UV photoelectrocatalytic degradation of \textit{m}-cresol pollutant using TiO$_2$ dip-coated stainless steel electrode system

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In the present study, the removal of \textit{m}-cresol in an aqueous medium was studied by the photoelectrocatalytic (PEC) degradation by the TiO$_2$ 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 \textit{m}-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 \textit{m}-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 \textit{m}-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$_2$ coated on stainless steel electrode is two times higher than the PCO method on the degradation of \textit{m}-cresol.

\textbf{Introduction}

In recent times, cresol compounds including \textit{m}-cresol, \textit{o}-cresol, and \textit{p}-cresol have widely used in various industries such as coal gasification plants, oil refining industries, pharmaceuticals, and varnish industries. Most notably, \textit{m}-cresol has the highest toxicity, a potential carcinogen, and \textit{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 \textit{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 \textit{m}-cresol from wastewater by photocatalytic oxidation (PCO) method using UV or solar irradiation with TiO$_2$ 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; Chiew 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 recombinated 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

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researchers (Roberto et al., 2000; Taicheng et al., 2004; Fang et al., 2002; Huseyn 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 (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 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 through the cheapest stainless steel electrodes assembly with UV light (8w, 352nm, 27mW/m$^2$). The performance of the PEC reactor on the degradation of m-cresol has 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

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 TiO$_2$ powder (Degussa 25, particle size – 0.3µ, Anatase/ rutile (3.6/1), crystalline form, surface area 56 m$^2$/g, band gap energy 3.2 eV) has used as the photocatalyst. In the PEC method, the 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 TiO$_2$ coating on a stainless steel electrode has made by trial and error. In the first trial, the TiO$_2$ powder and ethylene glycol have thoroughly mixed with the stirrer at the ratio of 1:1 (1.0g 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 120º C. Again, the same electrode has dried at a temperature of 450º 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 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 due to the ratio of 1:1. For the second trial, the same process has carried out to achieve the perfect TiO$_2$ coating on stainless steel electrode (anode) with the modification of the blended ratio of TiO$_2$ and ethylene glycol at 2:1 (1g TiO$_2$ powder and 0.5mL ethylene glycol) and also two drops of palm oil have added to get emulsion formation of TiO$_2$, which attributed to TiO$_2$ stability on stainless steel. The outcome of the second trial, there is no crack has developed on the stainless steel due to the emulsion formation of palm oil. From the result, it has concluded that the mixing ratio of 2:1 (TiO2 powder and ethylene glycol) created a good fit for the TiO$_2$ coatings on the stainless steel electrode, which has illustrated the Figure 1.

Figure 1: 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 $\text{H}_2\text{SO}_4$, which blended with a magnetic stirrer to ensure the complete mixing of the reagents. The electrodes ($\text{TiO}_2$ coated anode and cathode) assembly has kept inside of the quartz cell chamber with a distance of 1.0cm. The photoactivity of $\text{TiO}_2$ 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$_2$ 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.

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 $\text{TiO}_2$ powder (Degussa 25, particle size – 0.3μ, Anatase/rutile (3.6/1), crystalline form, surface area 56 m$^2$/g, band gap energy 3.2 eV) has used as the photocatalyst, which has thoroughly mixed with $m$-cresol synthetic solution. The photoactivity $\text{TiO}_2$ 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. Figure 2 illustrated the prototype PEC reactor.

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
\[
\text{COD (mg/l)} = \frac{(A-B) \times M \times 8 \times 1000}{\text{ml of sample}}
\]

Where:
- A – mL FAS used or blank
- B – mL FAS used for sample
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.

**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\(_2\) surface. As a result, it induces the adsorption of organic pollutants on the TiO\(_2\) 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\(_2\) produces more H\(^+\) 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\(_2\), 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$_2$ and H$_2$O (Gaya and Abdullah, 2008). The degradation of m-cresol pollutant using the TiO$_2$ thin film modified carbon sheet photoelectrode at the biased potential of 0.45V has investigated through the experiments were conducted with 5.0mg L$^{-1}$ 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$_2$ 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$_2$ 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$_2$ flat band potential across the foamed stainless steel supported TiO$_2$ 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$_2$ 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](image)

**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$_2$N$_3$ codoped TiO$_2$ 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 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 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 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

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

Thus, the rate of m – cresol has expressed as Eqn. 2

$$-\frac{dC}{dt} = k \ [C_0] \quad \text{--------- Equation (2)}$$

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

$$\frac{dC}{dC_0} = -kdt \quad \text{--------- Equation (3)}$$

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

$$\ln \frac{C}{C_0} = -kt \quad \text{--------- Equation (4)}$$

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 TiO$_2$ film electrodes is seen to obey the first-order or pseudo-first-order kinetics. The PEC degradation of organic pollutants using a 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 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$_2$ electrode

| Pollutant concentration | Source of light | Electrode | Reactor (counter electrode, assembly) | (counter reference) | $R^2$ | Kinetic constant, $k$ | Ref. |
|-------------------------|-----------------|-----------|--------------------------------------|---------------------|------|----------------------|------|
| PCP, 40 mg/L            | Inserted UV light 365 nm, 0.6 mW/cm$^2$ | TiO$_2$ film electrode | Single photoelectrochemical Compartment (stainless steel) | 0.983 | 0.0171 | Quan et al. 2007 |
| BPA, 11.2 mg/L          | UV 365 nm, 0.68 mW/cm$^2$ | TiO$_2$ multiporous thick-film electrode | Batch-scale photoreaction set-up three-electrode configuration (Pt foil, SCE) | 0.995 | 0.0178 | Xie, 2006 |
| MB, 20 mg/L             | UV 254 nm       | TiO$_2$/Ti mesh electrode | Typical three-electrode System (Pt wire, SCE) | 0.995( R) | 0.0178 | Li et al., 2007 |
| Malachite green, 1 x 10$^{-5}$ M | Visible light above 420 nm | TiO$_2$ film electrode | Two-compartment and three-electrode reactor (Pt foil, SCE) | 0.995 | 0.0314 | Yang and Pan, 2010 |
| Phenol, 100 mg/L        | Inserted UV light 365 nm, 0.6 mW/cm$^2$ | TiO$_2$/Ti photoanodes | Three-electrode configuration (KCl, SCE) | 0.0122 | 0.0314 | Zhou and Ma, 2009 |

Table 2: Kinetics elements for PEC and PCO methods

| m-cresol Concentration | Method of Treatment | Source of Light | Linear equation | Rate constant $k$ | $R^2$ |
|-----------------------|---------------------|-----------------|----------------|-------------------|------|
| 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$_2$ 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 TiO2 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.

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