner, Fe<sup>3+</sup> ions can enhance the life time for the electrons and holes by acting as both electron and hole traps.

Sakthivelet al., (2004) also investigated the performance of TiO<sub>2</sub> after supplementing with platinum (Pt) 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 hole recombination.

He reported that palladium also act as electron traps thereby preventing the generated electron from falling back to the valence band.

**Table 7: Reusability curve of Photo-degradation of 4-chlorophenol under 300nm UV light using 0.5%Pd-TiO<sub>2</sub>**

S/NO	TIME (min)	1 <sup>st</sup>		2 <sup>nd</sup>		3 <sup>rd</sup>		4 <sup>th</sup>	
		A (nm)	C (mMole)	A (nm)	C (mMole)	A (nm)	C (mMole)	A (nm)	C (mMole)
1	0	426.8	5.00	426.8	5.00	426.8	5.00	426.8	5.00
2	20	234.1	3.042	297.7	3.661	312.1	3.802	392.6	4.586
3	40	199	2.699	266.4	3.356	324.7	3.924	358.2	4.251
4	60	112.9	1.869	219.7	2.901	300	3.684	310.9	3.789
5	80	85.2	1.591	182.3	2.537	283.3	3.521	308.1	3.763
6	100	78	1.521	133.2	2.058	255	3.245	281.1	3.499
7	120	60	1.345	120.0	1.929	234.2	3.043	252.4	3.219



**Figure 7: Reusability curve of 4-chlorophenol photo-degradation using 0.5%Pd-TiO<sub>2</sub>**

### **Reusability of 0.5% pd/TiO<sub>2</sub> in the photo-degradation of 4-chlorophenol under 300nm light**

In this experiment, the resulting solution from the photocatalytic degradation of 4-chlorophenols were filtered, and the catalyst washed and dried, the dried catalyst were subsequently used again under the same experimental conditions with a fresh 4-cp solution. The reusability curves of 4-cp photo-degradation using 0.5% Pd/TiO<sub>2</sub> is shown in table 7 and Figure 7, generally showed a dramatic decrease in concentration of the 4-cp compound with time.

The Pd/TiO<sub>2</sub> was used for 4 times under the same reaction condition. There is successful degradation of the 4-cp up to 4 times which shows slight decrease in photo-degradation rates due to the blockage of active sites of pd/TiO<sub>2</sub> by organic pollutant thereby preventing light penetration of the UV light by photocatalyst material. The decrease in the photocatalytic efficiency due to subsequent usage may also be attributed to the loss of pd ion during recovery after usage which is called metal leaching. The 5.0 mmol concentration of 4-cp was reduced to 1.345 mmol at first time of usage, second usage 1.929 mmol, third usage 3.043 mmol and 3.219 mmol after fourth time re-use showing that catalyst is still active except for



the third and fourth time of usage which is attributed to metal leaching and blockage of active site by the pollutants.

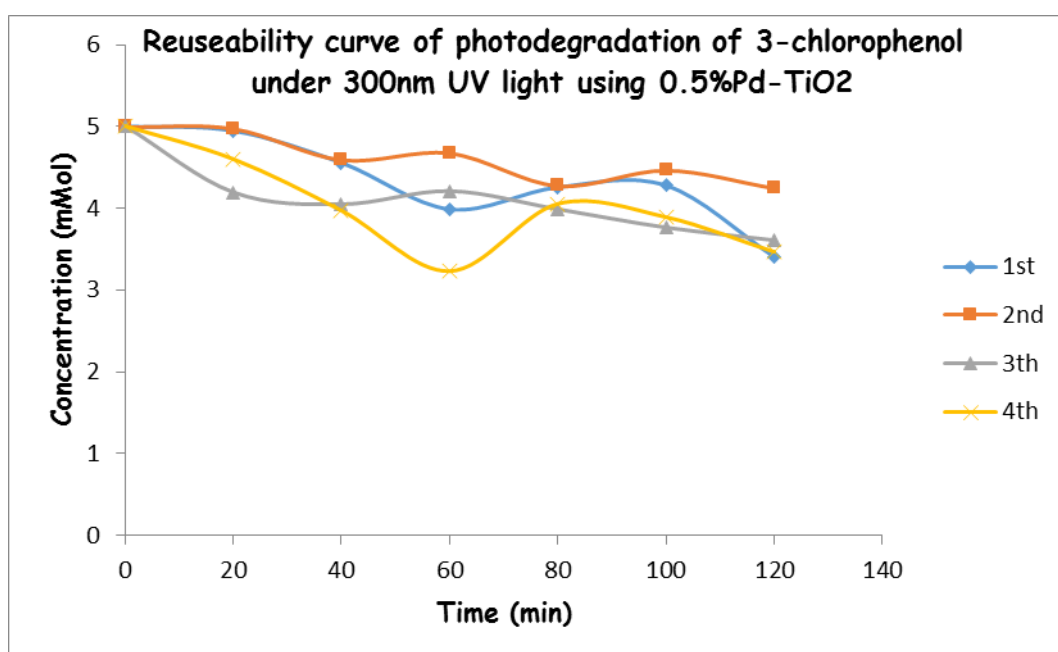
This conform with the work done by Yan et al., (2017) that TiO<sub>2</sub> catalyst loaded on glass fiber filters showed excellent re-usability on the photo-degradation of nitrobenzemne, and presented a photo-degradation rate of 95% at the first time and up to 75.9% even after 6 times of reusing by the treatment time of 12 hours.

This is similar to work done by Sarah et al., (2016) that the use of TiO<sub>2</sub> doped on Zn. The catalyst was re used for three times. It was observed that the photocatalytic nano composites under consideration do not show a significant decrease in their activity when the experiments were repeated three times using the same sample. It was reported that the slight decrease in activity after usage for 3 times may be attributed to the presence of organic contaminants on the surface of catalyst which will compete for the active sites of the photocatalyst and secondly the loss of the photocatalyst particles from the polymeric matrix. Silijaet al., (2013) also reported that the regeneration of the best catalyst 2% Au/TiO<sub>2</sub>, was done after each reaction, by centrifugation washing with water and further treatment at the calcination temperature of the catalyst that is at 200°C for 1 hour. The photocatalytic activity of the nano gold doped titania remains intact even up to ten consecutive experiments under the selected reaction conditions. This implies that the prepared catalyst can be active for several times of usage depending on the user carefulness in recovery of the used catalyst particles.

**Table 8: Photo-degradation of 3-chlorophenol under 300nm UV light using 0.5%Pd-TiO<sub>2</sub>**

S/NO	TIME (min)	1 <sup>st</sup>		2 <sup>nd</sup>		3 <sup>rd</sup>		4 <sup>th</sup>	
		A (nm)	C (mMole)	A (nm)	C (mMole)	A (nm)	C (mMole)	A (nm)	C (mMole)
1	0	204.4	5.000	204.4	5.000	204.4	5.000	204.4	5.000
2	20	200	4.946	202	4.977	150	4.189	176.8	4.596

	40	174.2	4.556	176	4.596	140.3	4.043	135.3	3.967
	60	136.8	3.989	182.3	4.679	151	4.205	86.5	3.228
	80	154.5	4.258	155	4.279	136.3	3.982	140.9	4.052
	100	155.9	4.279	168.4	4.468	121.6	3.759	130.1	3.888
	120	98.4	3.408	154	4.250	111.2	3.602	102.1	3.464



**Figure 8: Reusability curves of photo-degradation of 3-chlorophenol under 300nm UV light using 0.5%Pd-TiO<sub>2</sub>**

### Reusability of 0.5% pd-TiO<sub>2</sub> in the photo degradation of 3-chlorophenol under 300 nm light

The resulting solution from photocatalytic degradation of 3-cp were recovered as stated from 4-cp experiment. The catalyst was used for up to 4 times in degradation of 3-cp under the same experimental condition. Table 8 and figure 8 shows the re usability curve of 3-cp. It was

observed that the catalyst can also be used for up to 4 times with slight decrease in photo-degradation efficiency due to blockage of active site by pollutant contamination and metal leaching but there seem to be fluctuation in photo-degradation of 3-cp as compared to 4-cp due to inductive and mesomeric effect on OH group and Cl which more on ortho and para position than ortho and meta -position (Marianna, 2005). Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through the inductive effect, chlorine destabilizes the intermediate carbocation formed during the electrophilic substitution. Through resonance, chlorine tends to stabilize the carbocation and the effect is more pronounced at ortho and para position. This is why 4-Cp has smooth photocatalytic degradation than 3-Cp. It is well known according to Marianna, (2005) that the OH group is a very strong activator as well as ortho- and- para-directing on electrophilic aromatic substitution. Therefore a direct OH radical attack on electron rich positions should be expected. Halogen substituent are slightly deactivating but are also ortho-para-directing in this reaction. The inductive effect of the hydroxyl group due to the electronegativity of oxygen is the withdrawal of electrons. For the nucleophilic substitution the Cl group directs to the para-position in this reaction. In the case of radical reactions, a nucleophilic radical will react preferentially at the ortho-and para-position if the substituent is  $\Pi$ -acceptor and at the meta, if it is a  $\Pi$ -donor. The opposite situation occurs for an electrophilic radical. Cassady et al., (1994) in their investigation of chlorophenols and methyl chlorophenols with the use of fourier transformation ion cyclotron resonance mass spectrometry (FTMS), suggests that the relative position of the chloro-and hydroxyl groups may have greater effects on photo-dissociation than methyl group position

Boule et al., (1982) found that during direct photolysis, the dechlorination rate of 4-chlorophenol and 2-chlorophenol is faster than 3-chlorophenol.

This is similar to work done by Kuo, (1999) that the reaction rate for direct photolysis upon radiation at wavelength  $< 300$  nm decreases in the order 2,4-dichlorophenol  $>$  2-chlorophenol  $>$  2,4,6-trichlorophenol. These results indicated that the para-and-ortho positions are more active in direct photolysis. The increased occurrence of para-position in comparison with ortho-position in reaction is explained by the intermolecular hydrogen bonding between the ortho-positioned Cl atom and a hydrogen from the hydroxyl group. In

the case of ortho substituted chlorophenols, hydrogen bonds may be formed internally between CL and OH as well as externally between molecules of chlorophenol and water.

Bazylet al., (2001) described the molecular structures of phenol chloroderivatives and their complexes with water.

The cited paper indicated that the structure of compounds especially of a position of the chlorine atom relatives to the hydroxyl group determines the reactivity of chlorophenol in direct photolysis. The chlorine atom is photo-reactive in ortho-and-para-position than in meta position.

In conclusion, the photodegradation of 4-chlorophenol and 3-chlorophenol. The 4-chlorophenol gives a smoother and faster degradation due to the fact that para-and -ortho-position are more favourable to the cleavage of the C-CL bond than the meta-positions. The favourable para-and-ortho position are as a result of the inductive and mesomeric effects of OH and Cl groups.

## Conclusion

The photocatalytic degradation of 3-cp and 4-cp follows the first order reaction rate. The photocatalytic degradation of 3-cp and 4-cp using Ag/TiO<sub>2</sub> and pd/TiO<sub>2</sub> indicates that the photocatalytic efficacy of Ag/TiO<sub>2</sub> is greater than pd/TiO<sub>2</sub> due to the ability of Ag/TiO<sub>2</sub> to trap the excited electron easily than pd/TiO<sub>2</sub> and prevent the recombination of the excited electrons to the valence band. The re usability curve of the prepared catalyst indicates that the catalyst can be re- used up to 4 times without much loss in activity of the catalyst. The slight loss in activity is due to metal leaching and blockage of active sites of catalyst by the organic pollutants. In the photocatalytic degradation of 4-cp and 3-cp, the para and ortho position are more favourable to the cleavage of C-CL bond than the meta position. The favourable para and ortho position are a result of the inductive and mesomeric effects of OH and Cl groups.

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### Cite this article:

**Author(s),** <sup>1</sup>Aroh, A.O.,<sup>1</sup>Gimba, C.E.,<sup>1</sup>Omoniyi, K.I., <sup>1</sup>Abba, H. and <sup>2</sup>Yilleng, M.T. (2019). “Comparison of Photocatalytic Degradation of 4-Chlorophenol and 3-Chlorophenol Using Silver/Palladium Nanoparticles Doped On Tio<sub>2</sub>”, Name of the Journal: International Journal of Academic Research in Business, Arts and Science, (IJARBAS.COM), N, 232- 254 . **DOI:** 10.5281/zenodo.3367512, **Issue: 2, Vol.: 1, Article: 12, Month: August, Year: 2019.** Retrieved from <https://www.ijarbas.com/all-issues/current-articles/>

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