

## UV photoelectrocatalytic degradation of *m*-cresol pollutant using TiO<sub>2</sub> dip-coated stainless steel electrode system

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ARTICLE INFO	ABSTRACT
<p>Received : 15 June 2021  Revised : 01 August 2021  Accepted : 20 August 2021</p> <p>Available online: 19 November 2021</p> <p><b>Key Words:</b>  Dip-coated stainless steel electrode  <i>m</i>-cresol pollutant  Photocatalytic efficiency  Photoelectrocatalytic oxidation</p>	<p>In the present study, the removal of <i>m</i>-cresol in an aqueous medium was studied by the photoelectrocatalytic (PEC) degradation by the TiO<sub>2</sub> suspension on dip-coated stainless steel electrode under UV lamp of the wavelength of 352nm. The performance of the PEC method on the degradation of <i>m</i>-cresol was studied by made the comparison with the photocatalytic oxidation (PCO) method in terms of COD removal and kinetic study. In the PEC study on the degradation of <i>m</i>-cresol pollutant was studied by the various parameters such as initial concentration, pH, and the bias potential. The result found that the optimum degradation efficiency of <i>m</i>-cresol in the PEC and PCO methods were 79.6% and 39.8% at pH 5.0. The result showed that the kinetic constants (k) in the PEC and PCO methods were -0.0116 and -0.0058 under optimum conditions. The result found that the PEC method using TiO<sub>2</sub> coated on stainless steel electrode is two times higher than the PCO method on the degradation of <i>m</i>-cresol.</p>

### Introduction

In recent times, cresol compounds including *m*-cresol, *o*-cresol, and *p*-cresol have widely used in various industries such as coal gasification plants, oil refining industries, pharmaceuticals, and varnish industries. Most notably, *m*-cresol has the highest toxicity, a potential carcinogen, and *m*-cresol causes harmful effects on kidneys, liver, lungs, and central nervous system (Yang *et al.*, 2018; Sudipta and Somnath, 2012). In recent years, the experimental works (Fransico *et al.*, 2007; Kavitha and Palanivelu, 2003; Wataru *et al.*, 2006) have demonstrated the feasibility of removing *m*-cresol pollutants through the advanced oxidation process (AOP), incorporating chemical oxidation with the help of reagents such as ozone, Fenton's reagent, ozone/UV, and hydrogen peroxide/UV and the major drawback of chemical oxidation methods creating chemical sludges during its operation. Several authors (Feng and Cheng, 2004; Cristina *et al.*, 2007; Rajkumar *et al.*, 2005) have described the quick removal of *m*-cresol from wastewater by

photocatalytic oxidation (PCO) method using UV or solar irradiation with TiO<sub>2</sub> catalyst. PCO is an ambient temperature process that takes energy from solar or UV to produce highly reactive intermediates of high oxidizing or reducing potential, which then attacks and destroys the target compounds (Rita *et al.*, 1991; Michael *et al.*, 1995; Chewi *et al.*, 2008; Gaya and Abdullah, 2008). Two reactions occur in the photocatalytic process, one being the oxidation reaction by the photogenerated holes another one the reduction reaction by photogenerated electrons. The photocatalytic efficiency primarily depends on the concentration of photogenerated electrons and holes. However, the band energy gap is narrow (3.2eV) between photogenerated electrons and holes and quickly recombined with each other, which attribute to the decrease in the photocatalytic efficiency (Sayekti *et al.*, 2014). The photoelectrocatalytic (PEC) oxidation method is the combination of the electrochemical and a photocatalytic process. Many

researchers (Roberto *et al.*, 2000; Taicheng *et al.*, 2004; Fang *et al.*, 2002; Huseyin *et al.*, 2003; Li *et al.*, 2007; Fabiana *et al.*, 2009; Liao and Wei, 2010; Wenjie *et al.*, 2010) have demonstrated the PEC method, which is efficient when a photoanode, created by titanium dioxide ( $\text{TiO}_2$ ) coating on semiconductor has biased by an external potential under illumination, which pulls the photogenerated electrons to the cathode, thus minimizing electron-hole recombination within the catalyst and increasing the rate of oxidation of organics. Several authors (Li *et al.*, 2007; Xie, 2006; Yang and Pan, 2010) attempted to degrade organic pollutants from wastewater with the help of the PEC oxidation using Ti/Pt and diamond doped electrode. As a result, the PEC method is more effective. However, the electrodes such as platinum and diamond used in the PEC method are too costly. As of now, based on current information, the degradation of *m*-cresol by the PEC method using  $\text{TiO}_2$  coated with the cheapest stainless steel electrode system has not been reported. In this study, the PEC oxidation method on the degradation of *m*-cresol has investigated using  $\text{TiO}_2$  coated stainless steel electrodes assembly with UV light (8w, 352nm, 27mW/m<sup>2</sup>). The performance of the PEC degradation of *m*-cresol was investigated by made the comparison with the PCO method. Furthermore, in this work, the degradation efficiency of *m*-cresol was studied by the effect of different parameters (initial concentration, pH, bias potential, and COD removal) and kinetic model.

## Material and Methods

### Stock solution

A commercial reagent *m*-cresol in their highest available grade in Analar (AR) was employed to prepare the solution without doing any further purification. A stock solution of 10,000mg/l has prepared by taking 1ml of *m* – cresol and made up to 1L with the help of deionized water.

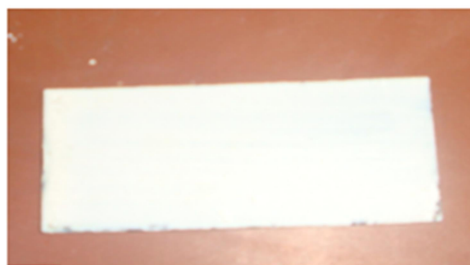
### Photoelectrocatalytic oxidation method

#### $\text{TiO}_2$ coatings on stainless steel

In this study, The Prototype PEC reactor has developed by combining the methods of electrochemical and photocatalytic oxidation. The performance of the PEC reactor on the degradation of *m*-cresol has investigated through the cheapest stainless steel electrodes (2.5cm×5cm×1mm) of the anode and cathode were used in the given buffer

solution. The  $\text{TiO}_2$  powder (Degussa 25, particle size – 0.3 $\mu$ , Anatase/ rutile (3.6/1), crystalline form, surface area 56 m<sup>2</sup> /g, band gap energy 3.2 eV) has used as the photocatalyst. In the PEC method, the  $\text{TiO}_2$  powder-coated on stainless steel using a dip coat method which used as the photoanode and the cathode used as a stainless steel electrode.

In the dip coat method, the  $\text{TiO}_2$  coating on a stainless steel electrode has made by trial and error. In the first trial, the  $\text{TiO}_2$  powder and ethylene glycol have thoroughly mixed with the stirrer at the ratio of 1:1 (1.0g  $\text{TiO}_2$  powder and 1.0mL ethylene glycol, which coated on a stainless steel electrode and it has dried in a hot air oven at a temperature of 120° C. Again, the same electrode has dried at a temperature of 450° C in the muffle furnace for one hour to complete removal of the ethylene glycol. In the first trial, the complete removal of the ethylene glycol could not take place in the above process because of the ratio of 1:1 mixer (1g  $\text{TiO}_2$  powder and 1mL ethylene glycol). As a result, it rendered the liquid form of the ethylene glycol, which did not stick on a stainless steel electrode. So, the crack has developed on the stainless steel electrode. Therefore, this is unfit for the  $\text{TiO}_2$  coating on stainless steel with a ratio of 1:1. For the second trial, the same process has carried out to achieve the perfect  $\text{TiO}_2$  coating on stainless steel electrode (anode) with the modification of the blended ratio of  $\text{TiO}_2$  and ethylene glycol at 2:1 (1g  $\text{TiO}_2$  powder and 0.5mL ethylene glycol) and also two drops of palm oil have added to get emulsion formation of  $\text{TiO}_2$ , which attributed to  $\text{TiO}_2$  stability on stainless steel. The outcome of the second trial, there is no crack has developed on the stainless steel due to emulsion formation of palm oil. From the result, it has concluded that the mixing ratio of 2:1 ( $\text{TiO}_2$  powder and ethylene glycol) created a good fit for the  $\text{TiO}_2$  coatings on the stainless steel electrode, which has illustrated the Figure 1.



**Figure 1:  $\text{TiO}_2$  coatings on stainless steel electrode (anode)**

### Development of prototype PEC reactor

The prototype PEC reactor has developed using the quartz cell chamber with a volume of 2 Litre, which contained a synthetic of *m*-cresol solution. The pH of the solution has adjusted to 3.0 with 0.1 M H<sub>2</sub>SO<sub>4</sub>, which blended with a magnetic stirrer to ensure the complete mixing of the reagents. The electrodes (TiO<sub>2</sub> coated anode and cathode) assembly has kept inside of the quartz cell chamber with a distance of 1.0cm. The photoactivity of TiO<sub>2</sub> coated stainless steel anode has illuminated by low-pressure UV lamp (Power capacity: 8W and wavelength: 352nm), which has fixed against the photoanode surface at the distance of 10.0cm. 1.0 Ampere DC two-terminal power supply has given across the electrodes assembly consisting of TiO<sub>2</sub> coated stainless steel anode and stainless steel cathode. The *m*-cresol sample has collected from the PEC reactor at regular 30.0 min intervals for a period of 2.0 hrs. Figure 2 illustrated the prototype PEC reactor.

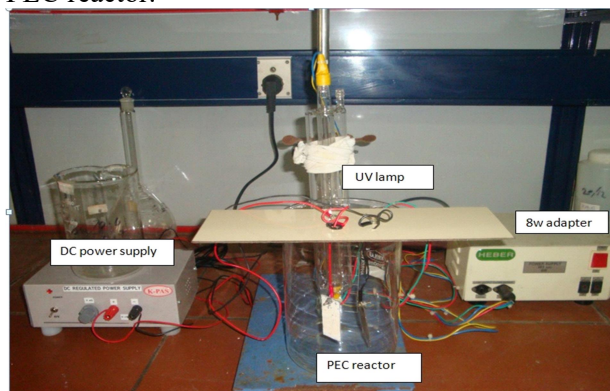


Figure 2: The Prototype PEC reactor

### Photocatalytic oxidation method

The performance of PEC degradation of *m*-cresol was investigated by made the comparison with the PCO method. The photocatalytic oxidation has carried out the same PEC quartz cell chamber without electrodes assembly. 1.0g of the TiO<sub>2</sub> powder (Degussa 25, particle size – 0.3μ, Anatase/rutile (3.6/1), crystalline form, surface area 56 m<sup>2</sup>/g, band gap energy 3.2 eV) has used as the photocatalyst, which has thoroughly mixed with *m*-cresol synthetic solution. The photoactivity TiO<sub>2</sub> surface in the PCO has illuminated by low-pressure UV lamp (Power capacity: 8W and wavelength: 352nm). The *m*-cresol sample has

collected from the PCO at regular 30.0 min intervals for a period of 2.0 hrs.

### Analysis, Instruments and procedure

#### 4 Amino Antipyrine Method

Visible Spectrometer (Model spectronica 20Geneys: made in the USA) was employed to assess the degradation rate of *m*-cresol concentration while before and after the PEC and PCO methods. The *m*-cresol concentration has determined by the 4-amino antipyrine method. 4-Aminoantipyrine reacts with *m*-cresol on oxidation with potassium ferricyanide to give light pink phenazone dye. The minimum detectable limit was 10μg (Annual Book of ASTM Standards, 1976). The degradation efficiency has estimated using the formula

$$\text{Degradation efficiency} = \frac{\text{initial absorbance} - \text{Absorbance at time (t)}}{\text{initial absorbance}} \times 100$$

### Chemical Oxygen Demand (COD)

Samples were measured in terms of COD to evaluate the removal efficiency of *m*-cresol in the PEC and PCO methods. The COD measurements were done by an open reflux dichromate titrimetric method as per the standard method procedures (Annual Book of ASTM Standards, 1976).

Calculation

$$\text{COD (mg/l)} = \frac{(A-B) \times M \times 8 \times 1000}{\text{mL of samp}}$$

Where;

A – mL FAS used or blank

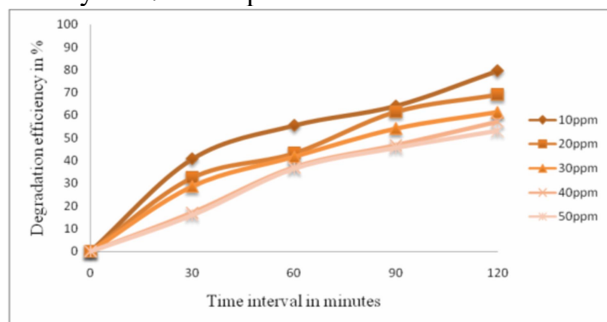
B – mL FAS used for sample

## Results and Discussion

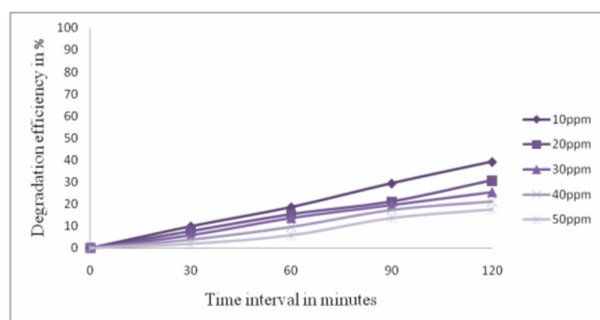
### Effect of initial concentration of *m*-cresol

The performance of the PEC and PCO methods the effect of initial concentration ranges of 10.0ppm – 50.0ppm has performed at 0-120 min contact time through the experiments made 3.0V bias potential at neutral pH (pH=7.0). The effect of initial concentration on the degradation of *m*-cresol using the PEC and PCO methods has depicted Fig.3a and Fig.3b, which has observed that the degradation efficiency of *m*-cresol has gradually increased from 0-120 minutes. As a result, the highest value of degradation rate of *m*-cresol has taken place at 10ppm concentration in the PEC (80 %) and PCO (40%) methods. In the PEC method, the degradation efficiency of *m*-cresol has decreased with increasing concentration of *m*-cresol

pollutants (Figure 3a and Figure 3b). The phenomenon may relate to the hydroxyl radicals were produced on the surface of the PEC anode during the reaction, which is higher than the mass of *m*-cresol pollutants at a lower concentration. As an outcome, it enhanced the efficient photocatalytic activity on *m*-cresol pollutants.



**Figure 3a: Effect of initial concentration on degradation of *m*-cresol using the PEC method**



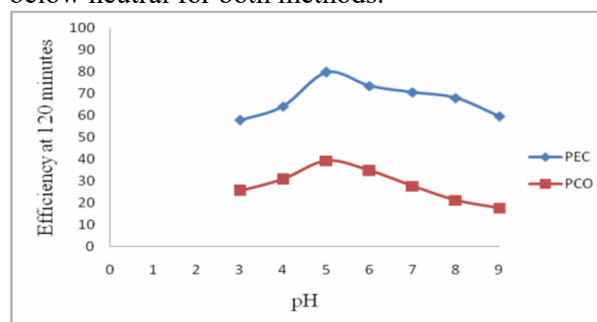
**Figure 3b: Effect of initial concentration on degradation *m*-cresol using the PCO method**

Generally, the degradation rate of organic pollutants increases with decreasing concentration. In other words, the degradation of organic pollutants has enhanced up until the optimized value. Beyond the optimal value, the degradation of organic pollutants continued to decrease (Yanzong *et al.*, 2012). Generally, there is a large quantity of hydroxyl radicals required to degrades the high concentration of pollutants, but the available quantity of hydroxyl radicals insufficient (Wang *et al.*, 2009a). The PEC oxidation has occurred only at the surface of the TiO<sub>2</sub> electrode, not in the quantity of solution. The reduction in *m*-cresol degradation rate at a higher initial concentration of *m*-cresol has clarified by the phenomenon the light intensity arrived at the TiO<sub>2</sub> film surface reduced due to lower transparency of the solution, which leads to diminished the in the hydroxyl radicals produced on

the TiO<sub>2</sub> surface (Ebrahim, 2018). From the above result, it has concluded that the degradation efficiency of *m*-cresol in the PEC method two times higher than the PCO method at an initial concentration of 10ppm at 120 minutes. The phenomenon has related to the PEC method generated more hydroxyl radicals than PCO, which induced the degradation efficiency of *m*-cresol.

### Effect of pH

The pH is an essential factor that estimates the degradation efficiency of *m*-cresol in the PEC and PCO methods because the pH value will modify the charge state of the TiO<sub>2</sub> surface. As a result, it induces the adsorption of organic pollutants on the TiO<sub>2</sub> surface (Yanzong *et al.*, 2012). In the PEC method, the effect of pH ranges of 3.0-9.0 has investigated through the experiments made with 10ppm *m*-cresol solution (operating parameters 3.0V bias potential and 120 min contact time were kept constant). The degradation of *m*-cresol took place in the PEC method when the UV lamp illuminated on the surface of the TiO<sub>2</sub> produces more H<sup>+</sup> ions on stainless steel photoanode, which attributed the adsorption of *m*-cresol species on the semiconductor surface. The same procedure has carried out in the PCO method with the absence of electrode assembly. The influence of pH 3.0-9.0 in the degradation of *m*-cresol in the PEC and PCO methods has illustrated the Figure 4. The degradation efficiency has attained a maximum of 79.6% and 39.8% at pH 5.0 in the PEC and PCO methods after it decreased from pH 5.0-9.0 (Figure 4). From the result, it has observed the effect of pH on the degradation of *m*-cresol is more effective below neutral for both methods.



**Figure 4: Effect of pH on degradation of *m*-cresol by using the PEC and PCO methods**

When the organic pollutant has adsorbed on the surface of TiO<sub>2</sub>, the reaction takes place between



hydroxide ions and positive holes. As a result, it renders the hydroxyl radical. Therefore, the positive hole ion enhances the oxidation of species at acidic pH (Yanzong, Z, *et al.*, 2012). The hydroxyl radical plays a predominant role in oxidizing the organic pollutant into CO<sub>2</sub> and H<sub>2</sub>O (Gaya and Abdullah, 2008). The degradation of *m*-cresol pollutant using the TiO<sub>2</sub> thin film modified carbon sheet photoelectrode at the biased potential of 0.45V has investigated through the experiments were conducted with 5.0mg L<sup>-1</sup> *m*-cresol in a buffer solution with the pH ranges of 3.0 – 11.0. As a result, the highest degradation has obtained at pH 4.0 (Ebrahim, 2018).

Even though the degradation efficiency of *m*-cresol has obtained maximum in the PCO method, the recombination of the holes and electrons takes place on the TiO<sub>2</sub> semiconductor surface. As an outcome, it reduces the adsorption capacity of 10ppm *m*-cresol species and also the degradation efficiency of *m*-cresol. From the above result, it has concluded that the effect of pH on the degradation of *m*-cresol in the PEC method is more effective than the PCO method at low pH.

#### Effect of bias potential

In the PEC method, the effectiveness of supported photocatalysts has improved by applying a positive potential ("bias") across the photoanode. The application of an applied voltage across the TiO<sub>2</sub> electrode facilitates to keep the photogenerated electrons apart from holes and also reduces their recombination, resulting in higher degradation efficiency of pollutant takes place (Vinodgopal *et al.*, 1993; Waldner *et al.*, 2007; Waldner *et al.*, 2007; Shinde *et al.*, 2009). The effect of bias potential ranges of 3.0 to 6.0 on the degradation of 10ppm *m*-cresol pollutants has performed in the PEC method through the experiment was conducted at pH 5.0. From this Figure 5, the maximum degradation efficiency of *m*-cresol has obtained at 80% in the PEC, where the applied voltage has increased from 3.0V to 6.0V and beyond 3.0V did not much enhance *m*-cresol degradation. It becomes stable. The phenomenon has related to the application of positive potential higher than the TiO<sub>2</sub> flat band potential across the foamed stainless steel supported TiO<sub>2</sub> photoelectrode could render a potential difference inside the film that forced the photogenerated holes and electrons to move in

inverse directions. As an outcome, the recombination of photoanode and electrode does not occur on the TiO<sub>2</sub> surface. Consequently, the amount of *m*-cresol degraded increased with the increase of the potential. Most of the photogenerated electrons were removed either by the electric field at 3.0V. Generally, in the PEC process, the degradation rate increased with an increasing potential bias, up until the optimized value. Beyond the optimal value, the recombination of electrons and holes has avoided that the attributes the bias potential led to no significant improvement in the PEC activity (Yanzong *et al.*, 2012).

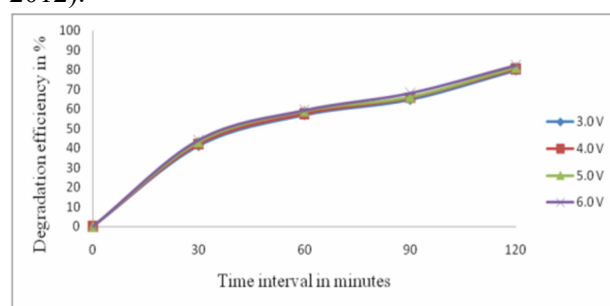
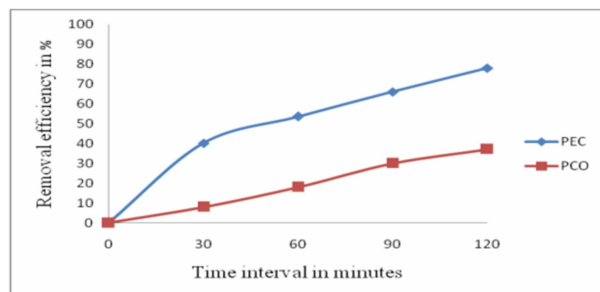


Figure 5: Effect of bias potential on degradation of *m*-cresol Using PEC method

#### Effect of COD Removal

COD removal is an important parameter the degradation of *m*-cresol pollutant (10ppm concentration) in the PEC and PCO method at pH 5.0 has investigated as compared with the PEC and PCO methods were shown Fig.6. The maximum degradation has obtained at 10ppm concentration of *m*-cresol in the PEC and PCO methods depicted 78.0% and 38.0% (Figure 6). The study on the degradation of refractory organic pollutants in the presence of a high concentration of chloride ions has investigated using the PEC, PCO, and electrochemical oxidation methods. As an outcome, the COD removal efficiency in the PEC, PCO, and electrochemical oxidation methods were about 47.4%, 38.0%, and 13.5% (Guiying, L, *et al.*, 2006). Another study has investigated through the experiments made on the degradation of landfill leachate using Cu<sub>2</sub>N<sub>3</sub> codoped TiO<sub>2</sub> electrode in the PEC method as compared with the PCO. In this profile, the COD removal efficiency has achieved using the PEC and PCO methods were about 68.7% and 21.7% (Xiao *et al.*, 2015).



**Figure 6: Effect of COD removal using the PEC and PCO methods**

From this Figure 6, the COD removal has obtained in the PEC method was two times higher than the PCO method. The phenomenon has related to the application of bias potential to the  $\text{TiO}_2$  electrode could not allow the recombination of electrons and holes and result in generated hydroxyl radicals via the reaction between the holes and electrons. As an outcome, the *m*-cresol pollutant has oxidized directly by hydroxyl radicals on the  $\text{TiO}_2$  electrode surface. From this result, it has concluded that the COD removal in the PEC method highly efficient than the PCO method.

#### Kinetics elements for PEC and PCO methods

Experiments on the PEC and PCO degradation of *m*-cresol conducted to compare *m*-cresol degradation efficiencies between them. The PEC and PCO experiments have carried out in acidic pH (pH=5.0) containing the 10ppm initial *m*-cresol concentration solution. Also, in this PEC process, an investigation has performed at a surface of the  $\text{TiO}_2$  stainless steel electrode biased at  $E = 3.0$  V. The Langmuir–Hinshelwood (L–H) kinetic model can be used to describe the PEC reaction (Yan *et al.*, 2003).

The PEC and photocatalytic oxidation of *m*-cresol belongs to first-order kinetics.

The chemical reaction has given in Equation. 1

$C \rightarrow \text{Coxidised}$  ----- Equation (1)

Thus, the rate of *m*-cresol has expressed as Eqn. 2  
 $-dC/dt = k [C_0]$  ----- Equation (2)

Rearranging the terms and given in Eqn.3 which represents the linear equation

$dC/dC_0 = -kdt$  ----- Equation (3)

Where, C- Concentration of *m*-cresol at any time

$C_0$  - Concentration of *m*-cresol at time  $t=0$

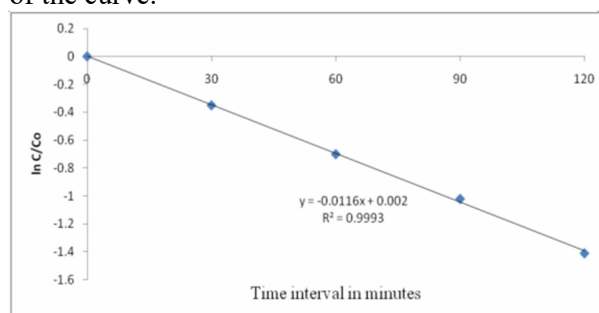
$k$  - Reaction rate constant

On integration of Eqn.3 becomes Eqn.4

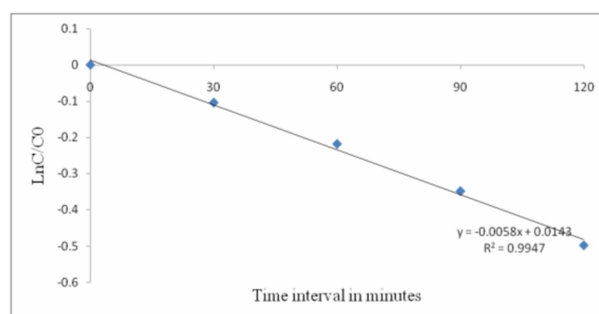
$\ln C/C_0 = -kt$  ----- Equation (4)

The slope of the plot  $\ln C/C_0$  versus  $t$  gives the value of reaction rate constant  $k$ .

The degradation of organic pollutants carried out in the PEC method using  $\text{TiO}_2$  film electrodes is seen to obey the first-order or pseudo-first-order kinetics. The PEC degradation of organic pollutants using a  $\text{TiO}_2$  film electrode illustrates the first-order kinetic constants and regression coefficients (Table 1). The experimental result of the PEC and PCO methods seem to fit in the equation of the first-ordered reaction model (Figure 7a and Figure 7b). Degradation of *m*-cresol pollutants in the PEC and PCO methods evaluated by considering the reaction rate constants in the kinetic equation via the slope of the curve.



**Figure 7a: Kinetics of PEC method on degradation of *m*-cresol**



**Figure 7b: Kinetics of PCO method on degradation of *m*-cresol**

The experimental results showed in Table 2 found that the rate constant  $k$  on the degradation of *m*-cresol in the PEC and PCO methods, which showed -0.0116 and - 0.0058 (2:1) respectively. These results demonstrate that the structure of the  $\text{TiO}_2$  coated stainless steel electrode and bias potential can significantly influence the kinetic constant. Hence, it has concluded that the degradation of *m*-cresol in the PEC proceeds two times faster than the PCO method.

**Table 1: Kinetic constant and regression coefficient for degradation of organic pollutant by the PEC method using TiO<sub>2</sub> electrode**

Pollutant concentration	Source of light	Electrode	Reactor electrode, (counter reference assembly)	R <sup>2</sup>	Kinetic constant, k	Ref.
PCP, 40 mg/L	Inserted UV light 365 nm, 0.6 mW/cm <sup>2</sup>	TiO <sub>2</sub> film electrode	Single photoelectrochemical Compartment (stainless steel)	0.983	0.0171	Quan <i>et al.</i> 2007
BPA, 11.2 mg/L	UV 365 nm, 0.68 mW/cm <sup>2</sup>	TiO <sub>2</sub> multiporous thick-film electrode	Batch-scale photoreaction set-up threeelectrode configuration (Pt foil, SCE)	-	0.0063	Xie, 2006
MB, 20 mg/L	UV 254 nm	TiO <sub>2</sub> /Ti mesh electrode	Typical three-electrode System (Pt wire, SCE)	0.995(R)	0.0178	Li <i>et al.</i> , 2007
Malachite green, 1 × 10 <sup>-5</sup> M	Visible light above 420 nm	TiO <sub>2</sub> film electrode	Two-compartment and three-electrode reactor (Pt foil, SCE)	-	0.0314	Yang and Pan, 2010
Phenol, 100 mg/L	Inserted UV light 365 nm, 0.6 mW/cm <sup>2</sup>	TiO <sub>2</sub> /Ti photoanodes	Three-electrode configuration (KCl, SCE)	-	0.0122	Zhou and Ma, 2009

**Table 2: Kinetics elements for PEC and PCO methods**

<i>m</i> -cresol Concentration	Method of Treatment	Source of Light	Linear equation	Rate constant k	R <sup>2</sup>
10 ppm	PEC	UV,352nm	Ln C/Co = -0.0116t	0.0116	0.9993
	PCO	UV,352nm	LnC/Co= -0.00586t	0.0058	0.9947

## Conclusion

In this study, the use of the PEC method was treating concentrated *m*-cresol pollutants have achieved a more effective and practicable manner as compared with the PCO method. In this experiment, the cheapest TiO<sub>2</sub> coated stainless steel electrode has taken as a photoanode to perform the degradation of *m*-cresol pollutants in the PEC. The experimental study of the PEC method has performed on degradation *m*-cresol appeared primarily depending on the initial *m*-cresol pollutant, pH, and bias potential. Given certain the PEC experimental conditions of pH value of 5.0, bias potential of 3.0V, and the removal efficiency

of COD was 78.0% as compared with the PCO method was 38.0%. COD removal of *m*-cresol in the PEC method was more efficient than the PCO method. Degradation of *m*-cresol in the PEC and PCO methods were followed first-order kinetic equation and result, in the kinetic constant in the PEC (-0.116) and PCO (-0.0058) were the ratio of 2:1. In this kinetic study, the degradation of *m*-cresol in the PEC method two times faster than the PCO method. The TiO<sub>2</sub> coated stainless steel photoanode in the PEC method has achieved the degradation of *m*-cresol via minimizing the recombination of photoinduced electrons and holes by a bias potential.

## References

- Chewi, H.C., Cheng Y .W., & Shin Juang, (2008). Influence of operating parameters on photocatalytic degradation of phenol in UV/TiO<sub>2</sub> process. *Chemical Engineering Journal*, 139(2), 322-329.
- Cristina, F., Pere-Lluis, C., Francesc, C., Jose, A.G., Rosa, M.R., Conchita, A., and Enric. (2007). Solar photoelectro-Fenton degradation of cresols using a flow reactor with aboron-doped diamond anode. *Applied Catalysis B: Environmental*, 75, 17-28.
- Ebrahim, Z., (2018). Electrochemically assisted photocatalytic removal of *m*-cresol using TiO<sub>2</sub> thin film-modified carbon sheet photoelectrode. *International Journal of Industrial Chemistry* 9, 285–294.

- Fabiana, M., Paschoal, M., Marc, A., & Maria, V.B. (2009). The photoelectrocatalytic oxidative treatment of textile wastewater containing disperses dyes. *Desalination*, 249 (3), 1350-1355.
- Fang, B.L., Xiang, Z.Li., Yue, H.K., & Xin, J.L. (2002). An innovative Ti/TiO<sub>2</sub> mesh Photoelectrode for methyl orange Photoelectrocatalytic degradation. *Journal of Environmental Science and Health*, 37(4), 623-640.
- Feng, H.E., & Cheng, L.E.I. (2004). Degradation kinetics and mechanism of phenol in photo – Fenton process. *Journal of Zhejiang University Science*, 5, 198-205.
- Fransico J, R., Javier, B., & Cristina, R. (2007). Elimination of benzene and chlorobenzene by photodegradation and ozonation process. *Chemical Engineering communications*, 194(6), 811-827.
- Gaya U.I., & Abdullah A.H. (2008). Heterogeneous Photocatalytic Degradation of Organic Contaminants over Titanium Dioxide: A Review of Fundamentals, Progress and Problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 9, 1-12. <https://www.researchgate.net/publication/222937056>
- Guiying, L., Taicheng, A., Jiaxin, C., Guoying, S., Jiamo, F., Fanzhong, C., Shanqing, Z., & Huijun, Zh. (2006). Photoelectrocatalytic decontamination of oilfield produced wastewater containing refractory organic pollutants in the presence of high concentration of chloride ions. *Journal of Hazardous Materials*, B138, 392-400.
- Huseyin, S., Jeosadaque, J. S., & Marc, A.A. (2003). Photoelectrocatalytic humic acid degradation kinetics and effect of pH, applied potential and inorganic ions. *Journal of Chemical Technology and Biotechnology*, 78,979-984.
- Kavitha, V., & Palanivelu K. (2003). Degradation of 2-chlorophenol by Fenton and Photo- Fenton process – a comparative study. *Journal of Environmental science and health, Part A*, 38, 1215 – 1231.
- Li, J., Zheng, L., Li, L., Xian, Y., & Jin, L. (2007). Fabrication of TiO<sub>2</sub>/Ti electrode by laser assisted anodic oxidation and its application on photoelectrocatalytic degradation of methylene blue. *Journal of Hazard Materials*. 139, 72-78.
- Li, X.Z., Liu, H.L., Li, F.B., & Mak, C.L. (2007). Photoelectrocatalytic Oxidation of Rhodamine B in aqueous solution using Ti/TiO<sub>2</sub> mesh Photoelectrodes. *Journal of Environmental Science and Health, Part A*, 37, 55 - 69.
- Michael, R.H., Scot, T.M., Wonyong, C., & Detlef, W.B. (1995). Environmental Applications of Semiconductor Photocatalysis. *Journal of chemical Reviews*, 95, 69-96.
- Quan, X., Ruan, X., Zhao, H., Chen, S., & Zhao, Y. (2007). Photoelectrocatalytic degradation of pentachlorophenol in aqueous solution using a TiO<sub>2</sub> nanotube film electrode. *Environmental Pollution* 147, 409-414.
- Rajkumar,D., Guk, K.J., & Palanivelu, K. (2005). Indirect Electrochemical Oxidation of Phenol in the Presence of Chloride for Wastewater treatment. *Chemical Engineering and technology*, 28, 98-105.
- Rita, T., Nick, S., Claudio, M., & Ezio, P. (1991). Photocatalyzed mineralization of cresols in aqueous media with irradiated titania. *Journal of Catalysis*, 128, 352-365.
- Roberto, J.C., Walter, A.Z., & Marc, A. A. (2000). Effects of pH and Applied Potential on Photocurrent and Oxidation Rate of Saline Solutions of Formic Acid in a Photoelectrocatalytic Reactor. *Environmental Science and Technology*, 34(16), 3443-3451.
- Sayekti, W., Candra, P., Teguh, E.S., & Edi, P. (2014). Photoelectrocatalytic Rhodamine B in using Ti/ TiO<sub>2</sub> Photoanode. *Journal of Environmental Protection*, 05(17), 1630-1640.
- Shinde., P.S, Patil, P.N., Bhosale, A., Bruger, G.N., Neumann, S.M., & Bhosale, C.H. (2009). UVA and solar light assisted photoelectrocatalytic degradation of AO7 dye in water using spray deposited TiO<sub>2</sub> thin films. *Applied Catalysis B: Environmental*, 89, 288-294.
- Sudipta, D., & Somnath, M. (2012). Kinetic modelling for removal of *m*-cresol from wastewater using mixed microbial culture in batch reactor. *Journal of Water Reuse and Desalination*, 3, 149-156.
- Taicheng, A., Wenbing, Z., Xianming, X., Guoying, S., Jiamo, F.,and Xihai, Z. (2004). Photoelectrocatalytic degradation of quinoline with a novel three-dimensional electrode-packed bed photocatalytic reactor. *Journal of Photochemistry and Photobiology A: Chemistry*, 161(2-3), 233-242.
- Vinodgopal, K., Hotchandani, S., & Kama P.V. (1993). Electrochemically assisted photocatalysis. TiO<sub>2</sub> particulate film electrodes for photocatalytic degradation of 4-chlorophenol, *Journal of Physical Chemistry A*, 97, 9040-9044.
- Waldner, G., Bruger, A., Gaikwad, N. S., & Neumann, S.M. (2007). WO<sub>3</sub> thin films for photoelectrochemical purification of water. *Chemosphere*, 67, 779-784.
- Waldner, G.R.G., & Michalle, N.S. (2007). Using photoelectrochemical measurements for distinguishing between direct and indirect hole transfer processes on anatase: Case of oxalic acid. *Electrochimica Acta*, 52, 2634-2639.
- Wang, N., Li, X., Wang, Y., Quan, X., & Chen, G. (2009a). Evaluation of bias potential enhanced photocatalytic degradation of 4-chlorophenol with TiO<sub>2</sub> nanotube



- fabricated by anodic oxidation method. *Chemical Engineering Journal*, 146, 30–35.
- Wataru, M., Masahiro, T., Hussein, T Z., & Yoshinori, K. (2006). Photodegradation of *o*-cresol in water by the H<sub>2</sub>O<sub>2</sub>/UV process. *Journal of Environmental science and health, Part A; Toxic/Hazardous Substances & Environmental Engineering*, 41, 1543 – 1558.
- Wenjie, Z., Yang, Y., & Xiaoxi, W, (2010). Photoelectrocatalytic degradation of methyl orange in TiO<sub>2</sub> suspension-Ti electrode system. *IEEE*, 2, 978-982.
- Xiao, Z., Yongxin, Z., Juan, Z., & Shaoqi, Z, (2015). Degradation Kinetics of Photoelectrocatalysis on Landfill Leachate Using Codoped TiO<sub>2</sub>/Ti Photoelectrodes. *Journal of Nanomaterials*, 1-11.
- Yan, X., Shi, H., & Wang, D, (2003). Photoelectrocatalytic degradation of phenol using a TiO<sub>2</sub>/Ni thin-film electrode. *Korean Journal of Chemical Engineering*. 20, 679–684.
- Yang, H., & Pan, C, (2010). Synthesis of carbon-modified TiO<sub>2</sub> nanotube arrays for enhancing the photocatalytic activity under the visible light. *Journal of Alloys and Compound*, 501, L8–L11.
- Yang, Y., Zhang, H., & Yan, Y. (2018). The preparation of Fe<sub>2</sub>O<sub>3</sub>-ZSM-5 catalysts by metal-organic chemical vapour deposition method for catalytic wet peroxide oxidation of *m*-cresol. *Royal Society open science*, 5(3), 171731
- Yanzong, Z., Xiaoyan, X., Yue, H., Xiaohong, Z., Fei, S., Shihuai, D., Hong, X., Xinyao, Y., Gang, Y., & Hong, P, (2012). Photoelectrocatalytic degradation of recalcitrant organic pollutants using TiO<sub>2</sub> film electrodes. *An overview Chemosphere*, 88, 145–154.
- Zhou, M., & Ma, X, (2009). Efficient photoelectrocatalytic activity of TiO<sub>2</sub>/Ti anode fabricated by metalorganic chemical vapor deposition (MOCVD). *Electrochemical Communications*. 11, 921–924.